Carbon Dioxide Storage in Unconventional Reservoirs Workshop: Summary of Recommendations

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Conversion factors

Multiply	By	To obtain
Length		
micrometer (μm)	3.937×10^{-5}	inch (in.)
meter (m)	3.281	foot (ft)
foot (ft)	0.3048	meter (m)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton (t)(1,000 kg) = 1 megagram (Mg)
kilogram (kg)	2.205	pound, avoirdupois (lb)
metric ton (t)(1,000 kg) = 1 megagram (Mg)	1.102	ton, short (2,000 lb)
billion metric tons = gigaton (Gt)	1.102	billion short tons

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Introduction

As mandated by the Energy Independence and Security Act (Public Law 110–140; U.S. Congress, 2007), the U.S. Geological Survey (USGS) recently completed a national assessment of geologic carbon dioxide (CO_2) storage resources (U.S. Geological Survey Geologic Carbon Dioxide Storage Resources Assessment Team, 2013a,b,c). The probabilistic methodology used to estimate storage resources is based on a volumetric calculation using geologic parameters within sedimentary formations (Burruss and others, 2009; Brennan and others, 2010; Blondes and others, 2013). The assessment only examined existing pore space accessible through residual and buoyant trapping within saline formations (sandstones, limestones, or dolostones) and therefore did not calculate storage capacity for reservoirs where changes to the rock (dissolution, mineralization, adsorption, hydraulic fracturing) contribute to CO_2 storage.

"Unconventional reservoirs"—reservoirs in which changes to the rock trap CO_2 and therefore contribute to CO_2 storage—including coal, shale, basalt, and ultramafic rocks, were the focus of a USGS workshop held March 28 and 29, 2012, at the National Conservation Training Center in Shepherdstown, West Virginia. The workshop was designed to help determine the next steps for the USGS regarding assessing CO_2 storage potential in unconventional reservoirs. The workshop consisted of presentations describing the current state of laboratory studies, modeling, and pilot projects and a discussion of the feasibility of CO_2 storage in coal, shale, basalt, and ultramafic rocks. The ultimate goals of the workshop were to determine whether an assessment of CO_2 storage capacity in unconventional reservoirs is warranted, and if so, to build a set of recommendations that could be used to develop a methodology to assess this storage capacity. At this stage, such an assessment would address only the technically available resource, independent of economic or policy factors.

The current assessment methodology for buoyant and residual trapping (Brennan and others, 2010) deals with geological storage of CO_2 between 3,000 feet (ft) (914 meters [m]) and 13,000 ft (3,962 m) depth. It also allows additional assessment of storage deeper than 13,000 ft (3,962 m), as formations warrant. The methodology is probabilistic instead of deterministic. Carbon dioxide is generally in a supercritical state at these depths, where it is a buoyant fluid that displaces water, oil, and gas and that can be contained in structural traps; CO_2 can also be held in place by residual trapping in pore spaces. Overlying sealing formations are required to prevent the stored CO_2 from escaping to the atmosphere. Based on the Safe Drinking Water Act of 1974 and U.S. Environmental Protection Agency (2009, 2010) underground injection controls that protect underground sources of drinking water, the salinity of groundwater in the assessed formations must be greater than 10,000 parts per million (ppm) of total dissolved solids.

The U.S. Department of Energy (DOE) also assesses potential CO_2 storage resource using a separate methodology (Goodman and others, 2013). The DOE publishes the National Carbon Sequestration Database and Geographic Information System (NATCARB), now being integrated into the Energy Data Exchange, and, with Natural Resources Canada and the Mexican Ministry of Energy, the North American Carbon Storage Atlas (North American Carbon Atlas Partnership, 2012; Wright and others, 2013). The DOE's storage resource estimates are based on technically accessible pore volumes for buoyant trapping, and do not consider regulatory or economic constraints. The DOE assessment for potential CO_2 storage in coal only considers "unminable" coal beds, which it defines as those that cannot be mined economically using today's technology. Although USGS and DOE assessments are fundamentally similar, they use different methodologies; the DOE's assessment is regional in scale, while USGS assessments consider each formation in a sedimentary basin individually; additionally, USGS assessments are fully probabilistic.

Based on the USGS and DOE assessments, potential CO_2 storage in U.S. coals, shales, basalts, and ultramafic rocks is orders of magnitude less than that in saline formations. Saline formations in the United States may be able to hold 2,300 to 3,700 billion metric tons (gigatons, Gt) of CO_2 (U.S. Geological Survey Geologic Carbon Dioxide Storage Resources Assessment Team, 2013a), but coal may only be able to hold 60 to 120 Gt of CO_2 (U.S. Department of Energy, National Energy Technology Laboratory, 2012). McGrail and others (2006) estimated that the Columbia River Basalt Group in the Western United States could hold 100 Gt of CO_2.

Because the mechanisms for CO_2 storage in organic-rich rocks are so different from those in ultramafic rocks, and because the state of knowledge regarding these mechanisms and the state of pilot carbon storage projects in these two groups of lithologies are so different, the workshop split into two groups to discuss these unconventional storage reservoirs separately. This document addresses the findings of the coals and organic-rich shales group first, and the findings of the group that considered storage in basalts and ultramafic rocks second.

Coal and Organic-Rich Shale

Coal—and, by extension, organic-rich shale—is an excellent lithology for storing CO_2, although the bulk volume of coal is orders of magnitude less than that of the sandstones and limestones typically considered for conventional geologic CO_2 storage. Coal has a CO_2 storage capacity per unit volume that is five or six times that of conventional reservoir rock because of the large internal surface area in coal's networks of micropores (Clarkson and Bustin, 1999; Shi and Durucan, 2005). Carbon dioxide adsorbs to the surfaces of organic material in coal and organic-rich shale, and is held there permanently by van der Waals forces unless pressure and temperature conditions change (Mastalerz and others, 2004). Some absorption of CO_2 into the coal may also occur (Reucroft and Sethuraman, 1987; Milewska-Duda and others, 2000). Formation volume and sorption characteristics (that is, how much CO_2 can be stored per unit volume) of coal and organic-rich shale would be the main inputs to a storage assessment calculation for these resources.

When the workshop participants discussed how to assess CO_2 storage in coal and shale, many questions arose. For example: What type of storage will be assessed—only sorption, or also buoyant trapping and residual trapping in pore spaces? How essential is a cap rock or sealing formation? There may be less need for sealing formations above unconventional storage reservoirs than above conventional storage reservoirs; for example, when CO_2 is adsorbed to or absorbed in coal or organic-rich shale, the CO_2 is immobile and does not leak if pressure and temperature remain constant. Injected CO_2 may not have to be in a supercritical state for it to be stored by adsorbtion and absorption in coal and organic-rich shale, so how might this affect the depth requirements for CO_2 storage? How will hydraulic fracturing affect storage potential, particularly in organic-rich shales? Will possible "utilization" of the stored CO_2 play a role? For example, CO_2 can be injected into hydrocarbon-bearing reservoirs to recover methane in a process called enhanced gas recovery. It may also be necessary to consider the effect of CO_2 on methane-producing microbial communities in the subsurface.

Porosity and Permeability

Coal is stress-sensitive and its porosity and permeability change with depth. Coal acts like a sponge: it shrinks when gas desorbs from it and swells when gas adsorbs to it. Following injection, adsorption of CO_2 to the coal surface occurs over days (Kovscek and others, 2006). Coal preferentially adsorbs CO_2 over methane or nitrogen, so at any given pressure, coal can adsorb several times as many molecules of CO_2 as of methane (Gentzis, 2000; Stanton and others, 2001; Gluskoter and others, 2002; Krooss and others, 2002; Burruss, 2003; Mastalerz and others, 2004; Busch and Gensterblum, 2011). Replacing adsorbed methane with adsorbed CO_2, then, requires additional volume causing coal to swell (Cui and others, 2007; Bustin and others, 2008; Hol and others, 2011). Coal permeability is likely to change over the lifetime of an injection project. These permeability changes can cause weakening and failure of the organic-rich matrix. Coal swelling, however, is a dynamic process and is therefore beyond a static calculation of maximum CO_2 storage capacity. It might be better addressed as a storage efficiency factor that can reduce capacity from a theoretical maximum to an expected "effective capacity."

Wet coal has less capacity to adsorb CO_2 than dry coal does, because water blocks some adsorption sites on the coal surface (Gensterblum and others, 2013). Wet environments, then, may present a challenge for assessing storage capacity as water saturation can reduce the theoretical maximum gas adsorption. The moisture content of coals should therefore be considered in a realistic assessment of coal's storage capacity—again, possibly as a storage efficiency factor.

Although swelling from gas adsorption is understood relatively well for coal, it is not yet known whether swelling is an important parameter for CO_2 storage in organic-rich shale (Heller and Zoback, 2014). Shale contains much less organic material than coal does, so the effect of this factor would be very different.

Understanding adsorption isotherms for coal, or quantifying the available pore space in organic-rich shale, could be the basis for a well-constrained assessment. Although these kinds of data are unavailable in many areas that have not been exploited for energy resource production, it may be possible to use coal rank or vitrinite reflectance to estimate adsorption characteristics.

Minability

Precisely what types of coal deposits would be considered—all coal, or some subset of coal—for an assessment of potential CO_2 storage in coal beds needs to be defined. In the past, CO_2 storage has only been considered in "unminable" coals—those that cannot be mined economically using current technology. This is an important issue because adding CO_2 to coal may render the coal unminable. Mining and burning coal that contains stored CO_2 would release the CO_2 back to the atmosphere and could create unsafe conditions for mine workers. The presence of CO_2 makes coal respond differently to stresses than an unmodified coal bed would, and, as discussed at the workshop, this change in response could contribute to roof falls, rock bursts, bumps, and floor heave (Koperna and others, 2013).

Defining unminable coal is difficult because the minability of coal changes by mining company, basin, and seam. It also changes as mining technology improves and as the global energy economy changes. Minability also may not strictly be the real question, because underground gasification or other techniques for in-place use of energy resources could allow energy to be extracted from coal beds without mining them conventionally.

The group consensus was to stop trying to distinguish minable and unminable coal because, technically, any coal could ultimately be mined. An assessment of potential CO_2 storage in any coal should be based on physical, non-economic criteria. The portions of this storage resource that are located in areas that could be mined—particularly areas that are of high economic value or that may be mined soon—could then be subtracted from the calculated total storage resource if necessary. This would be similar to the groundwater salinity cutoff in the existing storage assessment of residual and buoyant trapping—although it is physically possible to store CO_2 in formations that are underground sources of drinking water (less than 10,000 ppm total dissolved solids), this storage is generally prohibited and so CO_2 storage in these formations is not considered.

Organic-Rich Shale

Most discussions of storing CO_2 in organic-rich rocks focus on coal, but organic-rich shale is also a possible target lithology for CO_2 storage. Although this type of shale is unlikely to be a primary target for this storage, the possibility of extracting shale gas as a profitable byproduct of CO_2 storage makes it an attractive economic option. Workshop participants raised questions about which shales should be assessed—only shale from which gas, oil, or both have been produced, or all shale? The group reached the consensus that CO_2 storage capacity should be assessed in all organic-rich shales. Minimum criteria of maturity of at least 0.5 percent vitrinite reflectance (R_o) and about 1 percent total organic content were proposed, but it was noted that an organic content cutoff might need to vary by basin. For example, most shales used to store CO_2 would contain at least 3 percent total organic carbon, but some notable shales of less than 1 percent total organic carbon should also be assessed.

Environmental Concerns

Environmental concerns from CO_2 injection into coal and organic-rich shale include CO_2 leaking to the atmosphere, groundwater contamination, and induced seismicity.

Storage integrity—that is, preventing leaks—is an important risk factor in geologic CO_2 storage. Workshop questions included the following: How long can CO_2 stay in these rocks? Do reactions that occur between CO_2, other pore fluids, and the host rock during and after injection influence this storage? We need more information on storage capacity, the time required for injection and adsorption, and whether the host rock changes due to the presence of CO_2 over time: the first pilot projects involving CO_2 storage in coal only began in the 1990s. Monitoring of any CO_2 storage project—before injection to establish a baseline, during injection, and after injection—will be critically important.

Participants discussed whether an overlying low-permeability sealing formation is necessary for reducing risk associated with CO_2 storage in coal and organic-rich shale. Carbon dioxide would be stored in these lithologies almost entirely by sorption (regardless of the presence or absence of an overlying seal), and so the CO_2 would be fixed to the rock as long as pressure and temperature did not change after injection while the CO_2 is being stored. If pressure decreased, for example, some adsorbed CO_2 would tend to desorb in response. The general consensus was that sealing formations, like those required for CO_2 stored in conventional lithologies by buoyant trapping, would increase the safety factor. Therefore, it would be prudent to require the presence of sealing formations overlying any coals or organic-rich shales assessed as potential CO_2 storage formations.

Organic molecules (Kolak and Burruss, 2006) and toxic metals (Kharaka and others, 2006) liberated from the storage formation by the formation interacting with injected CO_2 could leak into water wells and aquifers. Some injected CO_2 itself may also leak into these wells and aquifers. One-third of U.S. drinking water is produced from wells tapping underground sources of drinking water (U.S. Environmental Protection Agency, 2012). We need to (a) understand the organic components that come from shale, oil, and coal beds, and (b) understand the toxicity of the organic components, and the reactions they

undergo underground. We know little about dissolved organic molecules, but they could allow early detection of CO_2 leaks into groundwater. Though potential groundwater contamination will be an operational concern, it does not affect the storage resource calculation.

Groundwater salinity does not place a physical limit on CO_2 storage, but it places a regulatory limit on where CO_2 can be injected, removing a large potential storage volume from consideration for storage. The current conventional assessment methodology (Brennan and others, 2010) uses 10,000 ppm total dissolved solids as a minimum.

Produced waters resulting from any CO_2 injection project must be disposed. Although this is an environmental concern, produced waters do not affect storage capacity and therefore are not an assessment consideration.

Although induced seismicity is a concern for safety, formation integrity, and public opinion, it is beyond the scope of an assessment. It is an operational concern that does not affect a calculation of potential storage capacity. It is assumed that injection will not fracture the host formation. Safe pressure rules can be determined locally for storage sites by monitoring the pressure during injection tests (for example, Gilliland and others, 2013). Participants also expressed concern about using formations for storage that have previously been hydraulically fractured for petroleum extraction, suggesting that poorly controlled hydraulic fracturing may have created paths for leakage or for unwanted lateral migration of fluids.

Summary

At the end of the coal and organic-rich shale discussion, the group assembled a list of the most important issues to consider for an assessment of CO_2 storage potential in this unconventional resource. These issues were formation geometry, including depth and volume; the adsorption capacity of the rock, determined by adsorption isotherm analysis if possible, otherwise by coal rank (for coals) or vitrinite reflectance and total organic content (for shales); and formation porosity. Secondary issues, less important for an assessment but still worth considering and reporting on, included formation permeability (above a certain minimum) and injectivity, the pore size distribution, and whether the formation has been hydraulically fractured or contains coal mines. The participants also suggested assessing (a) the total CO_2 storage resource that these lithologies represent and (b) the amount of CO_2 that could be stored if such storage only resulted from profitable enhanced gas recovery.

Any capacity assessment should start with observable variables that are important and relatively easy to determine. Observations include total volume of the target formation, adsorption isotherm data (or thermal maturity or coal rank to predict adsorption capacity where isotherms are unknown), the presence or absence of sealing formations, the presence or absence of underground sources of drinking water, the regional pressure-depth relationship, and total organic content of the target formation.

Basalts and Ultramafic Rocks

Storing CO_2 in mafic or ultramafic rocks, in which CO_2 reacts to form solid, stable carbonates, eliminates much of the risk of CO_2 leaking to the atmosphere or affecting nearby aquifers. Until recently, the costs of mineral carbonation technologies were prohibitive and were excluded from USGS geological assessments because the technology was unlikely to be used for large-scale storage of CO_2. However, new pilot studies have shown a decrease in the costs and reaction times of mineral carbonation.

During mineral carbonation, CO_2 reacts with magnesium, iron, and calcium silicate phases to form stable carbonates. The most energetically favorable phases that exist in place in large volumes are found in mafic and ultramafic rocks (for example, Seifritz, 1990; Lackner and others, 1995; Kelemen and Matter, 2008; Oelkers and others, 2008). Ultramafic rocks, including peridotite and serpentinite, contain abundant magnesium, iron, and calcium in the form of olivine and serpentine. Mafic rocks, including basalt, contain abundant magnesium, iron, and calcium in the volcanic glass. Previous studies have shown the areal extent of ultramafic and mafic rocks (Oelkers and others, 2008; Krevor and others, 2009; U.S. Department of Energy, National Energy Technology Laboratory, 2012) and estimates of storage capacity in deep sea basalts (Goldberg and Slagle, 2009) and the Columbia River Basalts in the United States (McGrail and others, 2006), yet there is no clear estimate of how much CO_2 could be stored in the mafic and ultramafic rocks of the United States.

The basalt and ultramafic rocks working group first examined the state of experimental research, modeling, and pilot projects and then addressed the feasibility of assessing potential long-term subsurface CO_2 storage by mineralization.

Recent Advances in Modeling and Experiments

Recent experiments related to the interaction of CO_2 with basalt or ultramafic rocks have improved the understanding of dissolution and precipitation kinetics for the relevant phases (for example, Daval and others, 2010; Stockmann and others,

2014), the kinetic differences between supercritical and aqueous CO_2 (for example, Schaef and others, 2011, 2013), the mutual solubilities between CO_2 and water (for example, Spycher and others, 2003; Spycher and Pruess, 2005), and the effect of catalysts on reaction rates (for example, Stolaroff, 2013).

Workshop participants presented results of a number of experiments, some of which had not yet been published. Research by the National Energy Technology Laboratory using Columbia River Basalt Group core samples from the Wallula pilot project (McGrail and others, 2011a,b) have shed light on the effect of supercritical CO_2 on basalt, the natural formation waters within the fractures and pore space, and pre-existing microbial communities (Lavalleur and Colwell, 2013). Bacteria were found to exist in all samples, and iron-rich carbonates and iron hydroxides formed when exposed to supercritical CO_2. Computed tomography (CT) scanners with resolutions of 240 micrometers to 1 micrometer (Crandall and Bromhal, 2013) are being used to image CO_2 flow at reservoir conditions through Grande Ronde Basalt from the Columbia River Basalt Group, and these images help researchers infer how subsurface CO_2 moves during pilot tests. Experiments on Columbia River Basalt samples at the Pacific Northwest National Laboratory show that mutual solubilities of CO_2 and water can have a large impact on reaction kinetics (McGrail and others, 2011b). The amount of CO_2 that can be dissolved in water varies little with pressure and temperature, yet water solubility in supercritical CO_2 is highly dependent on temperature at high pressures. Experiments with such water-rich supercritical CO_2 show the formation of carbonate layers, an increase in iron content, and long rods of amorphous silica after 180 days (McGrail and others, 2011b). The inclusion of SO_2 causes secondary sulfide minerals to form, removing sulfur species from the water-rich supercritical CO_2.

Hydrothermal autoclave experiments using crushed basalt samples from multiple locations show that the extents of reactions depend largely on temperature and basalt composition (Rosenbauer and others, 2012). In particular, the magnesium content of the rock is a good indicator of reaction extent. Other hydrothermal autoclave experiments were performed on olivine, the dominant mineral in ultramafic rocks (Johnson and others, 2014). These showed that an amorphous silica layer often forms on the surface of olivine crystals, but organic acids in the presence of CO_2 release magnesium from the olivine, increasing alkalinity and triggering carbonate precipitation and greater storage through mineralization. Further, flow mechanics of CO_2-rich fluids may provide ways to increase porosity and permeability in ultramafic rocks, enhancing the potential for CO_2 storage. Other laboratories are using autoclave experiments to specifically study dissolution and carbonate reaction kinetics. Experiments on olivine by Qiu and others (2012) show that temperature, pressure, pH, mineral surface properties, and experimental methods all affect dissolution rates: reactions occur more rapidly at higher temperatures, with greater concentrations of dissolved inorganic carbon in the fluid, and with smaller grains of olivine. Dissolution and precipitation modeling by Prigiobbe and Mazzotti (2013) supports such experiments. Dissolution rates were calculated for a range of temperatures and pH values and the presence of salts. Precipitation kinetics were then determined for the resulting magnesium carbonates.

Remaining gaps in experimental and modeling knowledge include a multi-laboratory consensus regarding reaction kinetics, updated thermodynamic data and activity models, and a better understanding of relative permeabilities.

Pilot Projects

Current pilot projects for CO_2 injection into basalt include CarbFix in Iceland (Gislason and others, 2010; Matter and others, 2011; Aradóttir and others, 2012) and the Wallula pilot project (McGrail and others, 2011a) in the Pacific Northwest.

Iceland, located on the Mid-Atlantic Ridge, is almost entirely composed of basalt. The Hellisheiði geothermal power plant releases 60,000 tons of magmatic CO_2 per year, and the CarbFix project plans to mix 2,000 tons per year of this CO_2 with water and inject it into basalt at a depth of about 1770 ft (540 m) (Matter and others, 2011; Aradóttir and others, 2012). The aqueous CO_2 will further mix with groundwater and react with the basalt to form stable carbonates. Five wells allow monitoring of subsurface fluid movement. Conservative tracers, trifluoromethyl sulfur pentafluoride (SF_5CF_3) and sulfur hexafluoride (SF_6), are used to determine how the injected fluid advects and disperses. Radiocarbon tagging distinguishes injected CO_2 from preexisting CO_2 (Matter and others, 2011). In January 2012, 175 tons of pure CO_2 was injected into the basalt target, and in July 2013, 73 tons of a mixture of CO_2 and H_2S was combined with 2,500 tons of water and was injected into the basalt target (Matter and others, 2014).

The Wallula pilot project (McGrail and others, 2011a,b) is a study of CO_2 injection into the Columbia River Basalt, a large continental flood basalt province covering parts of Washington, Oregon, and Idaho. The project is run by the Big Sky Carbon Sequestration Partnership, led by Montana State University and largely funded by the U.S. Department of Energy. The field site is located above some of the deepest and thickest basalt of the Columbia River Basalt Group in eastern Washington. The injection target is the Slack Canyon member of the Grande Ronde Basalt at a depth below 2,700 ft (823 m). Unlike the CarbFix pilot project, the Wallula pilot project injects supercritical rather than aqueous CO_2 into the subsurface. An extensive characterization process was completed (McGrail and others, 2009), including seismic analyses and simulation modeling, as well as hydrologic and microbiological testing. Injection of 1,000 tons of CO_2 into the Grande Ronde Basalt in eastern Washington began in July 2013 and monitoring activities are ongoing.

Future work for these and other pilot projects will seek a better understanding of basalt seal integrity, monitoring tools, and how lab experiments scale up to the field level.

Volumetric Equation for Storage by Mineralization

Several quantifiable parameters of a volumetric equation are necessary to complete a probabilistic assessment of potential mafic or ultramafic rock storage. The mappable area and thickness of a given rock body is the starting point for an assessment. The primary and secondary porosity, as well as the mineralogy and the proportion of unaltered rock, will determine how much of that rock will interact with CO_2. Dissolution and precipitation kinetics will be controlled by temperature, pressure, oxygen fugacity, water chemistry, and pH. Other parameters that may affect the availability of formations for CO_2 storage because of environmental concerns include water quality and toxic metal composition within trace mineral phases.

Conclusions

At the end of the workshop, participants agreed that sufficient knowledge exists to allow an assessment of the potential CO_2 storage resource in coals, organic-rich shales, and basalts. More work remains to be done before the storage resource in ultramafic rocks can be meaningfully assessed.

In order to assess the CO_2 storage capacity of coals and organic-rich shales, the workshop participants agreed that the following several factors are key: sorption mechanisms and capacity, pore fluid composition and saturation, thermal maturity, formation thickness, and whether hydrocarbons have been extracted from the formation previously (for example, by enhanced gas or oil recovery). In order to assess the CO_2 storage capacity of basalts, the workshop participants agreed that the key factors include temperature, pressure, pH, water chemistry, mineral chemistry, organic content, mineralogy, porosity, permeability, relative permeabilities, and CO_2 phase. Similar to the recent USGS residual and buoyant trapping assessment, the storage capacity for all unconventional reservoirs may be modeled with a volumetric equation starting with the extent of the rock unit, and adjusted using the key factors listed above and including reaction terms.

The ideas that were developed during this workshop can be used by USGS scientists to develop a methodology to assess the CO_2 storage resource in unconventional reservoirs. This methodology could then be released for public comment and peer review. After completing this development process, the USGS could then use the methodology to assess the CO_2 storage resource in unconventional reservoirs.

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