

Sequestration of Dissolved CO₂ in the Oriskany Formation

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Experiments were conducted to determine the solubility of CO₂ in a natural brine solution of the Oriskany formation under elevated temperature and pressure conditions. These data were collected at temperatures of 22 and 75 °C and pressures between 100 and 450 bar. Experimentally determined data were compared with CO₂ solubility predictions using a model developed by Duan and Sun (*Chem. Geol.* 2003, 193, 257–271). Model results compare well with Oriskany brine CO₂ solubility data collected experimentally, suggesting that the Duan and Sun model is a reliable tool for estimating solution CO₂ capacity in high salinity aquifers in the temperature and pressure range evaluated. The capacity for the Oriskany formation to sequester dissolved CO₂ was calculated using results of the solubility models, estimation of the density of CO₂ saturated brine, and available geographic information system (GIS) information on the formation depth and thickness. Results indicate that the Oriskany formation can hold approximately 0.36 gigatonnes of dissolved CO₂ if the full basin is considered. When only the region where supercritical CO₂ can exist (temperatures greater than 31 °C and pressures greater than 74 bar) is considered, the capacity of the Oriskany formation to sequester dissolved CO₂ is 0.31 gigatonnes. The capacity estimate considering the potential to sequester free-phase supercritical CO₂ if brine were displaced from formation pore space is 8.8 gigatonnes in the Oriskany formation.

Introduction

Carbon dioxide, an important greenhouse gas, has increased in atmospheric concentration from 280 ppm to 365 ppm since the industrial revolution (2). Anthropogenic CO₂ is considered a large factor in the measured increase in atmospheric CO₂. As of 1998, an estimated 75% of the world's energy needs were met by the combustion of fossil fuels (3, 4). The Intergovernmental Panel on Climate Change (IPCC) estimated that global emissions of carbon from fossil-fuel burning and cement production was approximately 7.8 gigatonnes of carbon in 2005 (5). This rate of emission is believed to exceed the assimilation capacity of oceans and

the terrestrial ecosystem and account for the observed increase in concentration of atmospheric CO₂ (6).

The principle modes for carbon management include (i) increasing the efficiency of energy conversion; (ii) using low-carbon or carbon-free energy sources; and (iii) capturing and sequestering CO₂ emissions. The latter strategy termed "CO₂ sequestration" has gained increased attention, as it permits continued use of fossil fuels for the generation of electric power while ensuring CO₂ emission reductions. Various CO₂ sequestration options, including ocean, terrestrial, geologic, advanced biological processes, and advanced chemical approaches, are currently being studied. Each of these options has significant technical and economic hurdles that need to be addressed before being considered feasible for full-scale application.

One potentially attractive approach for CO₂ sequestration is injection of CO₂ into geologic formations such as active and depleted oil and gas reservoirs, deep unmineable coal seams, basalt formations, and deep saline aquifers. The underlying principle of this method of sequestration lies in the premise that injected CO₂ will remain stored in the host rock for an extended period of time (i.e., hundreds of years or more). In addition to simple storage as free-phase CO₂ or a soluble component, geologic sequestration of CO₂ by injection into saline aquifer formations may have enhanced sequestration capacities and permanence due to conversion of CO₂ into carbonate minerals.

The United States Department of Energy envisions the geological sequestration of as much as one gigatonne of CO₂ per year by 2025 and perhaps as much as 4 gigatonnes per year by 2050 (7). Such reductions would act to mitigate domestic contribution to the increases in global atmospheric CO₂. Geological sequestration of anthropogenic CO₂ would rely on the contribution of several CO₂ trapping mechanisms: (1) hydrodynamic trapping—the physical trapping of CO₂ in a gaseous, liquid, or critical state in a subsurface formation; (2) solubility trapping—the trapping of CO₂ via the dissolution of CO₂ within a brine, petroleum, or other subsurface fluid; and (3) mineral trapping—the process of forming in situ, interstitial carbonate minerals from CO₂ and the host rock and formation waters (8). Demonstration efforts are already underway to verify the viability of the geological sequestration paradigm. For example, up to one million tons of CO₂ per year are being trapped at Sleipner West in the North Sea (9).

The current study addresses the potential of the Oriskany formation to serve as a soluble CO₂ trapping reservoir. Worldwide, deep saline aquifers such as those associated with the Oriskany formation are thought to have the potential to sequester from 1 to 130 gigatonnes of CO₂ during their useable lifetimes (10). However, due to variability in brine chemistry, extent of the formation, and varying reservoir conditions, the true capacity of these saline aquifers to sequester CO₂ must be determined individually. CO₂ is partially miscible in the host brine and offers the potential to interact chemically with the host rock and the brine itself. The injection of CO₂ into underground reservoirs is best accomplished with CO₂ pressurized to a supercritical fluid (11, 12). Conditions needed to produce supercritical CO₂, that is, above 31 °C and 73 bar, require potential sequestering formations to be of depths greater than approximately 800 m (13).

The Oriskany formation was selected for this study because it meets many of the criteria required of a potential sequestration horizon (7); some portions of the Oriskany have adequate porosity and permeability, are of sufficient extent to provide for the potential sequestration of significant volumes of CO₂, and are commonly found at depths greater

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than 800 m permitting CO₂ to be injected as a supercritical fluid. Also, a large number of fossil fuel-fired power plants are located in areas underlain by the Oriskany formation. This proximity makes the Oriskany formation an ideal candidate to serve as a CO₂ sink.

The focus of this paper is to evaluate the solubility of CO₂ in the Oriskany brine experimentally and compare these experimental results with predictions of the Duan and Sun (1) carbon dioxide solubility model. Results of the experiments and model predictions are used in conjunction with GIS data on unit thickness and depth, along with fluid density to estimate the capacity of the Oriskany formation to sequester CO₂ through solubility trapping.

Experimental Methods

Reactants were loaded into a flexible titanium reaction cell, which in turn was placed in a steel-alloy autoclave, as described by Seyfried et al. (14). Titanium exit tube and sampling valve were attached to the reaction cell, which allowed fluid to be removed during each experiment, permitting the chemical evolution of the reactive system to be monitored. Fluid samples were taken directly into glass, gas-tight syringes containing a small quantity of 45% (w/w) KOH, which prevents the loss of CO₂ during sample processing. A simplified schematic of the experimental apparatus is provided in the Supporting Information. Details of reactor loading and sampling method are also provided in the Supporting Information (reactor schematic, Figure S1, supplemental information).

Following sample collection, KOH-stabilized samples were analyzed to determine total CO₂ concentration. Samples were acidified using a perchloric acid solution and evolved CO₂ transported via inert carrier gas for subsequent measurement in a CO₂ coulometer, as is detailed in the Supporting Information.

Brine samples were collected from a well in the Oriskany Sandstone aquifer, in Indiana County, Pennsylvania, operated by Cabot Oil and Gas Corporation after purging at a formation depth of 2800 m following methods described by Lico and others (15). These high salinity samples (20 wt% NaCl equivalent) were stored at 4 °C for several months before being used in the experiments described herein. During this period, exposure to air occurred as a result of diffusion through high-density polyethylene storage bottles resulting in sample oxidation and precipitation of ferric hydroxide and a gradual decrease in brine pH over time. Filtered samples of this brine were used in all experiments; mean results of brine composition analysis (*n* = 9) are reported in Table 1 as mg per liter of brine.

Results and Discussion

Three sets of data were collected, two at 22 °C and one at 75 °C. At 22 °C, two liquids were examined, pure water and the Oriskany brine. The pure water samples were used as a control to compare experimentally determined values to those previously published and to those predicted by the Duan–Sun model (1). Only after sampling and analysis techniques had been adequately demonstrated with pure water (see Figure S2, Supporting Information) was analysis of CO₂ solubility in Oriskany brine samples initiated. Oriskany brine solution CO₂ solubility values were converted from moles per kg solution of brine to moles per kg solution of water using the percent of salt determined from the refractive index of the brine.

The Duan and Sun stand-alone solubility model (1) was designed specifically and exclusively to estimate carbon dioxide solubility. The model is not designed to address CO₂/solution/rock interactions but can provide very accurate estimates of CO₂ solubility in complex saline aqueous fluids

TABLE 1. Mean Composition of the Air-Exposed Oriskany Brine (*n* = 9)^a

	units	mean brine composition (\pm std dev)
Al ⁺⁺⁺	pH	2.72 (\pm 0.03)
Ba ²⁺	mg/L	>OL
Ca ²⁺	mg/L	847 (\pm 24)
Fe ^{+++/++}	mg/L	25130 (\pm 962)
K ⁺	mg/L	165 (\pm 11)
Mg ²⁺	mg/L	1930 (\pm 64)
Mn	mg/L	1540 (\pm 92)
Na ⁺	mg/L	5.33 (\pm 0.41)
P	mg/L	48733 (\pm 2903)
Si	mg/L	>OL
Sr ²⁺	mg/L	7 (\pm 1.5)
Cl ⁻	mg/L	11817 (\pm 448)
Br ⁻	mg/L	122930 (\pm 9196)

^a Standard deviations are noted parenthetically as a \pm value. All values were determined by inductively coupled plasma mass spectrometry, save chloride and bromide, which were determined by ion chromatography and pH, which was measured with selective electrode.

for temperatures between 0 and 260 °C and pressures between 0 and 2 kbar. The model uses an equation of state to calculate carbon dioxide solubility in pure water and, instead of a generalized fit to carbon dioxide solubility data in high salinity fluids, Pitzer specific interaction parameters (16) are used to adjust the solubility of carbon dioxide in fluids with elevated salinities to account for the “salting-out” effect.

As discussed by Allen and colleagues (17), all geochemical models require accurate estimation of the following data to produce reliable results: (1) fugacity of CO₂, (2) activities of charged and neutral aqueous species, and (3) equilibrium constants for all included free-phase fluids, aqueous species, and mineral phases. In addition, intercomparison of modeling results indicates that failure to adjust all equilibrium constants to account for elevated carbon dioxide pressures results in significant errors in both gas solubility and mineral formation estimates. Finally, it should be emphasized that the Duan and Sun model (1), as with other stand-alone solubility models, does not take mineral reactions into account and will, therefore, underestimate the ultimate capacity of aquifers to sequester carbon dioxide as a result of enhanced solubility and mineral trapping mechanisms. In general, it is difficult to confidently predict the ultimate sequestration capacity of deep saline aquifers, however, the Duan and Sun model (1), when applied correctly, is believed to provide a good estimate of initial solubility in complex saline solutions at formation appropriate conditions.

At each pressure condition, CO₂ concentrations were determined by taking the average of four replicate samples. Model predictions were calculated using the software package TK Solver, release 5 (UTS Software, Rockford, IL), to iteratively converge upon a solution and produce a table of predicted solubility values, plotted in Figure 1 with corresponding experimental results. It is important to note that the experiments were conducted not to rederive a solubility model but, rather, to test the applicability of the Duan and Sun model in predicting CO₂ solubility at elevated fluid salinities and CO₂ pressures.

The experimental data collected correlate well with the model-predicted solubility. CO₂ solubility decreases with increasing system temperature and salinity, as shown in both observed and predicted values. Observed experimental error can be attributed to the complexity of the apparatus and the relative rigidity of the titanium reaction cells, which can result in slight differences between actual sample pressure and

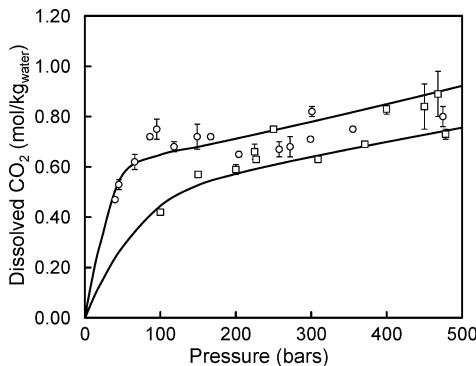


FIGURE 1. Solubility of CO_2 in Oriskany formation brine samples at 22 and 75 °C as a function of pressure. Solid lines represent Duan and Sun (2003) model predictions, open squares represent experimental data for Oriskany brine solubility at 22 °C, and circles represent experimental data for Oriskany brine solubility at 75 °C. Bars represent one standard deviation from the mean of quadruplicate measurements.

measured system pressure in the confining water surrounding the titanium cell. Although there is some scatter of experimental points, the data clearly demonstrate that the Duan and Sun model is appropriate for simulating CO_2 solubility in Oriskany brine. Following verification of the applicability of this model for estimation of Oriskany brine CO_2 solubility, further calculations were carried out to estimate the total CO_2 solubility capacity of the Oriskany sandstone aquifer.

Capacity Prediction Methods

Method of Estimating Solubility Storage Capacity in the Oriskany Formation. In the work described herein, an attempt was made to integrate a more rigorous and laboratory verified CO_2 solubility model (1) with a sophisticated model of CO_2 -saturated brine density (18) and geologic parameters of the target formation to develop a reliable estimate of total potential dissolved CO_2 storage capacity in the Oriskany formation.

The total quantity of CO_2 capable of being sequestered in any formation via solubility trapping can be predicted from the following expression:

$$\text{CO}_2 = v \times E \times p \times \delta \times \text{mCO}_2 \times M \quad (1)$$

where v is the total volume of the formation in km^3 , p is the estimated mean porosity of the formation, E is the CO_2 storage efficiency factor or the fraction of p that can be filled by CO_2 , δ is the density of the CO_2 saturated brine in kg/km^3 , mCO_2 is the concentration of CO_2 dissolved in the brine in mol/kg , M is the molar mass of CO_2 in g/mol , and CO_2 is the total mass of CO_2 in grams.

This equation assumes that the concentration of total inorganic carbon (TIC) prior to CO_2 injection is negligible, as compared to the CO_2 saturated condition, an assumption that is substantiated by a consideration of the matter by Bachu and Adams (18). In the case of the Oriskany formation, the formation volume was estimated using Oriskany formation thickness data reported by the Bureau of Economic Geology, University of Texas (19). The published formation thickness raster map has a pixel spatial resolution of 5000 m and a thickness resolution of 1 m. Formation volume was determined by multiplying the pixel area (25 km^2) times the formation thickness, as reported in each pixel; a raster representation of estimated formation volume was generated (see Figure S3, Supporting Information). Total estimated formation volume was then determined by summing these calculated volumes for all pixels in the data set. The effective volume for CO_2 solubility or volumetric is limited to the subset of the total pore volume that is accessible to the injected

CO_2 . To calculate the effective volume of brine available for sequestration in the formation, the formation volume for each pixel must be multiplied by both the estimated mean porosity of the formation and the estimated fraction of that pore volume that can be reached by CO_2 (referred to as an efficiency factor). Finally, the calculated effective pore volumes of all pixels are summed to arrive at a formation effective pore volume. The porosity of the Oriskany formation has been reported to vary from 0 to 12% (20–22), with the majority of the basin having a porosity between 7 and 12%. Of the total porosity, CO_2 storage efficiency factors are estimated to be between 1 and 4% for saline formations (23). Porosity vector data reported by the UT BEG (19) were rasterized with pixels within each porosity region assigned the midvalue of the reported porosity range. An average porosity of 8.4% was determined for the Oriskany formation by weighting the number of pixels assigned each mean porosity. This number is similar to the value of 10% used by the MRCSP to predict the amount of supercritical CO_2 potentially trapped in the pores of the Oriskany formation through hydrodynamic trapping (24). The concentration of CO_2 dissolved in the formation water is a function of the chemistry of the brine and the temperature and pressure of the brine at each point in the formation. The density of the CO_2 saturated brine is also a function of chemistry, temperature, and pressure.

The temperature of the Oriskany formation was based on the determination by the UT BEG derived from data of Opritz (25) and Harper and Patchen (22) and indicate a linear gradient as defined in eq 2. Similarly, pressure within the Oriskany formation was determined by the UT BEG using data from Harper and Patchen (22) and indicates a linear hydrostatic gradient as defined in eq 3

$$T = 63 + 0.0092 \times (\text{depth}) \quad (2)$$

$$P = 0.44 \times (\text{depth}) \quad (3)$$

where depth is in feet, temperature is in degrees Fahrenheit, and pressure is given in pounds per square inch.

Employing these correlations, a unique set of pressure and temperature values is defined for each depth value (see Figure S4, Supporting Information). When the depth to formation midpoint is used (depth to formation plus half of formation thickness), new raster files of average formation temperature (see Figures S5, Supporting Information) and pressure (not shown) were constructed.

These correlations for temperature and pressure as a function of depth (eqs 2 and 3, respectively) were also used to define the formation depth below, which free undissolved CO_2 is expected to remain as a supercritical fluid. As mentioned previously, the critical point for CO_2 occurs at a pressure of approximately 73 bar and 302 Kelvin. Using eq 3, a depth of 800 m correlates with a formation pressure of 79.63 bar, a value slightly above the supercritical point. For convenience, 800 m was used as the formation depth threshold below which CO_2 was assumed to remain supercritical in free-phase. A new raster was created to define the spatial subset of depth data that are associated with formation pressures, allowing for injected CO_2 to remain as a supercritical fluid in the formation.

It has been reported that the Oriskany formation waters vary in total dissolved solids (TDS) from 9990 to 343000 mg/L (26); the TDS of brine samples used in all experiments described herein (purge water from wells of the Cabot oil and gas company, PA) is 228000 mg/L. As the brine used in these calculations is within this reported range and as there is no published correlation between depth and TDS for the Oriskany formation, the chemistry of this sample is assumed to be representative of formation brine chemistry for all capacity estimate calculations. When relatively high salinity

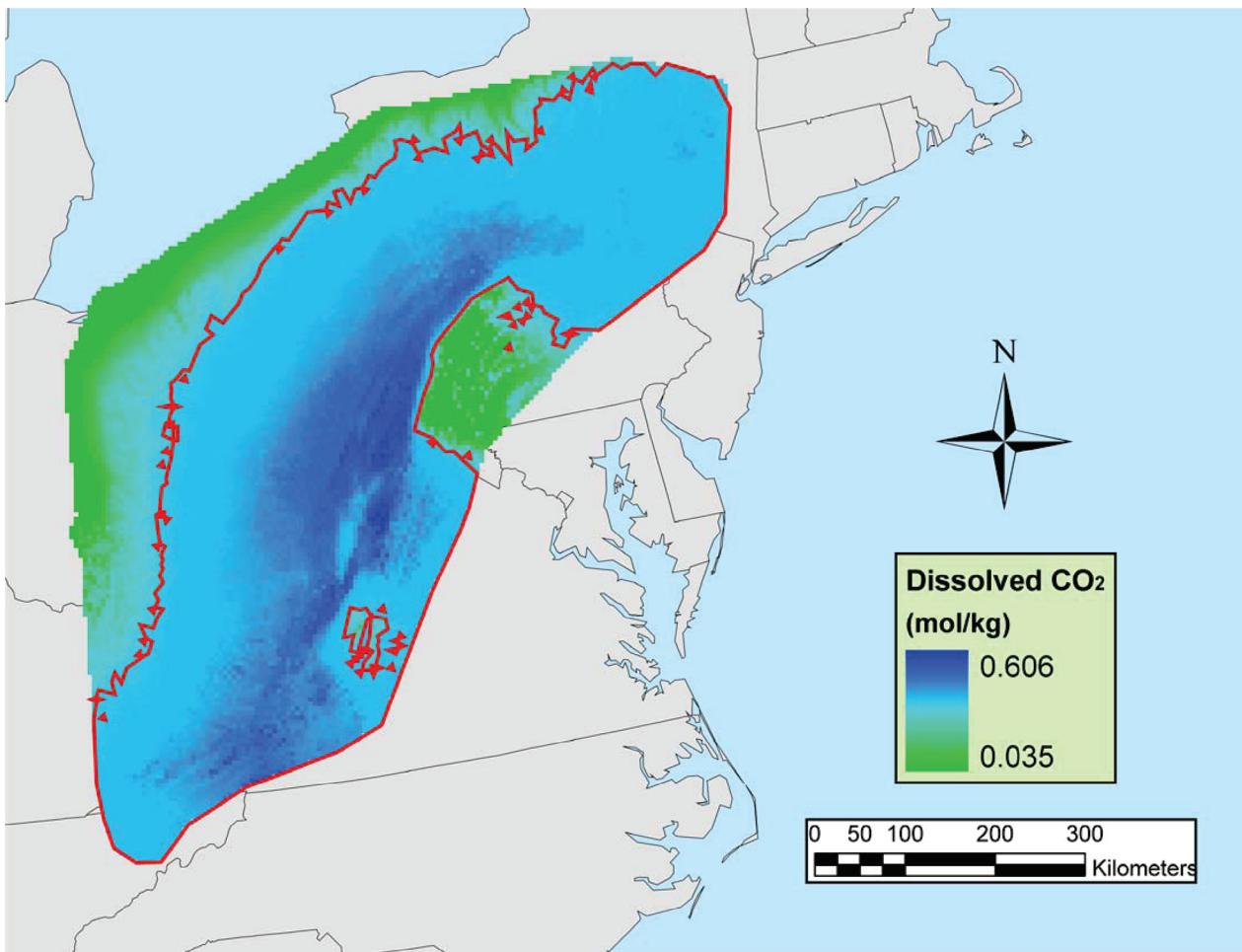


FIGURE 2. Raster of CO₂ concentration at formation midpoint depth (and corresponding temperature/pressure) was generated for the model Oriskany brine described in Table 1.

model brine is used, this results in a relatively low calculated CO₂ solubility and, therefore, a conservative formation capacity estimate. When this model brine composition and the correlation between temperature and, therefore, pressure is used, the concentration of CO₂ in the Oriskany brine was calculated. A polynomial was fit to the data to correlate temperature (and, therefore, pressure) to the formation of CO₂ concentration (shown in Figure S6, with correlation described in Table S1, Supporting Information). When this developed correlation is used, a raster of CO₂ concentration at formation midpoint depth (and corresponding temperature/pressure) was generated for the model brine (see Figure 2). Similarly, the density of CO₂ saturated brine at the brine chemistry, temperature and pressure was determined using equations described by Bachu and colleagues (27). From these data, a density–temperature correlation was constructed and a polynomial fit was determined (Figure S7 and Table S2, respectively, Supporting Information). A raster of CO₂ saturated brine density for the given brine composition at formation midpoint temperature and pressure was also generated.

Finally, all developed raster maps, including density, CO₂ concentration, and total formation volume, are used with estimated formation porosity and CO₂ molecular weight to calculate, according to eq 1, a new raster with each pixel value representing the CO₂ solubility capacity for the spatial subset represented by that pixel (in grams). By summing the CO₂ solubility capacity of each pixel, a value for total formation CO₂ solubility capacity was determined. When the calculated depth below which injected CO₂ would remain as a supercritical fluid was used, a second, slightly lower,

estimate was developed that is considered to be a practical solubility capacity.

Method for Estimating Volumetric Trapping of CO₂ in the Oriskany Formation. Volumetric storage capacity refers to the maximum potential storage in a sequestration target formation or subset of a target formation, assuming that all of the brine is displaced from the pore volume and replaced with free-phase CO₂, in this case, supercritical CO₂. This is in contrast to hydrodynamic trapping, a term which describes the more relevant scenario in which a plume of free-phase CO₂ is trapped within the flow system of the formation brine. Volumetric storage capacity for the Oriskany formation was determined by applying temperature and pressure correlations (eqs 2 and 3, respectively) with depth (see Figure S4, Supporting Information) to a detailed model of free-phase CO₂ density as a function of those parameters. When these relationships were used, the density of free-phase CO₂ was determined as a function of formation midpoint depth (as shown in Figure S8, Supporting Information). Correlation between free-phase CO₂ density and temperature at formation midpoint was defined (shown in Figure S9, Supporting Information) and a polynomial fit to these data (Table S3, Supporting Information). When this polynomial was used, a raster describing the density of free-phase CO₂ at formation midpoint was constructed using the previously described calculated raster of temperature at formation midpoint (Figure S5, Supporting Information). As this polynomial was fit to only temperature/density correlation in the temperature range corresponding with supercritical CO₂, the free-phase CO₂ density raster (Figure 3) was generated only for that spatial subset of the Oriskany formation with temperature/

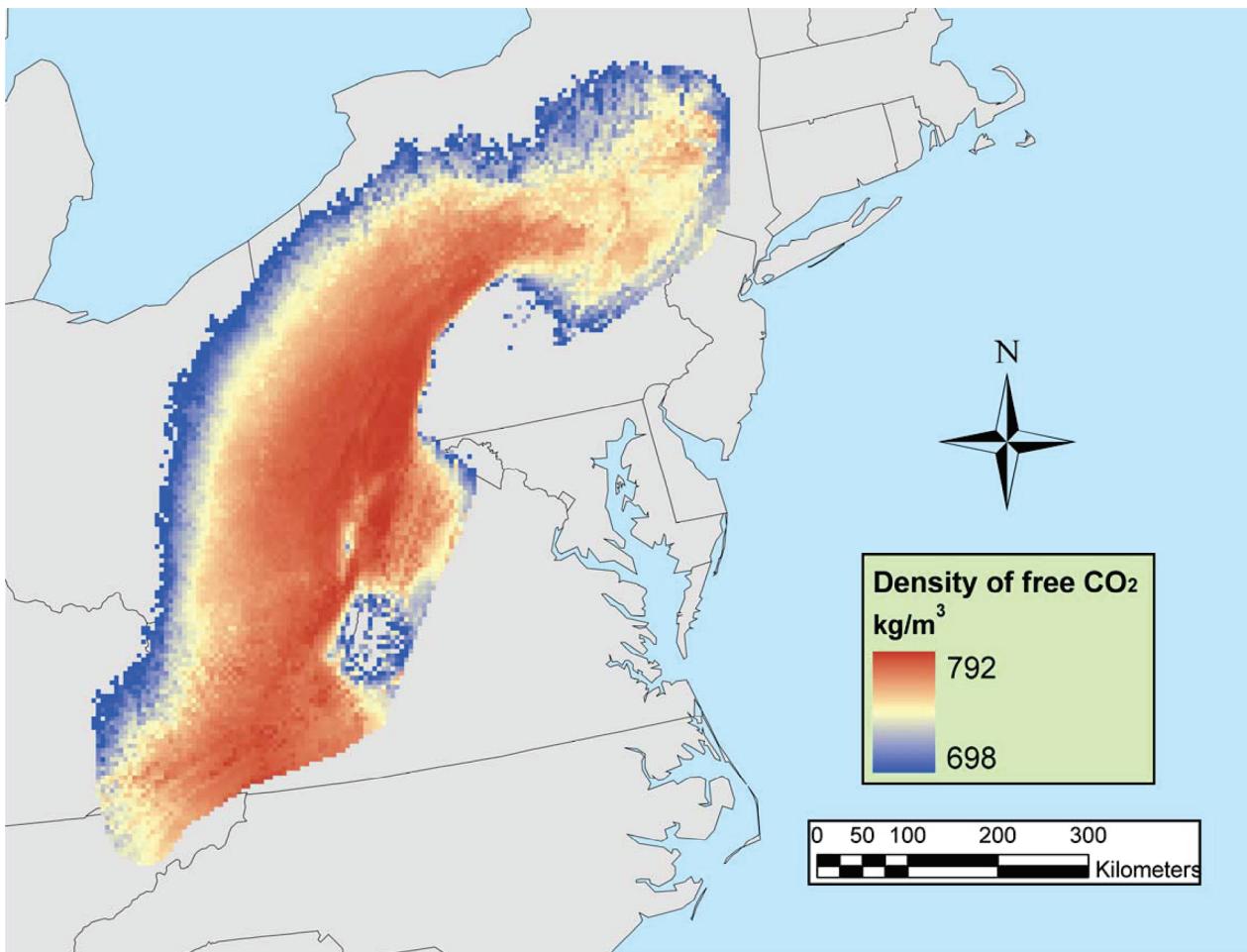


FIGURE 3. Raster of free-phase CO_2 density (kg/m^3) at Oriskany formation midpoint for the spatial subset capable of holding supercritical CO_2 , as determined using the free-phase CO_2 density model developed by Lemmon and colleagues (28) and the temperature and pressure/Oriskany formation depth correlation reported by Opritsa (25) and Harper and Patchen (22).

pressure sufficient to maintain supercritical CO_2 at the top of the formation (the vertical point with lowest temperature/pressure). This raster of formation midpoint free-phase CO_2 density in regions capable of holding supercritical CO_2 was then multiplied by the raster of formation volume of the Oriskany formation and again multiplied by the estimated mean porosity of the Oriskany formation (8.4%) and the CO_2 storage efficiency factor (4%). The raster resulting from this calculation estimated the mass of free-phase CO_2 that could be sequestered in each pixel ($5000 \text{ m} \times 5000 \text{ m}$) in the region of the Oriskany formation estimated to be appropriate for supercritical CO_2 volumetric trapping. The mass capacity estimates were summed for all pixels in this spatial subset, yielding a total free-phase CO_2 capacity estimate.

Results and Discussion of Capacity Estimates. Results indicate that the total volume of the Oriskany formation is 4194 km^3 . With an estimated average porosity of 8.4%, an estimated total pore volume of 352 km^3 was calculated with an available porosity of 14.1 km^3 CO_2 . Assuming that the available pore volume would be completely saturated with brine, the total mass of CO_2 that would be dissolved in pore water is estimated to be 0.36 gigatonnes. Considering only that spatial subset of the basin that is of sufficient depth (top of formation) to allow hydrodynamic trapping as supercritical CO_2 , the total capacity estimate reduces to 0.31 gigatonnes. The small difference in these capacity estimates is in agreement with the observation that most of the Oriskany basin is sufficiently deep to maintain free trapped CO_2 as supercritical fluid and that CO_2 solubility is significantly greater in regions of greater formation pressure. In the second

estimate of formation, volumetric CO_2 sequestration capacity, in which complete displacement of brine from available pore volume of the supercritical region of the Oriskany formation was assumed, a free-phase CO_2 -bearing capacity of 8.8 gigatonnes was determined.

As described in the background section, geologic sequestration of CO_2 in deep saline aquifers is expected to manifest as a combination of hydrodynamic trapping, solubility trapping, and mineral trapping through precipitation of mineral carbonates. Current thinking on this topic holds that volumetric trapping will initially predominate, with the contribution of CO_2 dissolution increasing with time and mineralization contributing significantly only after a very long time (18). In addition to having different time scales, each trapping mechanism has a different degree of permanency. Hydrodynamic trapping requires containment of free-phase CO_2 and, as such, is contingent on the long-term integrity of the cap rock and the slow migration of fluid from the reservoir. Hydrodynamically trapped, free-phase CO_2 is, therefore, most prone to leakage from the target reservoir and considered to be the least permanent trapping mechanism. Dissolution is considered to be a more stable and permanent form of trapping, as compared to hydrodynamic trapping, since dissolved CO_2 does not occupy discrete space in the formation, does not exert pressure on the cap rock in excess of formation pressure, and will not degas unless brine deviates from formation pressure/temperature conditions. Finally, trapping of CO_2 in deep saline aquifers as relatively insoluble mineral carbonates is considered to be the most permanent means of CO_2 storage.

Estimates described herein consider two extreme cases: one in which all of the CO₂ is present as carbonate species in brine solution (maximum solubility trapping in the formation brine) and another in which all brine is displaced from the supercritical region of the formation and replaced with free-phase CO₂. For several reasons, neither of these cases describes a realistic injection scenario: CO₂ dissolution into the brine is dramatically limited in rate by the low pore volume to matrix ratio (limited fluid convection) and low free-phase CO₂/brine interfacial area. Complete displacement of brine from all pores is also unrealistic because brine occupies capillary pores of very small diameter as well as pores with limited continuity to the larger pore structure from which it would be difficult to force the native brine. Finally, displacement of large volumes of relatively incompressible brine from the formation would require high conductivity through the confined formation. As hydraulic conductivity in the Oriskany formation is believed to be very low (19), such large-scale brine displacement is not expected. It is also undesirable, because displacement of such a huge volume of brine would drive it from the formation, causing probable CO₂ leakage to the atmosphere and brine contamination of fresh water sources.

A more likely scenario will involve local injection of a moderate volume slug (relative to total formation pore volume) of free-phase CO₂ that would initially remain as a discrete CO₂ plume but dissolve over the course of hundreds or thousands of years into formation brine that was initially displaced but migrated back as CO₂ dissolution progressed. After the onset of CO₂ dissolution, disequilibrium between the brine and the host rock would result in increasing mineral carbonation, allowing for additional dissolution of CO₂ into the formation brine. For example, one site-specific CO₂ simplified CO₂ transport simulation (Mt. Simon brine formation) by Gupta and others (29) describes dissolution of only 8% of the injected CO₂ 500 years after a 50 year CO₂ injection at a loading rate of 1 Mt/year. In this simulated case, brine is displaced only locally (plume predicted to spread only 3500 m), with most of the CO₂ remaining in the free-phase and some predicted dissolution (again, mineralization was neglected in this model). To promote additional dissolution, a larger number of injection points with lower CO₂ loading rates would be required.

Neither capacity estimate provides a realistic CO₂ capacity for the Oriskany formation; rather, these values serve as outer bounds of CO₂-bearing capacity. Simply put, the reported volumetric capacity estimate describes the maximum amount of CO₂ that could be stored in the formation, while the reported solubility estimate describes the maximum amount of CO₂ that could be injected into the formation if solubility trapping of all injected CO₂ was the ultimate goal. It is recognized, however, that mineralization may also contribute significantly to ultimate CO₂ storage capacity, provided the host rock is sufficiently reactive.

A similar examination of the Oriskany formation volumetric capacity in the supercritical region was conducted by the MRCSP in 2005 (24). In that effort, a CO₂ storage effectiveness factor of 10% was assumed and a capacity estimate of 19 gigatonnes was determined. Adjusting this estimate to account for the revised effective porosity fraction of 4% (23), the MRCSP estimate would be approximately 7.6 gigatonnes, a value similar to the 8.8 gigatonnes of volumetric capacity determined herein.

The solubility trapping capacity estimate of the Oriskany basin described herein is more than an order of magnitude greater (per unit volume) than that of the Viking Aquifer of the Alberta basin generated by Bachu and Adams (19): the Alberta basin is approximately 1,681,000 km³, with an estimated ultimate dissolved CO₂ capacity of 198.7 Gt CO₂ in the entire formation and 106.6 Gt CO₂ in the region where

CO₂ will remain a dense fluid. The substantially larger predicted solubility capacity of the Viking formation of the Alberta basin arises from the larger total formation volume (1,681,000 km³ in the Alberta basin vs 4194 km³ in the Oriskany), the substantially lower salinity of the Viking formation (10000–80000 mg/L in the Viking aquifer vs 9990–343000 mg/L in the Oriskany), and the substantially larger porosity of the Viking aquifer (5–35% vs 3–12% in the Oriskany).

Ultimately, more reliable estimates of effective storage capacity will require increased spatial resolution of key formation properties such as brine composition, porosity, and formation mineralogy. While much of this data may be available in historic mineral exploration logs, accessing it will require time- and labor-intensive investigation of analog data repositories. It is likely that additional characterization will be focused at and around specific proposed injection sites. Finally, to gain a better understanding of the role of mineral sequestration in ultimate formation sequestration capacity, additional laboratory and field (*in situ*) investigation of brine/CO₂/rock interaction kinetics and thermodynamic equilibria will be required.

As was predicted by the Duan and Sun CO₂ solubility model (1), solubility of CO₂ in high salinity Oriskany sandstone formation brine samples is slightly lower at 75 °C than at 22 °C. Both Oriskany brine samples exhibited significantly lower CO₂ solubility than was observed in pure water solutions, as is expected as a result of the CO₂ salting-out effect. Also, as predicted, CO₂ solubility generally increases with increasing system pressure. Model predictions compared favorably with results of experimental solubility determination, suggesting that the Duan and Sun (1) model is a reliable tool for estimating solution CO₂ capacity in high salinity aquifers in the temperature and pressure range evaluated. The estimate of the capacity of the Oriskany formation to store CO₂ through solubility trapping using the model of Duan and Sun (1) along with formation thickness, depth, chemistry, and temperature and pressure data is 0.36 gigatonnes (0.31 gigatonnes in the spatial subset associated with supercritical CO₂ injection).

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Supporting Information Available

Information provided in support of this manuscript includes description of experimental apparatus, coulometric method for CO₂ analysis, and details of intermediate steps in volumetric and solubility capacity estimates. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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