ABSTRACT

The Jurassic Navajo Sandstone on the Colorado Plateau of Utah may be considered for sequestration of CO$_2$, because it is thick, widely distributed, has a high porosity and permeability, is typically horizontal to gently folded, is favorably located with respect to seal strata, and underlies many large point sources of CO$_2$. However, faulting common on the Colorado Plateau may provide pathways for leakage of the CO$_2$ similar to present-day geysers and CO$_2$-charged springs. Natural groundwater present in the Navajo Sandstone includes a range of low-salinity, moderate-salinity with high bicarbonate, and high-salinity waters. Higher salinity waters may have moved from deeper strata under artesian pressures or originated from solution of evaporite in pre-Jurassic rocks. These characteristics make the Navajo Sandstone an excellent analog for examining the geochemistry of CO$_2$ injection into deep saline aquifers. The storativity of CO$_2$ in solution is a function of the solubility of CO$_2$ in these waters, which is dependent on salinity, temperature, and pressure. Geochemical modeling shows that the coolest, least saline water can contain the most CO$_2$ in solution. Dissolving CO$_2$ in the water lowers the pH, so that no minerals precipitate, and the Navajo Sandstone contains only small amounts of mineral that may consume the H$^+$. The reaction of the acidic water produced by dissolving CO$_2$ with K-feldspar and minor clays and calcite in the sandstone throughout 500 yr consumes little H$^+$ and produces only small amounts of product minerals. The Navajo Sandstone likely would not store significant CO$_2$ as mineral precipitate, and thus, stored volumes of CO$_2$ would be limited by its solubility in the in-situ water and storage as free CO$_2$ in pore space.
INTRODUCTION

Large quantities of anthropogenic CO₂ generated by burning fossil fuels are contributing to a rise in CO₂ concentrations in the Earth’s atmosphere. Average releases at United States power plants are 2.7 million t of CO₂ each year, with large power plants releasing more than 18 million t (Hovorka et al., 2001). This has led to concerns that growth in concentrations of CO₂ in the atmosphere is contributing to a greenhouse effect that is affecting global climate. Despite uncertainty in estimating the impact of CO₂ emissions on future climate, the general scientific consensus is that CO₂ emissions should be minimized (Intergovernmental Panel on Climate Change, 2001). One element of a multifaceted strategy for limiting CO₂ emissions is to sequester CO₂ in geologic formations. Carbon dioxide can be stored in the subsurface as (1) a dissolved constituent in naturally occurring groundwater; (2) mineral precipitates produced by chemical reactions; and (3) free CO₂ as a supercritical fluid in the pore spaces of reservoir rock (Gunter and Perkins, 1993; Bachu et al., 1994; Law and Bachu, 1996; Perkins and Gunter, 1996; van der Meer, 1996; Pruess et al., 2001; Bachu and Adams, 2003).

Regional-scale sedimentary aquifers in subsurface geological structures offer a large storage capacity for CO₂ (Hendriks and Blok, 1993; Law and Bachu, 1996; McPherson and Cole, 2000; Lackner, 2003). Deeper aquifers are more attractive than shallow aquifers (van der Meer, 1993; Bergman and Winter, 1995). The aquifer should be capped by a regional aquitard, the depth should be more than 800 m (2600 ft) deep, and the aquifer should possess adequate porosity and permeability (Bachu et al., 1994). The residence or traveltime in regional aquifers is of the order of thousands to millions of years (Bachu et al., 1994). Deep brines absorb less CO₂ than low-salinity waters, but additional storage capacity may be provided because of water-rock reactions; in fact, large amounts of carbonate minerals can precipitate in some cases (Gunter and Perkins, 1993). The acidity produced by dissolving CO₂ may be consumed by dissolution of calcite and by reaction with alumino-silicate minerals such as feldspar if they are sufficiently abundant (Gunter and Perkins, 1993). However, some numerical modeling has shown that only small amounts of the carbonates are precipitated because they are quite soluble under the reservoir conditions of high CO₂ pressure and resulting low pH. The ferrous carbonate siderite can trap CO₂ if organic matter, petroleum, or some other reductant can chemically reduce the iron. Long-term CO₂ storage may lead to a decrease in porosity because of mineral precipitates and alteration. Alteration product hydrous alumino-silicates generally occupy larger volumes than the precursor minerals (Pruess et al., 2001).

The process of collecting the CO₂ at a point source (e.g., a power plant or gas field production well), transporting it to a well site, and injecting it into a subsurface reservoir is commercially proven, and commercial geologic sequestration has begun in natural
Assessing the viability of a CO₂ sequestration reservoir requires studying the basic geology of a sequestration site, evaluating potential pathways for leakage, and performing geochemical analyses that help to determine the likely behavior of CO₂ introduced to the reservoir-seal system (Law and Bachu, 1996). Numerical modeling of the fluid flow and geochemical processes is necessary to understand the long-term sequestration of CO₂ because chemical reactions with aluminosilicates and fluid flow in the porous reservoirs are slow and cannot be duplicated in laboratory experiments (Pruess et al., 2001).

Injection of CO₂ into petroleum reservoirs for secondary recovery may also provide an indication of the nature of fluid-rock interaction. For example, CO₂ has been injected into the Pennsylvanian–Permain Weber Sandstone, an eolian deposit (Fryberger, 1979) with mineralogy and sedimentary petrography similar to the Navajo Sandstone (Bowker and Shuler, 1991). The Weber Sandstone is the major petroleum-producing reservoir at the Rangely field, Colorado. Much of the Weber Sandstone is cemented with ferroan calcite, ferroan dolomite, and illite, and interstratified illite-smectite cements comprise approximately 5% of the sandstone. The pH of the brine produced from wells decreased from 7.5 to 4.5 from initiation to end of injection. The concentrations of Fe, Ca, and Mg in produced brine increased as a function of solution of carbonate, clays, and feldspars. The pH increased from 3.5 at injection wells to 4.5 at production wells. No net change in permeability was observed as a consequence of CO₂ injection (Bowker and Shuler, 1991).

Kharaka et al. (2006) investigated the potential for CO₂ storage in a saline aquifer. They injected 1600 t of CO₂ into the Frio Formation, a regional oil reservoir in the United States Gulf Coast. Injection of CO₂ resulted in a sharp drop in pH to 5.9 and increases in alkalinity and dissolved Fe. The solution of carbonate and iron oxyhydroxides buffered the pH, which geochemical models show would otherwise have dropped to 3.

This study focuses on the geochemical aspects of CO₂ sequestration in faulted and folded eolian Navajo Sandstone located in the Colorado Plateau region of Utah (Figure 1). Issues addressed include (1) the chemical characteristics of water naturally present in the these sandstones; (2) the chemical characteristics of water that may flow into the sandstones from aquifers with contrasting water types; (3) the solubility of CO₂ in these waters; (4) the geochemical consequences of solution of CO₂ in the diverse water types; (5) mixing of waters derived from aquifers beneath the Navajo; and (6) the reaction of CO₂-charged waters with reactive minerals in the sandstones and overlying seal rocks. The likely effects of mineral dissolution and precipitation are also evaluated.

The Colorado Plateau province is an elevated block of mildly deformed rocks and thickened crust encompassing an area of $3.6 \times 10^6$ km$^2$ ($1.4 \times 10^6$ mi$^2$) centered around the four corners of Utah, Colorado, Arizona, and New Mexico. The upper geologic section of the Colorado Plateau comprises a thick Mesozoic sedimentary sequence that includes permeable Jurassic eolian sandstones (prospective sequestration reservoirs) beneath a Late Jurassic to Cretaceous sedimentary sequence that includes low-permeability mudstone, shale, and carbonate beds (prospective reservoir seals).

Several factors make the Colorado Plateau region of Utah an attractive target for CO₂ sequestration (Haszeldine et al., 2005). Natural CO₂ reservoirs already exist to show sequestration feasibility and provide natural reservoir analogs. Allis et al. (2001) identified 12 major CO₂ accumulations with more than 30 billion m$^3$ (1059 billion ft$^3$) of gas in place. Some reservoirs have already been partially depleted through drilling and production. Other CO₂ reservoirs are releasing CO₂ to the atmosphere through fault-related breaches in seal rocks and geysering drill holes (Shipton et al., 2004).

Mantle degassing, metamorphism of carbonate sediments, and oxidation of hydrocarbons are among possible sources of this CO₂ (Shipton et al., 2004). Helium isotopes suggest that only a minor mantle component is present, and carbon isotopes suggest that the probable source is thermal decarbonation of carbonate sediments within the contact aureoles of igneous intrusions (Shipton et al., 2004).

Large, coal-fired power plants operating in the region produce CO₂, and new power plants are planned. The CO₂ produced may be sequestered in favorable sedimentary strata (Allis et al., 2001). Wastewater from coal-bed gas production is presently injected into the Navajo Sandstone (Conway et al., 1997). The eolian Navajo Sandstone forms a well-studied and extensive candidate sequestration reservoir with high porosity and permeability, relatively simple chemical and mineralogical composition, and good reservoir seals, although faults may permit the seals to leak (Shipton et al., 2004; Heath et al., in press).
METHODS

The geochemistry of CO$_2$ sequestration in the Navajo Sandstone is evaluated using petrographic examination, whole-rock chemistry, clay mineralogy, calculated modal mineralogy, and geochemical modeling. Samples of Navajo Sandstone were collected in outcrop on the Colorado Plateau. Sampling areas and detailed sample localities are given in Beitler et al. (2005) and Bowen (2005). Samples of host rock ($n = 74$) representing diagenetic types were submitted to Actlabs for whole-rock analyses by inductively coupled plasma–mass spectroscopy for major, minor, and trace elements. Clay minerals were extracted from 10-g samples of host rock by mild hand grinding in a mortar and then peptizing in water. Centrifuging separated the less than 2-µm-size fraction. Centrifuged slurry was smeared on glass slides for x-ray diffraction analyses. Thin sections ($n = 66$) were stained for K-feldspar and examined in the petrographic microscope. Polished sections were examined under reflected light. The modal mineralogical composition of Navajo Sandstone samples was calculated using a linear, least-squares fit of whole-rock chemistry, mineral composition, and mineral mass abundance described by Parry et al. (1980). Petrography, bedding, thickness, permeability, porosity, and mineralogy
of subsurface samples studied by Lindquist (1983) from the Nugget Formation, an equivalent to the Navajo Sandstone, in southwestern Wyoming are similar to petrography and mineralogy of outcrop samples in this study, suggesting that outcrop samples adequately represent the Navajo Sandstone.

Geochemical reaction paths for mixing of different waters, for the reaction of CO₂-charged waters with Navajo Sandstone, and for leakage of CO₂-charged waters through faults were calculated using The Geochemists Workbench (Bethke, 1998). Model calculations were done for a temperature of 60°C and 100 bars (1450 psi), well above the critical temperature for CO₂ of 31°C and 74 bars (1073 psi). Water chemistry typical of the Navajo Sandstone used in the model calculations was from Hood and Patterson (1984), Kimball (1992), and Spangler et al. (1996).

### STRATIGRAPHY

The sequence of Mesozoic sedimentary rocks on the Colorado Plateau of southeastern Utah includes three permeable eolian sandstone units of the Glen Canyon Group that are exposed on the flanks of the regional Laramide uplifts (Figure 2). The eolian Wingate Formation, the Navajo Sandstone, and the Entrada Sandstone are targets of this work and are the site of deep-water injection (Conway et al., 1997). The Kayenta Formation that separates the Wingate Formation from the overlying Navajo Sandstone is fluvial, and the Chinle (fluvial) and Moenkopi (marine) formations beneath the Wingate Formation are fine-grained aquitards. The Carmel Formation that forms a seal unit above the Navajo Sandstone represents a complex sabkha sequence of sandstone, siltstone, mudstone, limestone, anhydrite, and gypsum.

### THE NAVAJO SANDSTONE

The Early Jurassic Navajo Sandstone and its related equivalents, the Nugget Sandstone of northern Utah and Wyoming and the Aztec Sandstone of Nevada, form the largest eolian dune deposit in North America (Blakey et al., 1988; Peterson and Turner-Peterson, 1989; Blakey, 1994). The Navajo Sandstone is the thickest, most laterally extensive (Figure 1), and most permeable unit in the Mesozoic section of the Colorado Pla-
teau. In the eastern half of the Colorado Plateau, the Navajo Sandstone and its equivalents cover an area of more than 3.5 \times 10^5 km^2 (1.35 \times 10^5 mi^2), with deposits more than 670 m (1213 ft) thick, and a volume of up to 1.4 \times 10^5 km^3 (3.35 \times 10^4 mi^3) (Blakey, 1988). The thickest parts of the Navajo Sandstone (up to 700 m [2300 ft]) occur in southwestern Utah, which represents the main accumulation of eolian sand. The eolian sandstone is characterized by high-angle, large-scale cross-stratification and striking red to white variations associated with primary depositional patterns and extensive bleaching caused by fluid migration (Chan et al., 2000; Parry et al., 2004). Wingate Sandstone, Navajo Sandstone, and Kayenta Formation are extensively bleached along steeply dipping eastern limbs, along the flanks, and along the remaining crests of the San Rafael swell, Circle Cliffs uplift, Kaibab uplift, and Monument uplift (Figure 1) (Beitler et al., 2003). Bleached sandstone contains less calcite and dolomite cement, less hematite, and more K-feldspar alteration to clay (Beitler et al., 2005). The Navajo Sandstone is a fine-grained quartz arenite that is texturally mature, and fine to medium grained. Cordova (1978) divided the Navajo Sandstone into three informal units. Although there are some internal stratigraphic differences, Hood and Danielson (1979), Hurlow (1998), and others, however, suggest that the entire formation can be represented as one relatively homogeneous unit particularly for injection and chemical-reaction modeling purposes. The Navajo Sandstone is unconformably overlain by the J-2 unconformity (Figure 2). The Navajo Sandstone is known as an important groundwater aquifer throughout much of the Colorado Plateau (Cordova, 1978; Hood and Patterson, 1984; Howells, 1990; Kimball, 1992; Spangler et al., 1996; Hurlow, 1998).

In various areas of Utah, the Navajo Sandstone typically contains different facies units such as cross-bedded dune sandstone; massive, uniform sandstone (sometimes with contorted cross-strata); horizontal stratified interdune sandstone; and some carbonate playa and interdune deposits (e.g., Verlander, 1995; Thomas et al., 2000). In addition, internal stratification with some thin horizons of very high permeability (grain flow laminae of Hunter, 1977) occur along dune foresets, and very low-permeability horizons up to 30 cm (12 in.) thick lie at the base of some dune sequences (wind ripple laminae of Hunter, 1977, with finer grained sand, silt, and mud). Dune sets typically range in thickness from 4 to 20 m (13 to 66 ft) thick in the northern San Rafael swell (S in Figure 1), but can also be several tens of meters thick elsewhere.
Beitler et al. (2005) interpret bleaching patterns of the normally red Navajo Sandstone to indicate the pathways of paleofluid flow. Bleaching on a regional scale occurs on the crests of uplifts and commonly occurs at structural inflections. On an outcrop scale, bleaching is restricted by low-permeability deformation bands, interdune limestone-chert layers, and fine-grained to muddy wind ripple laminations (Beitler et al., 2005). These relationships suggest that flow and storativity of CO$_2$ are determined by regional-scale characteristics.
Locally, another eolian unit, the Page Sandstone, overlies the Navajo Sandstone (Figure 2) (Blakey, 1994). Because the Page Sandstone is similar in lithology and facies and occurs only locally, it can be treated as part of the Navajo Sandstone for modeling purposes.

THE CARMEL FORMATION

The Carmel Formation overlies the Navajo Sandstone and/or the Page Sandstone where present throughout most of the Colorado Plateau (Wright and Dickey, 1963). The Carmel Formation is a heterogeneous sabkha sequence of interbedded sandstone, siltstone, mudstone, limestone, anhydrite, and gypsum that overlies the Navajo Sandstone and forms the primary seal that would limit upward migration of CO₂ from the Navajo Sandstone reservoir. The Carmel Formation reaches a maximum thickness of 400 m (1312 ft) and averages more than 100 m (330 ft) across much of the Colorado Plateau region. Anhydrite and alabaster gypsum beds in the upper Carmel Formation comprise 50% of the unit. Individual gypsum beds are more than 2 m (6.6 ft) thick (Trimble and Doelling, 1978). Calcite cement is common in the clastic strata, but silica, gypsum, and hematite cements are also present (Wright and Dickey, 1963; Doelling, 1975; Trimble and Doelling, 1978; Doelling and Davis, 1989; Doelling et al., 2000). Mercury injection porosimetry reported by White et al. (2005) shows that anhydrite with displacement pressures of 30–60 bars (435–870 psi) forms the most effective seal. The Mancos Shale is the next most effective seal. Thus, the gypsum beds (anhydrite in the subsurface) in the Carmel Formation may form a good seal stratum.

STRUCTURE

Monoclinal folds, anticlines, domes, basins, and faults deform the generally flat-lying Navajo Sandstone and overlying Carmel Formation (Hunt, 1956; Davis, 1999). Early Tertiary compression formed a series of monoclines, with the Navajo Sandstone dipping at angles in excess of 60° to the east (e.g., the Kaibab, Circle Cliffs, Monument, and San Rafael monoclines) (Figure 1). The Navajo Sandstone has been removed from much of the crest area of these broad, asymmetrical monoclines, which are bounded by steeply dipping, blind, reverse faults (Davis, 1999; Bump and Davis, 2003). Deformation bands are common in the steep parts of these structures. The deformation bands significantly reduce the porosity and permeability of fault-affected rocks (Antonellini and Aydin, 1994; Shipton et al., 2002). Shipton et al. (2002) and Sigda and Wilson (2003) show that hydraulic conductivity is three orders of magnitude less in cataclastic deformation bands than in undeformed sandstone. Smaller basins occur between the monocline uplifts, such as the Henry Mountain Basin between the Circle Cliffs and Monument uplifts (Figure 1).

The Navajo Sandstone has also been folded into broad anticlines and domes that provide adequate structural traps for storage of buoyant CO₂ fluids, including the Farnham Dome field (Morgan and Chidsey, 1991). Northwest-trending anticlines and associated faults occur in east-central Utah underlain by thick evaporite beds. The evaporite beds of the Pennsylvanian Paradox Formation have been deformed to produce eight, northwest-southeast–trending salt anticlines, where the salt is locally thickened to more than 4 km (2.5 mi) (Cater, 1970). Salt intrusion structures were covered by 2 km (1.2 mi) of post-Triassic sedimentary rocks (Doelling, 1988), and exhumed about 37 Ma (Nuccio and Condon, 1996). Salt was dissolved by groundwater, forming the Moab and Lisbon Valley graben. The salt anticlines lie above and parallel to basement faults.

Northward-trending fault-bounded blocks of the geographical High Plateaus are bounded by Basin and Range normal faults that include, from west to east, the Hurricane, Sevier, and Paunsaugunt faults. Finally, a series of domes and folds are related to Tertiary laccolithic intrusions in the Henry, La Sal, and Abajo Mountains.

Abundant, closely spaced faults displace Jurassic and Cretaceous formation along the northern part of the Kaibab monocline, the Escalante anticline, and the San Rafael swell. The Teasdale fault zone forms the northern margin of the Miners Mountain uplift. Trace lengths of some of the faults are many kilometers (Davis, 1999). Faults in the Navajo Sandstone are related to regional trends, such as the northwest-striking set of faults that cut the San Rafael swell and the central part of the Colorado Plateau (Witkind, 1991; Bump and Davis, 2003) or the north- and north-northeast–striking trend observed near the transition with the Basin and Range (Witkind, 1991). Small faults in the Navajo Sandstone are typically deformation-band faults where grain crushing along narrow zones results in low-permeability surfaces or networks (Antonellini
and Aydin, 1994; Shipton et al., 2002). Faulting and fracturing may have an important effect on the variability of permeability in the Navajo Sandstone and the overlying Carmel Formation.

PETROGRAPHY OF THE NAVAJO SANDSTONE

The Navajo Sandstone averages 89% quartz. Alteration of detrital feldspars to illite, illite-smectite, and kaolinite is common. Interstratified illite-smectite is R > 3 ordered (each smectite layer is surrounded by more than three illite layers) and contains 90% illite layers. Detrital quartz grains are sometimes coated with iron oxide, illite, and/or illite-smectite. Where quartz overgrowths are present, these grain coatings postdate the quartz overgrowths. Most of the sand grains are quartz, but K-feldspar grains are scattered throughout. The sand grains are mostly 0.1–0.25 mm (0.004–0.009 in.) in size and are commonly coated with 2–4-μm-thick illite and hematite. Illite also occasionally fills pore space. Kaolinite commonly occurs as pore fillings, and calcite cement is sporadic.

NAVAJO SANDSTONE MODAL MINERALOGY

Mineral abundances of the phases that affect CO₂ sequestration were calculated by linear least-squares fit of mineral abundance, mineral composition, and rock composition. Mg was calculated as dolomite; the remaining Ca was calculated as calcite; K, Al, and Si were fit to kaolinite, K-feldspar, and K-mica; and the remaining Si was calculated as quartz. The results of modal mineralogical calculations for 74 samples are shown in Figure 3. In decreasing weight percent abundance, K-feldspar averages 4.6%, illite averages 4%, kaolinite averages 1.8%, and calcite averages 0.81%.

PERMEABILITY AND POROSITY

The most common controls on sandstone matrix porosity and permeability are thermal maturity, composition, sorting, and grain size. Porosity and permeability of the Navajo Sandstone are also related to mineral cements and deformation. Porosity of undeformed sandstone ranges from 10 to 30% (Cooley et al., 1969; Dunn et al., 1973; Cordova, 1978; Hood and Patterson, 1984; Freethey and Cordy, 1991; Shipton et al., 2002). Shipton et al. (2002) note that deformation bands that develop in response to faulting can reduce the original sandstone porosity from an initial 19 down to 12%.

Laboratory-scale permeability measurements of undeformed Navajo Sandstone yield values ranging from 50 to 5000 md (Weigel, 1986; Antonellini and Aydin, 1994; Shipton et al., 2002). Locally, permeability values of up to 9000 md are observed (Shipton et al., 2002). In-situ well tests yield permeability estimates that range from 80 to 13,000 md (Heilweil et al., 2000). The 2.5 order of magnitude variation in permeability of Navajo Sandstone reflects both facies variations and the consequences of faulting and fracturing.

When considering CO₂ injection into a sandstone reservoir, relative permeability relationships for the sandstone with respect to water and CO₂ must be identified.
because the relative proportion of water and liquid or supercritical CO₂ in the pore space will vary as a function of time and space in the reservoir. Unfortunately, few data are available for estimating these relationships for CO₂-water systems. Consequently, Pasala et al. (2003) and Ennis-King et al. (2004) used models developed by van Genuchten (1980) and Corey (1986) to compute plausible relative permeability curves for sandstone.

GROUNDCWATER CHARACTERISTICS

In several locations, the Navajo Sandstone is a natural reservoir for CO₂-charged waters (e.g., Morgan and Chidsey, 1991). Natural water in the Navajo Sandstone in the northern San Rafael swell varies from fresh to moderately saline (Table 1) (see Hood and Patterson, 1984; Kimball, 1992; Spangler et al., 1996; Heath et al., in press). Groundwater in the Navajo Sandstone includes brines with salinities of nearly 20,000 mg/L dissolved solids and low-salinity water (Kimball, 1992; Spangler et al., 1996). Water with salinities in the range of 3000–10,000 mg/L occurs in the southeasternmost part of Utah, and very saline to briny water with salinities of 10,000–35,000 and 35,000–400,000 mg/L (Table 1) underlies the moderately saline groundwater near areas underlain by evaporite beds in southeastern Utah (Howells, 1990). The lowest salinity water is of the calcium, magnesium bicarbonate type. Higher salinity water contains significant sulfate and chloride that results from interformational leakage from below the Navajo Sandstone caused by relatively high artesian pressures and likely conduction pathways along faults (Hood and Patterson, 1984). Very saline waters in aquifers below the Navajo Sandstone are in the Pennsylvanian Paradox Formation, which has dissolved evaporite salts, and Mississippian limestones. The saline waters may leak through the Triassic Moenkopi and Chinle formations into the Navajo Sandstone along prominent faults in the region. Typical waters from below the Navajo include late Paleozoic Paradox, Kaibab, Coconino, and Little Grand Wash fault waters shown in the trilinear diagram in Figure 4. Waters from the Navajo Sandstone that contain substantial bicarbonate include Woodside, Farnham, and Crystal Geyser locations (Figures 1, 4).

GEOCHEMICAL MODELING

Injection of CO₂ into water-saturated, porous rock forms regions of free CO₂ and CO₂-saturated water. During injection, the dissolution of CO₂ in water lowers the pH as aqueous CO₂ dissociates into H⁺ and HCO₃⁻. The ionizable hydrogen is capable of driving chemical reactions with aluminosilicate and carbonate minerals in the rock. Significant amounts of water remain in the pore space after maximum saturation with free supercritical CO₂. The original details of this water-rock reaction depend on the chemical composition of the groundwater. We illustrate this interaction by first calculating the solubility of CO₂ in water of varying salinities, modeling the consequences of adding CO₂ to two waters of contrasting composition, mixing contrasting waters, and modeling reaction of two contrasting waters with minerals in the Navajo Sandstone.

In the simulations, water compositions from Table 1 were used, dissolved SiO₂ was set at quartz saturation, Al³⁺ was set at kaolinite saturation, and K⁺ was set at muscovite saturation because of the common occurrence of these minerals. The four stages in the geochemical simulation are (1) the equilibrium state of the fluid was

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca</th>
<th>Mg</th>
<th>Na + K</th>
<th>HCO₃</th>
<th>SO₄</th>
<th>Cl</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farnham</td>
<td>874</td>
<td>61</td>
<td>422</td>
<td>3070</td>
<td>586</td>
<td>172</td>
<td>3607 (0.36 wt.%)</td>
</tr>
<tr>
<td>Paradox</td>
<td>76,200</td>
<td>9480</td>
<td>58,300</td>
<td>919</td>
<td>49</td>
<td>249,000</td>
<td>394,000 (39 wt.%)</td>
</tr>
<tr>
<td>Mississippian</td>
<td>10,120</td>
<td>1410</td>
<td>86,830</td>
<td>366</td>
<td>300</td>
<td>155,000</td>
<td>254,500 (25 wt.%)</td>
</tr>
<tr>
<td>Low salinity</td>
<td>56</td>
<td>52</td>
<td>14, 6.1</td>
<td>305</td>
<td>100</td>
<td>14</td>
<td>402</td>
</tr>
</tbody>
</table>

*Concentrations are from Hood and Patterson (1984) in milligrams per liter.
calculated, (2) equilibrium fluids could then be mixed, (3) CO$_2$ was reacted with the equilibrium fluid, and (4) the equilibrium CO$_2$-charged fluid was reacted with K-feldspar.

**CO$_2$ SOLUBILITY**

The solubility of CO$_2$ in natural water in sandstone aquifers is a function of temperature, pressure of CO$_2$, and salinity of the water. The likely temperature range for sequestration is from a surface temperature of about 20°C to a temperature of approximately 80°C at a depth of a few kilometers. Maximum CO$_2$ pressure would be between hydrostatic and lithostatic pressure at the aquifer depth. Salinity in water from our study area ranges from fresh to 20 wt.% dissolved salts. Stored CO$_2$ would likely be a dense (between 0.6 and 0.8 g/cm$^3$), supercritical fluid at 60°C and 100 bars (1450 psi) pressure considered here. CO$_2$ would occur as a dense, supercritical fluid phase, as a dissolved constituent in groundwater, and as a reactant with minerals in the reservoir rock. The solubility of CO$_2$ was calculated in water of various salinities using the equations and coefficients of Duan and Sun (2003) and shown in Figure 5. The solubility of CO$_2$ decreases systematically as salinity increases.

![Figure 4. Piper diagram showing the compositions of some typical groundwater in the Navajo Sandstone and from other stratigraphic units on the Colorado Plateau. Water compositions are taken from Hood and Patterson (1984).](image)
For example, with fresh water at a CO₂ pressure of 50 bars (725 psi), the solubility is 29.5 g/kg of water at 60°C, decreasing to 14 g/kg in a 20 wt.% (4.28 molal) salt solution. In a 2 wt.% (0.35 molal) salt solution, the solubility of CO₂ is 61.34 g/kg of water at 20°C and CO₂ pressure of 100 bars (1450 psi) that decreases to less than 35.7 g at 80°C. Solubility increases with increasing pressure of CO₂. For example, increasing CO₂ from 10 to 100 bars (145 to 1450 psi) in a 10 wt.% (1.90 molal) salt solution at 60°C increases the solubility from 5.04 to 31.27 g/kg of water.

**CO₂ REACTION WITH WATER**

Adding CO₂ to water that contains constituents other than Na and Cl may result in saturation of the water with carbonate minerals. Water from Mississippian aquifers contains significant calcium and magnesium. Adding CO₂ to this water could result in the precipitation of dolomite and calcite. If the pH is buffered at 6.0 by reaction with minerals in the rock, then the addition of approximately 0.5 mol of CO₂/kg of water would result in precipitation of 10.4 g of dolomite and 1.9 g of calcite. These mineral precipitates would occupy 4.5 cm³ (0.27 in.³) of pore space. Adding CO₂ to water that is discharged from a CO₂ geyser (Crystal Geyser) could result in the initial precipitation of 2.26 g of dolomite at a pH of 5.5. The dolomite would dissolve as additional CO₂ is added, and the pH falls to 4.5. However, the Navajo Sandstone is notably lacking in appropriate mineral buffers. Little calcite is present (average = 0.81 wt.%), and reactions with the principal aluminosilicate mineral K-feldspar are very slow.

Adding 2.37 mol of CO₂ to water typical of the Navajo Sandstone in Farnham Dome (0.36 wt.% salinity) raises $P_{CO₂}$ to 138 bars (2001 psi) and lowers the pH to 3.8 (Figure 6). No minerals reach saturation at this low pH value. If the Navajo Sandstone contains calcite at these conditions, then pH is buffered by CO₂-H₂O-calcite at a higher value of 4.6, but no minerals are precipitated (Figure 6). The buffer involves solution of 0.13 cm³ (0.007 in.³) of calcite in 1 kg of fluid.

Adding 0.85 mol of CO₂ to water typical of Mississippian aquifers (25 wt.% salinity) raises $P_{CO₂}$ to 138 bars (2001 psi) and lowers the pH to 3.2 (Figure 6). Despite the higher Ca levels in this water, no minerals reach saturation. If the pH is buffered by calcite at 4.7, then 4.5 cm³ (0.27 in.³) of calcite dissolves. Note that the average Navajo Sandstone contains 31 cm³ (1.9 in.³) of calcite in 5000 cm³ (305 in.³) of rock with 1000 cm³ (61 in.³) of pore space (20% porosity).

**WATER MIXING**

Mixing of waters of diverse composition may result in mineral precipitation with attendant changes in porosity and permeability. The effect is most pronounced.

![Figure 5. Solubility of CO₂ in waters of varying salinity in terms of weight percent NaCl. Solubilities are calculated at 60 °C using the equations of Duan and Sun (2003).](image-url)
when water that contains substantial bicarbonate from shallow, low-salinity aquifers is mixed with calcium-magnesium brine from deeper aquifers. Mixing bicarbonate water from Farnham Dome with saline brine from a Mississippian aquifer results in the initial precipitation of dolomite and dawsonite (NaAlCO3(OH)2) as shown in Figure 7. The dolomite begins to dissolve with increasing mixing fraction of saline water because of dilution of the bicarbonate content of Farnham Dome water. Dawsonite was also formed in the CO2 injection model experiments of White et al. (2005) and in the CO2 reaction models of Kharaka et al. (2006). Moore et al. (2005) observed dawsonite in the Springerville-St. Johns field, Arizona and New Mexico, where CO2 leaks to the surface.

**REACTION OF WATER AND CO2 WITH ROCK**

The consequences of reacting aquifer waters with reactive minerals in the rock as CO2 is added were evaluated by treating CO2 as a reactant along with feldspar in the rock. Calcite and clay were not treated as reactants because the solutions were saturated or nearly saturated with these minerals, and addition as reactant simply results in the precipitation of the amount of reactant added. Clays and carbonates instead became products in the reactions. Reaction products are a function of the proportion of reacting CO2 compared with rock mineral reactants. The reaction of K-feldspar with fluid is slow compared to the rate at which CO2 dissolves. Therefore, the reaction simulations proceeded as follows. First, the equilibrium state of the fluid was calculated; then CO2 was reacted with the equilibrium fluid; and finally, the fluid was reacted with K-feldspar.

The reaction rate law for K-feldspar reacting to product clay minerals used in the simulations is (Bethke, 1998)

$$rate = A_s k_+ a_{H^+} (1 - Q/K) \text{ in mol/cm}^2/\text{s} \quad (1)$$

where $A_s$ is the surface area; $k_+$ is the rate constant; $a_{H^+}$ is the activity of hydrogen ion; $Q$ is the reaction quotient; and $K$ is the equilibrium constant. The overall rate of reaction of K-feldspar in the rock is rate multiplied by surface area in square centimeters per gram times the number of grams of K-feldspar in the rock. The rate constant $k_+$ at 25°C is $1.168 \times 10^{-14}$ mol/cm²/s, and the activation energy is 51.7 kJ/mol (Blum and Stillings, 1995). The rate constant at an elevated temperature may be calculated using the Arrhenius equation

$$k_+ = A e^{-E/RT} \quad (2)$$

where $A$ is the pre-exponential factor $1.347 \times 10^{-5}$, $E$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. The rate constant calculated for 60°C is $1.047 \times 10^{-13}$ mol/cm²/s.
The mean grain size of K-feldspar in the Navajo Sandstone from measurements of Hood and Patterson (1984) and from our own measurements is 0.125 mm (0.0049 in.). The specific surface area of K-feldspar is 374 cm²/g (57.9 in.²/g), calculated using the equation of Brantley and Mellot (2000). The reaction of low-salinity Farnham Dome water saturated with CO₂ at 138 bars (2001 psi) CO₂ pressure is shown in Figure 8. No significant mineralogical changes occur within the first few years. Kaolinite precipitates and then dissolves as muscovite begins to precipitate. The maximum kaolinite reaches 4 g or 1.5 cm³/kg of water (0.091 in.³/kg of water). A tiny quantity, 0.02 g, of alunite also precipitates then dissolves. Muscovite continues to precipitate over the 500-yr time span of the simulation, reaching a maximum of 51 g or 18 cm³ (1.09 in.³). The solution reaches dolomite saturation at about 225 yr, and 0.08 g (0.03 cm³; 0.0018 in.³) of dolomite has precipitated in 500 yr. K-feldspar available for reaction was 488 g or 191 cm³ (11.6 in.³). After 500 yr, 42 cm³ (2.5 in.³) had reacted to 22% of the total available K-feldspar.

Reaction of high-salinity Mississippian formation water saturated with CO₂ at 138 bars (2001 psi) produces no aluminosilicate clays. The solution reaches saturation with dawsonite (NaAl(CO₃)(OH)₂) within the first year; and after 500 yr, 95 g (39 cm³; 2.37 in.³) of dawsonite precipitated along with 8 g (3 cm³; 0.18 in.³) of dolomite (Figure 9a). After 500 yr, 72 cm³ (4.4 in.³) of K-feldspar had reacted (38% of the total). Suppression of dawsonite results in the precipitation and then dissolution of 5.8 g (2.2 cm³; 0.13 in.³) of kaolinite within the first 10 cm³ (0.61 in.³) of K-feldspar reaction. At 500 yr of reaction time, 80.5 g (28.4 cm³; 1.73 in.³) of muscovite, 9.5 g (3.3 cm³; 0.20 in.³) of dolomite, and 6.1 g (2.3 cm³; 0.14 in.³) of calcite precipitate (Figure 9b).

**LEAKAGE OF CO₂ ALONG FAULTS**

Oil and gas fields in the Navajo Sandstone and its equivalent Nugget Sandstone include the Anschutz Ranch, Anschutz Ranch East, Farnham Dome, Lodgepole, and...
Pineview, and the most recently discovered Covenant fields (Hill and Bereskin, 1996; Brown, 2005). The presence of oil, natural gas, and CO₂ reservoirs, together with modeling studies, shows that reservoirs and seals exist that can contain gas for long periods of time (White et al., 2002; Allis et al., 2003). However, some natural CO₂ reservoirs have failed to contain the gas in the past and are leaking today. The Carmel Formation has sustained the same sequence of structural deformation as that in the Navajo Sandstone and is therefore broken in places by faults and fracture zones. Some of these faults are known to transmit CO₂ through the reservoir seal. Two fault systems have provided conduits for discharge of CO₂ from the subsurface. The Crystal Geyser and surrounding springs along the Little Grand Wash fault system discharge CO₂-charged waters and deposit travertine, both modern and ancient. The Little Grand Wash fault brings CO₂-charged water from the Navajo Sandstone to a borehole where the CO₂ and water are regularly discharged in geyser activity. Ten Mile Geyser and Torrey’s Spring also discharge CO₂-charged waters from the Salt Wash fault system with the attendant deposition of travertine. The CO₂ discharge appears in the form of slow leaks instead of catastrophic discharges. The presence of travertine terraces, tufa, and calcite-filled vein structures, CO₂ geysers, and CO₂-charged springs at the Little Grand Wash and Salt Wash fault zones suggests that CO₂-charged water has been discharging from the fault throughout recent geologic time (Dockrill et al., 2004; Shipton et al., 2004; Heath et al., in press). Travertine has formed from the leakage of CO₂ adjacent to fault zones from the Springerville-St. Johns field over a long period of time (Allis et al., 2002; Moore et al., 2005). Thus, the fault zones that breach the reservoir seals do not appear to have been sealed by mineral precipitation from CO₂-charged water in the fault zone.

The geochemical modeling of the interaction of CO₂-charged water with minerals in the Navajo Sandstone described above results in water that is saturated with carbonate minerals calcite and dolomite because of the solution of calcite cement in the sandstone and the consumption of hydrogen ion by reaction with detrital feldspar in the sandstone. Leakage of this water to the surface or into shallower aquifers would result in decreased pressure, CO₂ loss, and a rise in pH. Carbonate minerals would reach supersaturation and precipitate along the flow path and as travertine at the surface. Calculating the consequence of CO₂ loss indicates that less than 1 cm³ (0.061 in.³) of carbonate mineral precipitates per kilogram of water as CO₂ pressure is lowered to 1 bar (14.5 psi). Negligible quantities of dolomite and clay minerals are precipitated. These calculations are consistent with observed CO₂ leakage from faults that results in precipitation of travertine, but does not result in sealing the fault conduit as seepage continues today (Shipton et al., 2004).

Modeling studies of White et al. (2005) suggest that neither the Wingate nor the Navajo Sandstones can contain CO₂ for long periods of time along the transect that was modeled and are not suitable for storage because of leakage through seals.

**CONSEQUENCES OF ROCK-FLUID INTERACTION**

A small amount of clay mineral (modeled as muscovite) precipitated in the Farnham Dome simulation (51 g., 18 cm³ [1.09 in.³]). The total pore space containing 1 kg of water was 1000 cm³ (61 in.³), so the pore volume occupied by clay is very small (1.8% of the total pore space), decreasing the porosity from the assumed 20% to 19.6%. The decrease in porosity probably would have a negligible effect on permeability.

The formation of clay minerals as CO₂ reacts with K-feldspar in the rock affects permeability in two ways. The clay minerals fill pore space and reduce porosity, and more significantly, the kaolinite platelets and illite fibers can break loose during fluid flow and partially block pore throats, the main cause of permeability reduction (Vinopal and Taylor, 1999). Several empirical relations have been developed to predict the effect of clay abundance on permeability. The relationship developed by Baker et al. (2000) for sandstones in the Carnarvon Basin in Western Australia is

\[
\log k = (0.137\phi - 0.821\ Mgs - 0.0476\ Cv - 1.81\ R_o + 2.18)
\]

(3)

where \( k \) = permeability in millidarcys; \( \phi \) = porosity in %; \( Mgs \) = mean grain size in \( \phi \) units; \( Cv \) = total clay volume %; and \( R_o \) = vitrinite reflectance in %. This equation accounts for 87% of the permeability variation, with most predicted values within one order of magnitude of measured permeability.

Bloch (1991) formulated a second empirical relationship between permeability and clay content. According to Bloch (1991), the most important factors in sandstone permeability are detrital composition, grain
size, sorting, and temperature-pressure history. The empirical equation is

$$\log k = (1.34 \text{Mgs} + 4.08(1/\text{So}))$$

$$+ 3.42 \left( \frac{\text{rigid grain content}}{100} \right) - 4.67$$

where $k$ = permeability in millidarcys; Mgs = grain size in millimeters; and So = Trask coefficient = $(Q_1/Q_3)^{0.5}$, where $Q_1 = \text{particle size in millimeters having 75\% of the sample smaller in size}$; and $Q_3 = \text{particle size in millimeters having 25\% of the sample smaller in size}$ (Trask, 1932, p. 71; Krumbein and Pettijohn, 1938, p. 230–231). This equation is valid for sandstones with less than 5\% pore-filling cement.

The contribution of varying clay content on permeability for the empirical equations of Bloch (1991) and Baker et al. (2000) is plotted in Figure 10, together with the measured permeability and clay content of samples of Navajo Sandstone from the northern part of the San Rafael swell. The two equations are in reasonable agreement, but neither equation predicts the Navajo Sandstone permeability. Both equations predict a negligible change in permeability with a change in clay content of a few volume percent.

In the simulations of CO$_2$ injection into the Navajo Sandstone, a small amount of calcite is dissolved, increasing the porosity by a small amount. Later, dolomite and dawsonite are precipitated in pore space, decreasing the porosity. The maximum porosity change is precipitation of 39 cm$^3$ (2.37 in.$^3$) of dawsonite, which amounts to a decrease in porosity from 20 to 19.2\%. These changes in porosity probably are insignificant in terms of permeability. It takes, on average, a 4\% porosity increase to cause a one-order-of-magnitude change in permeability (Archie, 1950).

**DISCUSSION**

To understand and use a potential CO$_2$ sequestration site, the influence of rock mineralogy and groundwater chemistry should be examined. The temperature, pressure, and salinity of groundwater into which the CO$_2$ is to be injected determine the CO$_2$ solubility. As CO$_2$ is injected, the pH is substantially reduced, unless mineral buffers are present. This decrease in pH inhibits the precipitation of carbonate minerals and sequestration of CO$_2$ in solid phases. The CO$_2$ thus remains either in solution in the natural groundwater or as a separate CO$_2$ phase.

The quantity of CO$_2$ that can be stored in solution in groundwater is determined by the CO$_2$ solubility and by the quantity of groundwater into which the CO$_2$ can be dissolved. Injection of CO$_2$ into a dynamic groundwater system in which the regional groundwater flow field continually supplies unsaturated water to the injection site and sweeps away saturated groundwater down the flow path would result in greater storativity than injection into a static or low-gradient groundwater system. The San Rafael swell region of the Colorado Plateau (Figure 1) is bounded on the west by high plateau recharge regions, and the regional groundwater flow is from west to east at a nominal velocity of about 2 cm/day (0.08 in./day) (White et al., 2005). Such groundwater flow in an injection well would continually present unsaturated water at the site of injection and remove CO$_2$-saturated water.

The Navajo Sandstone provides the porosity, permeability, structure, and seal for an effective CO$_2$ sequestration reservoir. However, only small amounts of reactive minerals are present to consume the acidity

**Figure 10.** Calculated permeability as a function of clay content of sandstone using the equation of Bloch (1991) and Baker et al. (2000). Superimposed are measured permeabilities and clay contents of Navajo Sandstone samples.
produced by dissolving CO$_2$ in the water naturally present in the Navajo Sandstone. The primary reactant is K-feldspar, with an average abundance of 4.6 wt.%, but the reaction rate is slow. The maximum K-feldspar abundance is about 8.5 wt.%. Consequently, little CO$_2$ can be stored as carbonate minerals. Storage of CO$_2$ as precipitate would require the selection of alternative strata such as the Permian Kaibab Limestone, which is also favorably positioned with regard to seals and would also exhibit a favorable structure.

We show that CO$_2$ would be stored as a dissolved phase in the water and as free CO$_2$, and thus, the total volume that can be stored is a function of the volume of water in the system, its chemistry, the rock porosity, density of CO$_2$ at storage depth conditions, and the rates of groundwater movement in the system. These results have important implications for any sequestration site because clean eolian sandstones have many of the attributes required for candidate sites.

The fact that the porosity and permeability of Navajo Sandstone are little affected by CO$_2$ injection suggests that coupled multiphase flow and geochemical reaction simulators that also represent temporal changes in permeability are not required in evaluating prospective CO$_2$ sequestration strategies in the undeformed Navajo Sandstone. Because the mineral composition of faulted Navajo Sandstone differs little from that of the undeformed sandstone, this conclusion also applies to deformed Navajo Sandstone. Depending on the mineral composition of faulted Carmel Formation seal rocks, however, a fully coupled simulator should be used to evaluate the potential for fault-controlled leakage from the sandstone reservoir.

The CO$_2$-charged waters injected into the Navajo Sandstone reach or nearly reach saturation with the carbonate minerals calcite and dolomite. Upward leakage through faults in the Carmel seal would result in systematic decreases in CO$_2$ pressure as the fluids travel toward the surface. The decrease in CO$_2$ pressure leads to supersaturation in the carbonate minerals and precipitation of carbonate within the fault fractures and as travertine at the surface as has been observed in the natural, fault-controlled leakage on the Little Grand Wash fault and Salt Wash fault systems (Shipton et al., 2004). This precipitation has not completely sealed the leakage along the faults as seepage continues today. The effectiveness of sealing with carbonate precipitate is related to the coupling between precipitation rate and fluid flux rate through the seal leakage, but in the models described above, carbonate precipitation is an ineffective seal.

**CONCLUSIONS**

More CO$_2$ can be stored in solution in aquifers at lower temperature and lower salinity because CO$_2$ solubility in water decreases as salinity and temperature increase. Addition of CO$_2$ to groundwater reservoirs with dissolved calcium and magnesium may store CO$_2$ as mineral precipitate, providing that pH is buffered by reaction with rock, but the mineral precipitate plugs the pore volume and permeability. The volume of mineral precipitate is related to the proportion of reactant CO$_2$ compared to the proportion of reactant mineral in the rock. The Navajo Sandstone contains little reactant mineral that would consume H$^+$ at a sufficient rate to provide effective buffering. Therefore, little CO$_2$ can be stored as mineral precipitate. Careful studies should be done to evaluate the potential for fault-controlled leakage from the sandstone reservoir through the underlying Carmel Formation seal rocks.

The potential for sequestering CO$_2$ in the Jurassic Navajo Sandstone is promising because of its favorable hydrologic properties, geographic distribution, thickness, geologic structure, seal strata, and mineralogy. The presence of petroleum, natural gas, and CO$_2$ reservoirs in the Jurassic Navajo Sandstone suggests that long-term storage is possible. Present-day leakage from natural CO$_2$ reservoirs along faults is indicative of a leakage risk.

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