



Scientific drilling and downhole fluid sampling of a natural CO₂ reservoir, Green River, Utah

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1 Introduction

Understanding the geochemical behaviour of gaseous and supercritical carbon dioxide stored in geological reservoirs, over a range of timescales, is crucial for quantifying leakage risk and the geochemical evolution of the stored CO₂ through the life of an individual storage site (e.g. Bickle, 2009). Dissolution of the stored CO₂ into reservoir brine will likely form an important mechanism for stabilizing the CO₂ in geological reservoirs (e.g. Gilfillan et al., 2009; see review in Kampman et al., 2013a). Reactions between the acidified CO₂-charged brine and reservoir minerals might enhance the long-term storage of CO₂ by precipitation of carbonate minerals, or facilitate leakage by corroding cap rocks and fault seals. Understanding the fluid–fluid and fluid–rock reactions that may retard the migration of CO₂ from deep storage sites to the surface is also of critical importance for demonstrating the retentive capacity of the geological overburden above deep storage reservoirs.

Modelling the progress of the fluid–rock reactions is limited by uncertainties in the absolute mineral surface reaction rates and the unknown significance of other rate limiting steps such as CO₂ dissolution, and rates of fluid and solute transport (Knauss et al., 2005; White and Brantley, 2003). Investigating natural accumulations of CO₂ can provide insight

into the consequences for geological materials from long-term exposure of supercritical CO₂ and acidic CO₂-charged brine. Whilst it is expected that a well-sited CO₂ storage facility will not leak, some natural CO₂ reservoirs (such as the Green River site) have conductive features where CO₂ and CO₂-charged fluids are able to escape from depth to surface. These can provide sampling opportunities and insights into processes that may inhibit CO₂ migration through the overburden, such as dissolution into shallow reservoirs, capillary trapping of CO₂ gas or precipitation of carbonate minerals.

Deep geological storage of anthropogenic CO₂ will involve injection at depths > 800 m up to several kilometres, where the CO₂ is in a supercritical state and formation temperatures can range from ~ 30 to > 80 °C. The geochemical reactions occurring in CO₂ reservoirs, including dissolution into brine, and the subsequent reaction of the CO₂-charged brine with reservoir minerals are all sensitive to temperature. However, thermodynamic parameters such as the degree of CO₂ and mineral saturation in the fluid, or physical parameters related to flow of the CO₂, or surface properties of the minerals are equally as important in controlling the rates of these geochemical processes. Observations from shallow reservoirs containing CO₂-charged brine are thus extremely informative on the fundamental physical and geochemical processes controlling these reactions, and

processes that may inhibit CO₂ migration to the surface. The current state of knowledge of fluid flow and geochemical processes occurring during the storage of CO₂ in sedimentary basins is reviewed in Kampman et al. (2013a) and Jun et al. (2012). Natural analogue sites are reviewed in Baines and Worden (2004) and fluid–rock reactions in natural accumulations of CO₂ are reviewed in Bickle et al. (2013). The behaviour of cap rocks is reviewed in Song and Zhang (2012) and geochemical processes occurring during CO₂ leakage are reviewed in Harvey et al. (2012).

2 Project objectives

The fundamental goals of this project are to characterise and understand the mineralogical, geochemical, petrophysical and geomechanical consequences of long-term exposure of supercritical CO₂, CO₂-gas and CO₂-charged fluids on reservoir rocks, cap rocks and fault zone materials. This will improve our predictions of the long-term security of anthropogenic CO₂ geological storage sites. Data gathered during the extensive laboratory study of samples collected during drilling will be used to define or verify coupled models, like reactive transport (flow and geochemical reactions) or geochemical-mechanical models; these are ongoing projects at Shell Global Solutions International and the University of Cambridge. Despite the wide occurrence of natural CO₂ reservoirs, by their nature the critical parts of the reservoirs are buried and can only be accessed by drilling. If cap rocks, reservoir rocks or fault systems within reservoirs are exposed, not only will the CO₂-bearing fluids have already escaped, but the mineralogy and chemistry of the reservoir rocks will be altered by diagenetic and weathering reactions; thus the critical aspects of a breached system can only be inferred by indirect means. For these reasons the scientific drilling project had two primary objectives: (i) the recovery and preservation of core-samples from reservoir and cap-rocks exposed to CO₂ and CO₂-rich fluids; and (ii) the recovery of uncontaminated fluids at formation pressures from the target reservoirs using a wireline fluid sampler, and the analysis and collection of their dissolved gas load and fluid pH at surface. In this contribution we focus on the drilling operation itself and the sample recovery, and provide a brief description of the fluid sampling results. Details of the study of the core-samples and fluid geochemistry are ongoing; the initial results are presented in Kampman et al. (2013b), and detailed analyses of the reservoir and cap rock core-samples will be presented in future publications.

3 Green River CO₂ System

Numerous natural accumulations of supercritical CO₂ and CO₂-dominant gases occur throughout the greater Colorado Plateau and Southern Rocky Mountains region (Allis et al., 2001; reviewed in Bickle et al., 2013). A small number of

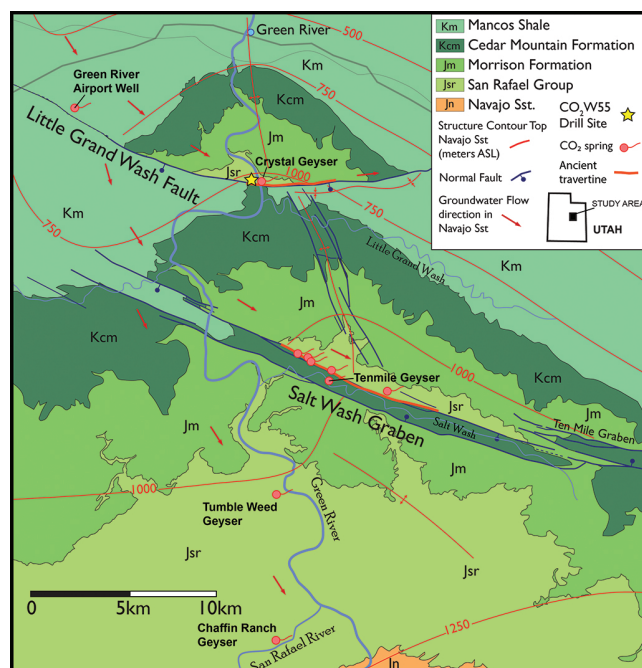


Figure 1. Geological map of the Green River anticline showing locations of the Little Grand Wash and Salt Wash Graben normal fault systems, CO₂-springs and location of drill hole CO2W55 (base map redrawn after Doelling, 2001 and Kampman et al., 2009). The distribution of ancient travertine mounds along the faults is highlighted, reflecting sites of paleo-CO₂ leakage (drawn from maps in Dockrill and Shipton, 2010). Structure contours are the height of the top surface of the Navajo Sandstone above sea level, the main shallow CO₂ bearing reservoir. Groundwater flow trajectories in the Navajo Sandstone are also shown (after Hood and Patterson, 1984 and maps in Kampman et al., 2009). Meteoric fluid flows from recharge zones in the San Rafael Swell to the northwest to zones of discharge in the Green River. The CO₂ and CO₂-charged brine flowing up the faults, mix with meteoric fluids in the Navajo Sandstone and flow parallel to the faults where they are sealing, and to the south-east where they are transmissive, being driven by the regional gradient in groundwater head.

these accumulations possess fault-associated, surface travertine deposits attesting to CO₂ leakage in the recent and geological past; the Springerville-St Johns Field, Arizona; Farnham Dome, Utah; and Green River, Utah. Of these only the Green River accumulation, and the St Johns Dome site (Allis et al., 2005, Gilfillan et al., 2011) are known to be naturally leaking in the present day.

Oil exploration drilling along the Green River anticline (Fig. 1) has encountered accumulations of CO₂-charged brine in the Navajo Sandstone at depths of ~200–340 m; CO₂ gas and CO₂-charged brine in the Jurassic Wingate sandstones at depths of ~400–500 m; accumulations of supercritical CO₂ and CO₂-charged brine in the Permian White Rim Sandstone at depths of ~800–900 m; and supercritical CO₂ and CO₂-charged brine in Carboniferous

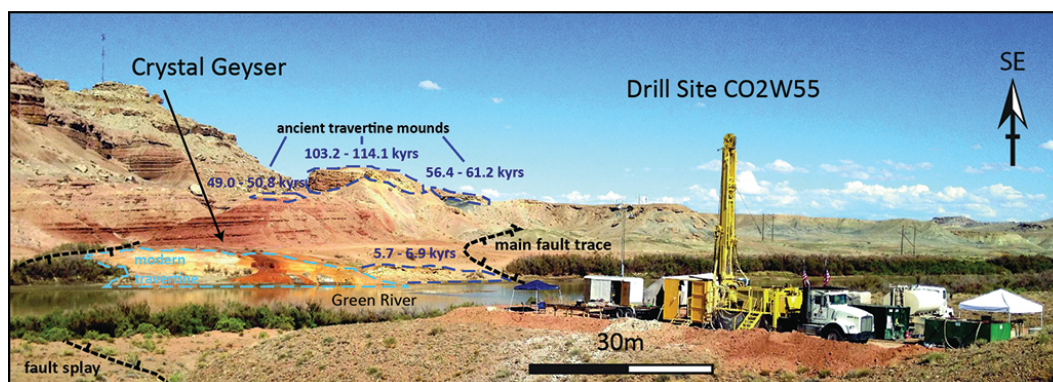


Figure 2. Field photograph of the drill site of well CO2W55 showing the CS4002 Truck Mounted Core Drill in the foreground and the travertine mound formed by Crystal Geyser on the opposite bank of the Green River. Also shown are the main fault trace of the Little Grand Wash Fault, and the local fault splays. Ancient travertine mounds form away from the main fault trace, within the footwall block of the fault, above the main fault damage zone through which CO₂ and CO₂-charged brine escape to surface. Travertine mound ages from Burnside et al. (2013) are also shown.

(Pennsylvanian and Mississippian) aged carbonate and evaporite deposits at depths > 900 m (J. Beach, Delta Petroleum, personal communication, 2007, e.g. Navajo Sandstone – Greentown State 36-11, API 4301931462; Wingate – Greentown Federal 26-43D, API 4301931547; White Rim – Greentown Federal 35-12, API 4301931507). CO₂ and CO₂-laden water leaks to the surface along the crest of the Green River anticline through a number of abandoned petroleum exploration wells and through the damage zone of the footwall block of the Little Grand Wash and Salt Wash normal fault systems (Figs. 1–3; Dockrill and Shipton, 2010; Shipton et al., 2004, 2005). These large normal faults (~35 km lateral extent) contain a clay gouge core. From surface mapping and projection onto Allen diagrams it is likely that they are laterally sealing towards the centre of the faults, with throws of 250–300 m, becoming laterally transmissive towards the fault tips, where reservoir–reservoir rock is juxtaposed (Dockrill and Shipton, 2010). Buoyant supercritical and gaseous CO₂ is thought to accumulate at the anticlinal crest adjacent to the two faults, beneath the south dipping fault seals. The localization of CO₂ leakage to the crest of the anticline reflects this, where open fractures in the fault damage zone allow CO₂ and CO₂-charged water to escape upwards from the deep supercritical CO₂ reservoirs (e.g. Pasala et al., 2013). In addition, an oil seep within the Little Grand Wash fault damage zone, near its intersection with the anticline crest, has been compositionally fingerprinted to Pennsylvanian strata at local depths of > 2 km, demonstrating migration of fluid from significant depths within the basin (Shipton et al., 2004). CO₂-leakage points away from the faults (Fig. 1; Tumble Weed Geyser and Chaffin Ranch Geyser) occur where exploration or water-well drill holes penetrate fluids in the Navajo Sandstone flowing horizontally away from the fault tips (Kampman et al., 2009).

U-Th dating of travertine mounds at surface shows a protracted history of CO₂ leakage over the past ~400 000 yr (Burnside et al., 2013), characterized by successive pulses of CO₂ degassing (Kampman et al., 2012). Over the last 135 000 yr pulsed leakage from the faults has occurred at the transition from local glacial to interglacial conditions. This has been likely triggered by changes in the hydraulic conductivity of the fault damage zone driven by changes in hydrology, pore fluid pressures and regional stresses following local climatic warming and crustal unloading (Kampman et al., 2012).

The stacked sequence of reservoirs, the relatively shallow depth (160–350 m) of the upper CO₂-bearing reservoir, the Navajo Sandstone and the prior knowledge of the site made it an excellent drilling target (Assayag et al., 2009; Baer and Rigby, 1978; Burnside et al., 2013; Dockrill and Shipton, 2010; Evans et al., 2004; Gouveia and Friedmann, 2006; Gouveia et al., 2005; Han et al., 2013; Heath, 2004; Kampman et al., 2009, 2012; Shipton et al., 2004, 2005; Wigley et al., 2012, 2013a, b; Wilkinson et al., 2009).

4 Drilling operations

Drilling of CO2W55 was carried out from 2 to 28 July 2012 using a CS4002 Truck Mounted Core Drill (Figs. 2–3). The drill site was located on the footwall block of Little Grand Wash Fault (38.93792° N, 110.13892° W; 1238 m Elev.), ~250 m to the west of Crystal Geyser – an abandoned petroleum exploration well, that now hosts a CO₂-driven cold water geyser (Fig. 3; Assayag et al., 2009; Baer and Rigby, 1978; Gouveia and Friedmann, 2006; Gouveia et al., 2005; Han et al., 2013). The initial drilling plan was to recover core by diamond drilling through a series of cap rock–reservoir pairs, from the Entrada Sandstone through to the base of the Permian White Rim Sandstone, at a proposed

depth of ~815 metres below surface (m b.s.). The target CO₂-reservoir intervals included Jurassic and Permian sandstones of the Navajo, Wingate and White Rim formations, and cap rocks of the Carmel, Kayenta, Chinle and Moenkopi Formations. For technical reasons related to high volumes of fluid returns to surface, driven by degassing of the CO₂-charged brine within the well bore and expansion of the exsolved CO₂ gas during coring, drilling ceased at 322.5 m b.s. near the base of the Navajo Sandstone.

The hole was drilled vertically using DOSECC's hybrid coring system to recover core to a depth of 282 m b.s., with core recovery > 99 %, after which point the drill hole was completed by rotary drilling to a total depth of 322.5 m b.s. On-site processing of the core involved rinsing the core with water to remove drilling mud, core description, photographing and selective anaerobic bagging of important core sections in nitrogen-flushed vacuum-packed aluminised bags. Six samples of cap rock were also placed in preservation cells under axial-compression (G-clamped), to reduce mechanic degradation of the core, and for later testing in the laboratory of their transport properties (porosity, permeability, capillary entry pressure). Initial core descriptions were conducted based on macroscopic and microscopic investigations of the material. Fluid returns to surface from transmissive formations were sampled at the well head during drilling, filtered on-site through 0.2 µm nylon filters and stored in pre-cleaned high-density polyethylene bottles, prewashed with filtrate, one sample acidified to pH ~2–3 with 6M HCl and one un-acidified sample, for chemical analyses. Additional downhole fluid sampling was conducted in the Navajo Sandstone and is discussed in detail below. Downhole logging of the hole was not conducted due to the depth of cementation required to control fluid inflow into the drill hole (see below), with the cement layer impeding analysis using traditional formation logging tools.

The drill hole was spudded on 6 July; we initially drilled from 0 to 10.2 m b.s. with a 5-5/8 inch nominal (142.88 mm) diameter tricone rock bit, through the regolith to the “earthy” member of the Entrada Formation, and installed a temporary top casing of PVC pipe. Diamond coring with HQ core bits proceeded from 10.2 m down to 163.4 m b.s., through the “earthy” and “sandy” members of the Entrada Formation, at a penetration rate of ~70 m d⁻¹, to a point roughly ~14.0 m into the more competent underlying Carmel Formation (149 m b.s.). A bentonite based drilling mud was used with Max Gel and M-I Wate polymers, and a Soda Ash pH modifier was added during drilling within the Navajo Sandstone. The hole was re-drilled from 10.2 to 163 m b.s. with an 8-3/4 inch (222.25 mm) tricone rock bit, and permanent 6-5/8 inch (168.28 mm) diameter steel casing was cemented in place. Significantly, free CO₂ gas and CO₂-charged fluids were first encountered in the basal 35–150 m of the Entrada Sandstone, which is open to the surface in this region, indicating that thin siltstone layers (such as those within the Entrada) can act as effective seals to the upward migration

of CO₂ and CO₂-charged fluids. Zones of CO₂-bearing fluids were identified based on the presence of CO₂-degassing and bubbling observed in intervals of core during washing, and CO₂-charged fluid returns to surface. The CO₂ gas pockets were identified during tripping out of the rods from the drill hole, where the gas/fluid ratio in fluid returns to surface would rapidly increase when the base of the rods encountered a zone in the formation containing CO₂ gas.

The Entrada Formation overlies the Carmel Formation, which in turn acts as the regional cap rock for the Navajo sandstone. As expected, the Carmel Formation produced no water while drilling with the exception of a conducting fault damage zone at ~188 m b.s. Drilling was smooth through the Carmel Formation, at a penetration rate of ~20 m d⁻¹, into the Navajo Sandstone, where the penetration rates increased to around ~50 m d⁻¹. Within the Navajo Sandstone, the reservoir overpressure and gas lift generated from degassing of the CO₂-charged brine within the wellbore began to return water to the surface. Shut in pressures were recorded periodically during drilling. Zero shut in pressure was observed during drilling through the Entrada Sandstone, Carmel Formation and through much of the upper Navajo Sandstone, suggesting pressure communication between the formations transected by the drill hole and Crystal Geyser (which as a flowing well acts as a pressure release). Within the Navajo Sandstone a maximum shut-in pressure of 13.8 bar was measured at surface at a drill hole depth of 221 m b.s., equivalent to a downhole pressure of 35.5 bar and formation overpressure of 12.8 bar. No continuous free gas flow (other than that degassed from the fluid within the well-bore) was observed at the well head whilst drilling in the Navajo Sandstone, even when the hole was unweighted with drilling mud, suggesting that the drill hole did not penetrate a free CO₂-gas cap within the Navajo Sandstone, or at least not a substantial one.

At around ~200 m b.s. the drilling mud used to weight the hole began to escape into the formation and became diluted by rapid inflow of formation fluid, resulting in partial unweighting of the hole, and an increase in water returns to surface. In order to alleviate the problem of heavy water returns and excessive gas lift at ~245 m b.s., the hole was cemented to seal this interval, and re-drilled. At 227.4 m b.s. we switched from HQ to NQ coring, and continued through the Navajo Sandstone to 282.2 m b.s. Following continued trouble with pressure control, gas lift and heavy water returns at 282 m b.s., the hole was again conditioned and then cemented. As the Navajo Sandstone is a relatively homogeneous unit it was decided to continue drilling with an 3-7/8 inch (98.43 mm) tricone bit until 322.5 m, an estimated 3 m into the Kayenta Formation, to take a final water sample at the base of the Navajo before the hole was plugged with cement and abandoned.

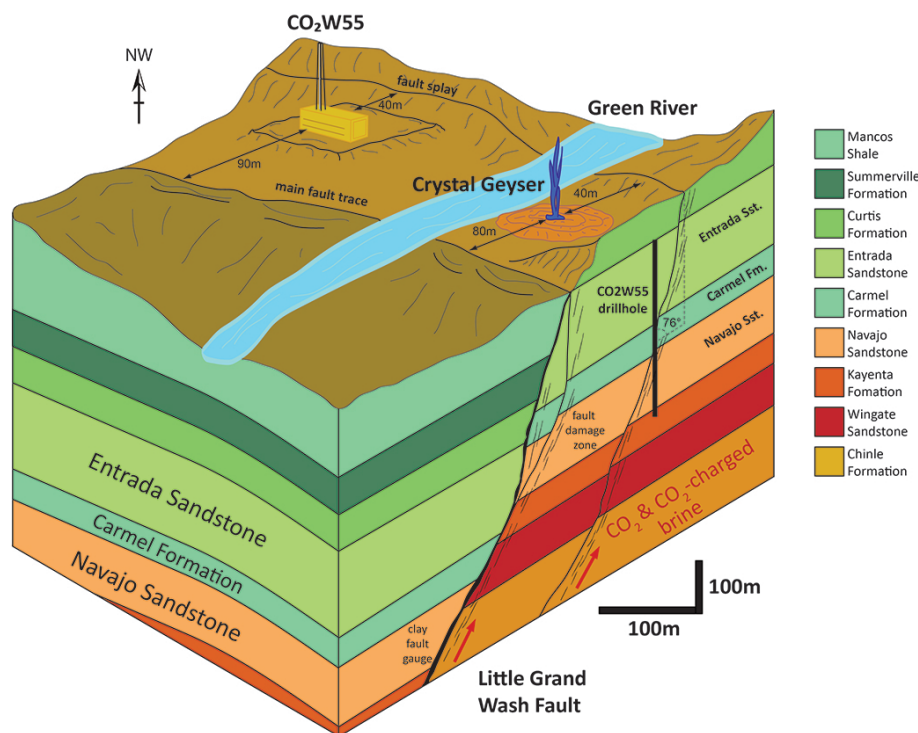


Figure 3. Cross section of the region surrounding drill hole CO2W55 showing the location of the Little Grand Wash fault system, including the northerly fault transacted by the drill hole (limited exposure precluded mapping this at surface), and the CO₂-driven cold water geyser at Crystal Geyser. The transect taken by the drill hole is projected on the left-side of the figure. The general structure of the fault is also shown using information from field mapping and in Shipton et al. (2004) and Dockrill and Shipton (2010).

5 Downhole fluid sampling at low pressure

Collecting uncontaminated and undegassed CO₂-rich fluid samples was a key objective of the Green River Drilling project. These CO₂-rich fluids contain a significant dissolved gas load, which will degas if exposed to pressures lower than the formation pressures. To prevent this, fluids were collected downhole at formation pressure by using the Leutert Bottom Hole Positive Displacement Sampler (Fig. 4a; PDS sampler) during the course of drilling (see also Kietäväinen et al., 2013 and Regenspurg et al., 2010 for examples of use of the tool in completed wells). Four fluid samples (~0.6 L) were collected from within the Navajo Sandstone formation at depths of 206 m b.s., 224 m b.s., 276 m b.s. and 322 m b.s. The use of the PDS sampler to recover pressurized fluid samples, fluid subsampling and the extraction of the fluid dissolved gas load for later compositional analysis in the laboratory is described in Regenspurg et al. (2010). Additional methods to analyse the dissolved CO₂ load of the fluid and fluid pH at high pressure in the field are discussed below.

We wanted the collected fluid samples to be (i) as little contaminated with drilling mud as possible and (ii) not depressurized and allowed to degas CO₂. The following protocol was initiated following a process of trial and error. Fluid sampling was conducted during the course of drilling

the hole to avoid the need to pack in individual target sample depths. Drilling commenced to a predetermined sample depth at which point a fluid sample was taken. The PDS sampler is designed with a clock that opens the sampler after a set time and fills at a slow rate controlled by the down-hole pressure, an internal flow regulator and the pressure of an internal transfer fluid. The clock was set to allow enough time for the sampler to reach the base of the hole on wireline, for the natural overpressure to flush out the drilling mud, and for the formation pressure to recover. To do this a blow out preventer (BOP) was fitted with a lubricator assembly, the PDS sampler was lowered to the base of the hole, and the rods were then pulled up ~1.5 m, allowing formation water to flow for about 15–45 min, flushing drilling mud out of the hole using the natural overpressure of the formation. Following the flushing procedure, the well was shut in at the BOP, allowing pressure recovery for 1–2 h. The PDS sampler was then left down the hole for 5–6 h after the clock triggered to open the sampler. The long filling time was necessary because of the low reservoir pressures of ~35 bars, and the primary design of the tool for use at high formation pressures. Different combinations of flow regulator and internal transfer fluid pressure were attempted, but the filling time could not be reduced. Complete filling of the sampler with formation fluid triggers the sampler to close, trapping the fluid at the

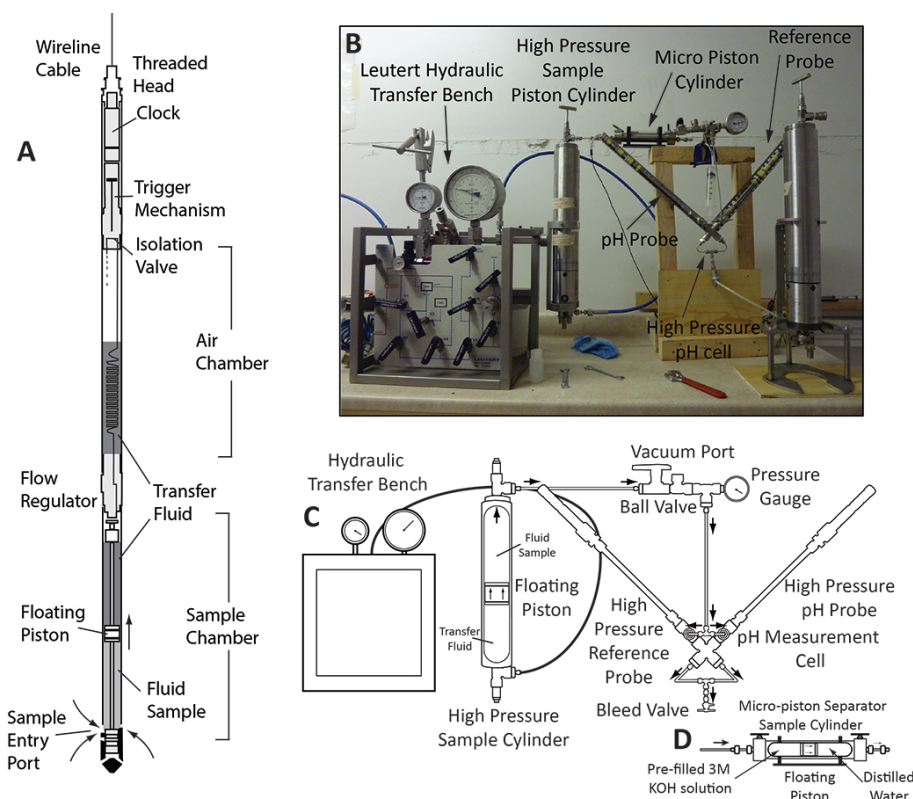


Figure 4. (A) Leutert Bottom Hole Positive Displacement Sampler (PDS sampler). (B) Laboratory set-up for extraction of high pressure fluid samples from the downhole fluid sampler for analysis of fluid CO₂ content and pH, in the field. (C) Shows the set-up for analysis of pH on pressurized samples. (D) The micro-piston cylinder used for the “alkalinity capture” of the dissolved CO₂.

formation pressure, after which the sampler can be recovered to surface on wireline.

The recovered fluid samples in the downhole sampler were transferred at pressure into high pressure piston separator sample cylinders, using a hydraulic transfer pump, to ensure the fluid did not degas (Fig. 4). A ~20–30 mL aliquot of the fluid was pumped from the piston sample cylinder through a high-pressure pH probe assembly, initially filled with a reference solution at the estimated formation pressure, and containing high pressure pH and reference probe (Corr Instruments). The pH cell was flushed with formation fluid until a stable pH was attained. A second aliquot of sample was pumped at pressure into a 30 mL micro piston separator. This was filled with 15 mL of 3M KOH solution, to capture the dissolved CO₂ in solution by conversion to CO₃²⁻ and precipitation as K₂CO₃, from which total CO₂ concentration could be determined by Gran titration. A sample of the exsolved CO₂ gas, for analysis of carbon and noble gas isotopic compositions, was then collected from the piston sample cylinder by connecting a length of refrigeration grade copper tubing to the pressure cylinder with high pressure lines, fittings and valves. These were in turn connected to pressure gauges and a roughing pump, to allow complete evacuation of atmosphere from the line and copper tubing before filling. The

piston sample cylinder was allowed to depressurise rapidly, by the removal of back pressure across the separator piston, and the exsolved gas was collected into the copper tubing which was then sealed by cold welding with an aluminium sample bracket equipped with steel compression jaws. It is hoped that the vigorous degassing and much higher solubility of the noble gases in the CO₂ phase will enable quantitative noble gas recovery from the fluid, although the analyses are still pending and partial recovery should not impact the isotope ratios of the noble gases. The remaining fluid was then pumped through 0.2 µm nylon filters and stored in pre-cleaned high-density polyethylene bottles, prewashed with filtrate, one sample acidified to pH ~2–3 with 6M HCl and one un-acidified sample for chemical analyses.

6 CO₂W55 core stratigraphy

The drill hole from the surface to 25 m.b.s. encountered marine and lacustrine red siltstones facies of the “earthy” Entrada Sandstone member, that grade into the 125 m-thick bleached aeolian dune deposits of the lower Entrada Sandstone, with intercalated marginal marine and sabkha influences throughout (see Crabaugh and Kocurek, 1993). Sandstone units of the upper Entrada contain sporadic

hydrocarbon and bitumen bearing zones, typically beneath siltstone seals from 35 to 50 m b.s. A series of sharp sub-horizontal contacts separate unbleached red siltstone and sandstone units from the bleached basal sandstone units. Steep bleached-unbleached contacts are observed around high-angle open fractures in the unbleached upper sandstone and siltstone units of the Entrada Sandstone. A complete sedimentary log of the cored interval is shown in Fig. 5 and examples of important intervals of the core are shown in Fig. 6. The total recovered thickness of Entrada Sandstone (~149 m) exceeds thickness estimates to the west and south (125 m) (O'Sullivan, 1981), indicating local thickening of the interval.

Below the Entrada Sandstone lies the Carmel Formation (top at 149 m b.s.), a 50 m-thick complex package consisting of three laterally gradational lithofacies: (i) interbedded, unfossiliferous red and grey shale and bedded gypsum; (ii) red and grey claystone/siltstone; and (iii) fine-grained sandstone. These are interpreted as marine sediments deposited in quiet, subtidal conditions under the influence of periodic hypersaline water (see Blakey et al., 1996 and references therein). Faulting at depths between 156 to 173 m b.s. has resulted in the formation of a ~17 m thick fracture zone comprising a ~7 m thick core containing centimetre to metre scale blocks of siltstone and shale breccia hosted in beds of remobilized gypsum. The core is bound by a fracture zone of gypsum-filled open fractures, of ~2 m thickness in the hangwall and ~8 m thickness in the footwall. Slickenlines and millimetre to centimetre displacements were observed on some fracture surfaces. The fracture zone in the footwall block was found to be transmissive, and surface returns of fluid were sampled. The recovered thickness of the Carmel Formation is consistent with regional estimates of 45–65 m, suggesting little loss of section. The limestone beds typical of the lower 1/3 of the Carmel Formation elsewhere (O'Sullivan, 1981) are locally thinned to ~2 m thickness, compared to a thickness of 10–15 m in the San Rafael Swell, 35 km to the west. The Carmel Formation forms a regional seal for the underlying Jurassic Navajo Sandstone (Peterson and Turner-Peterson, 1989).

In the CO2W55 core the Navajo Sandstone is comprised of thick sets of high-angle, cross-bedded, well-sorted, fine- to medium-grained sandstones with intercalated inter-dune facies sandstones which are typical of this aeolian deposit (see Verlander, 1995 and references therein). A thin zone of hydrocarbon bearing sandstone is present from 202 to 204 m b.s., beneath the Carmel Formation cap rock. Within the entire cored interval the unit is bleached from its typical red colour, to pale pink and white due to dissolution of hematite coatings originally present on the sand grains. Bleaching is most intense around open fractures and these are frequently mineralized with assemblages of gypsum and pyrite.

Such sandstone bleaching is a common feature within the Jurassic sandstones of the Paradox Basin and wider geo-

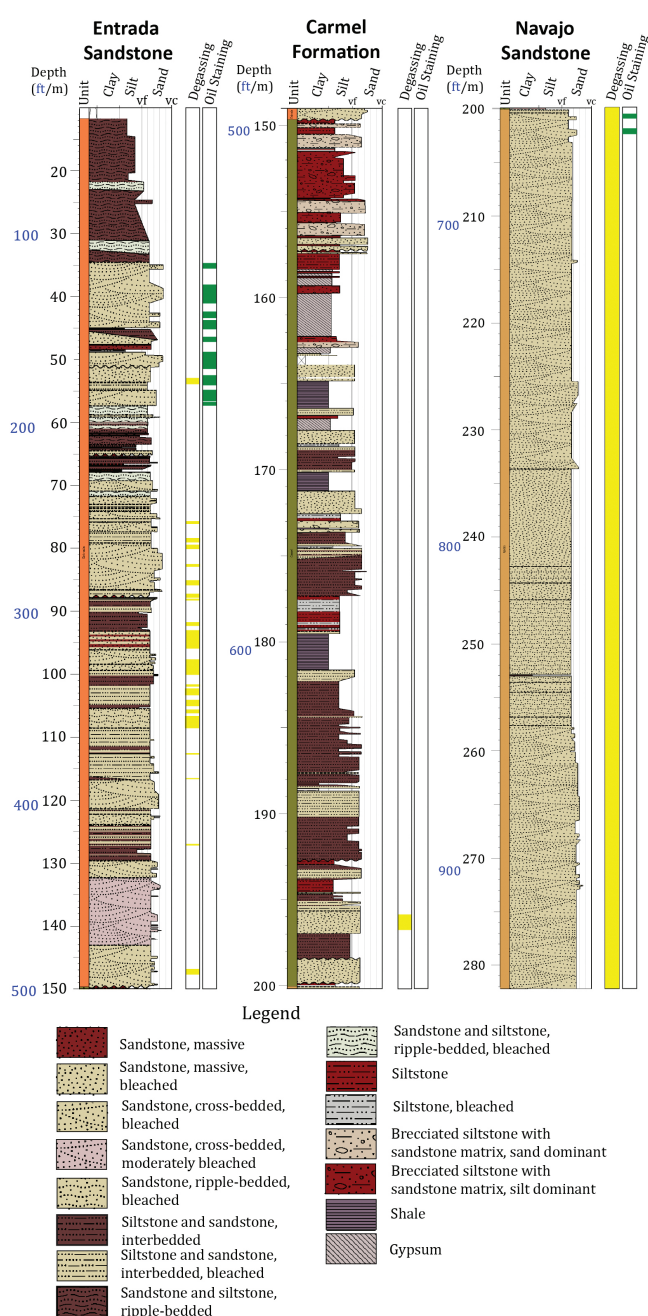


Figure 5. Sedimentary log of the core recovered from drill hole CO2W55 showing the main geological features of the three units, the Entrada Sandstone, Carmel Formation and Navajo Sandstone, transacted by the drill hole. Zones of CO₂-degassing core and hydrocarbon bearing zones are also shown.

graphic region. This has variously been attributed to bleaching by buoyant hydrocarbons and methane rich brine (Beitler et al., 2003, 2005; Chan et al., 2000; Garden et al., 2001; Parry et al., 2004, 2009) and by dense CO₂-charged brine containing methane or sulfide reductants (Loope et al., 2010, 2011; Potter-McIntyre et al., 2013; Wigley et al., 2012,

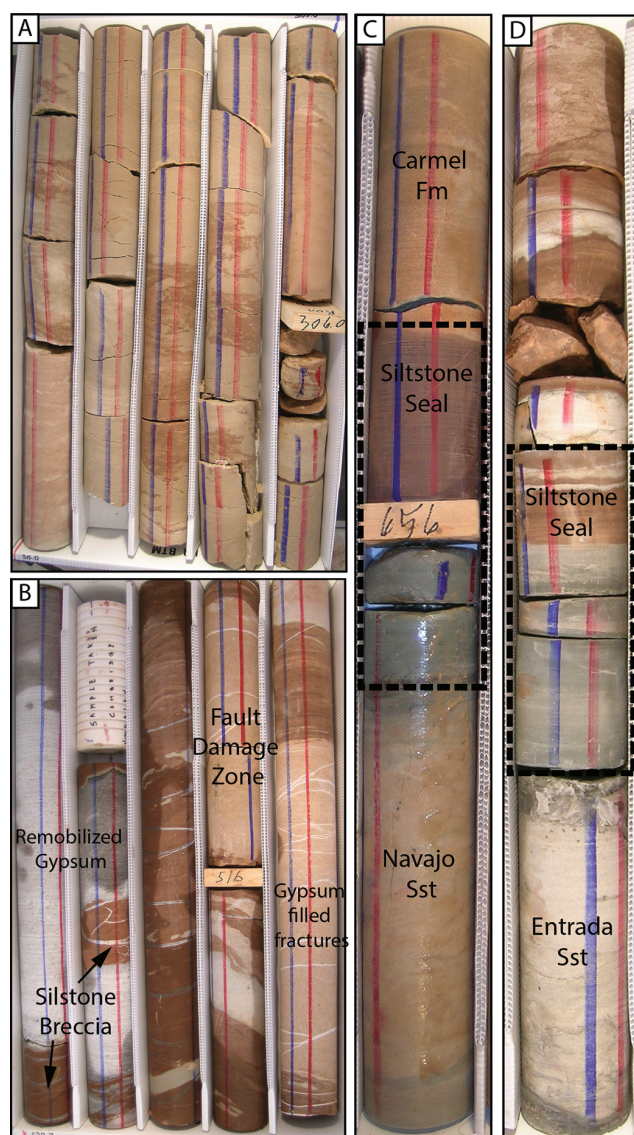
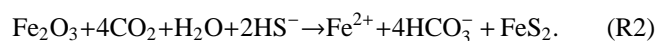
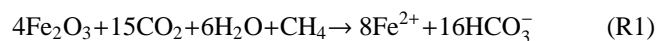


Figure 6. (A) Bleached basal sandstones of the Entrada Sandstone hosting CO₂ charged fluids. Fracturing of the core occurs at surface due to exsolution of CO₂ gas from the fluids held in core porosity. The relative permeabilities of water and gas result in a build-up of gas within the pore space, which expands causing the cores to break apart. (B) Sections of the fault core and damage zone from the Carmel formation showing fractured blocks of siltstone residing in remobilized gypsum horizons and pervasive fracturing of the core in the footwall fault damage zone. (C) and (D) Siltstone-sandstone contacts from CO₂-hosting sections of the Entrada and Navajo Sandstones showing bleaching and alteration of the originally red siltstones over a 10 cm distance by diffusion of volatiles into the reservoir cap rocks.

2013a, 2013b). Ferric iron bearing hematite is relatively insoluble in water at low temperatures and its dissolution requires a source of acidity and a chemical agent to reduce insoluble Fe³⁺ to soluble Fe²⁺. Such acid-reductive disso-

lution is possible with a wide range of naturally occurring sources of acidity (e.g. CO₂, organic acids, H₂S) and reductants (e.g. CH₄, HS⁻, H₂S) and different combinations most likely act as the bleaching agent in different places. At Green River bleaching of exhumed portions of the Entrada Sandstone has previously been attributed to the passage of CO₂-charged brine, with minor quantities of dissolved CH₄. The presence of these CO₂-rich brine has been inferred from analysis of CO₂-CH₄ bearing fluid inclusions within secondary mineral phases and the isotopic composition of secondary carbonate cements associated with the bleaching (Wigley et al., 2012, 2013b). In addition, bleached portions of the exhumed Entrada studied by Wigley et al. (2012, 2013a, b) contain assemblages of gypsum and pyrite in open fractures, although the pyrite is rarely preserved (typically as inclusions within gypsum) due to oxidative weathering at the surface. Such assemblages are more commonly preserved within the CO₂W55 core as fracture coatings around intensely bleached open fractures in the Navajo and Entrada Sandstones. At Green River the sandstone bleaching may occur through a series of linked reactions involving a range of reduced species following reaction stoichiometries such as



Mineralogical, petrographic and isotopic analysis of the bleach units and bleaching related mineral assemblages will form a focus of future analyses. The lower portions (5–10 cm) of many of the sealing siltstone layers in the Entrada and Carmel formations are also bleached where they are in contact with CO₂-hosting reservoir sandstones, suggesting upwards penetration of volatiles by diffusion, mineral dissolution and alteration of the cap rock mineralogy.

7 Fluid sampling results

Initial results of the downhole and surface fluid sampling results are presented in Fig. 7, full details of the fluid geochemical analyses and results can be found in Kampman et al. (2013b). The Na⁺ and Cl⁻ concentrations of the fluids are fairly constant through the Entrada Sandstone, the fault damage zone in the Carmel and in the upper Navajo Sandstone (Fig. 7a–b). Within the Navajo Sandstone Na⁺ and Cl⁻ concentrations increase systematically towards the base of the formation, and this broad salinity profile reflects mixing between dense brine flowing along the base of the formation, fed by active inflow from the main fault zone, and dilute meteoric fluid flowing horizontally into the fault. Dissolved CO₂ concentrations in the Navajo Sandstone determined by titration of “alkalinity captured” samples and calculated from the measured in situ pH and fluid alkalinity (Fig. 7c) are in good agreement (Fig. 7d). CO₂ concentrations are close

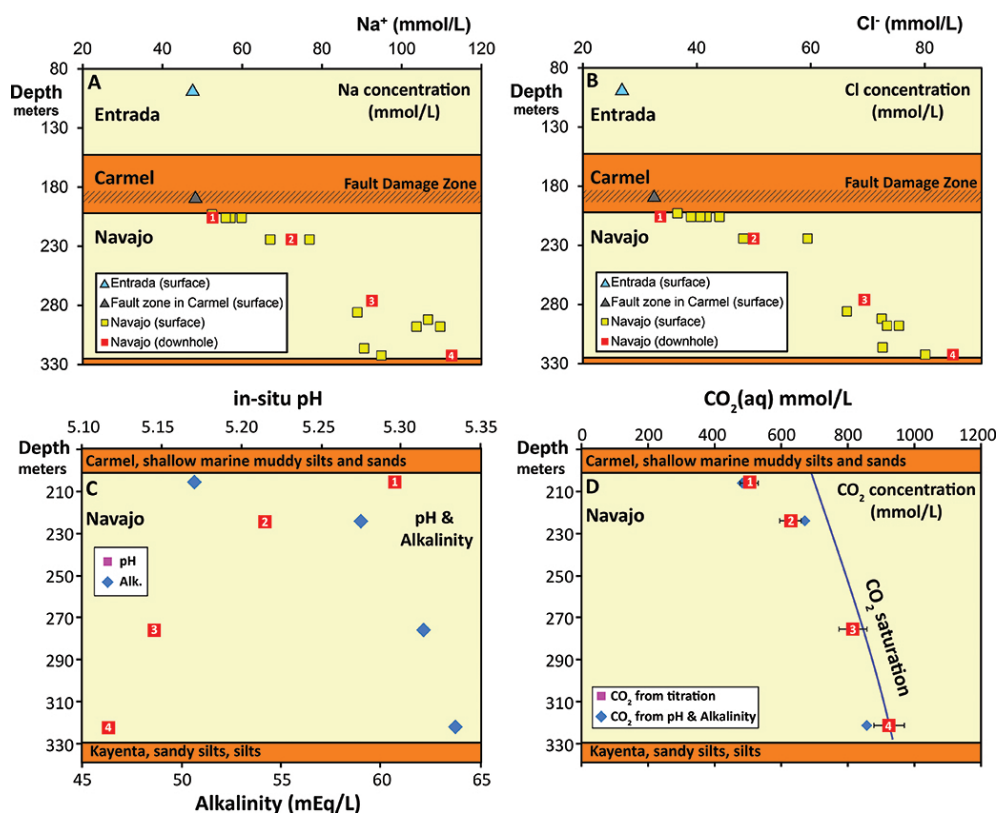


Figure 7. Preliminary results from the surface and downhole fluid sampling campaign. (A–B) Na^+ and Cl^- concentrations in downhole and surface sampled fluids. The geochemical profiles illustrate inflow of CO_2 -charged brine at base of the formation and mixing between brine flowing through the faults and meteoric fluid flowing horizontally into the fault zone. (C) In situ pH measured on pressurized samples and alkalinity determined by Gran titration in the field. (D) Dissolved CO_2 concentrations measured directly on titrated samples and recalculated from measured pH and alkalinity. Also shown is the theoretical CO_2 solubility curved calculated for a hydrostatic pressure gradient, local geothermal gradient and measured salinity profile using the equations of Duan et al. (2006).

to saturation at the base of the formation and decrease upwards due to mixing between the CO_2 -saturated brine and CO_2 -undersaturated meteoric fluid higher in the formation. These results suggest that the Navajo Sandstone is being fed by active inflow of CO_2 -saturated brine through the damage zone of the main Little Grand Wash Fault, and that the fluid sampling successfully captures this dynamic process.

8 Conclusions

For the first time, core of a cap rock/reservoir pair and accompanying downhole fluid samples from a naturally CO_2 -charged reservoir have been obtained. Surface and downhole fluid sampling reveals that the sandstone formations are being fed by active inflow of CO_2 -saturated brine through fault fracture networks; with the CO_2 -charged brine being sourced from supercritical reservoirs of CO_2 at depth within the basin. The sandstone and siltstone units are bleached from their typical red colour where they are in contact with the CO_2 -charged fluids. Narrow zones of mineralogical al-

teration are observed in the cap rock units in contact with the CO_2 -charged reservoir sandstones.

Forthcoming analysis will include mineralogical, petrographic, geochemical and geomechanical studies of the CO_2 -reservoir rocks and reservoir cap rocks. Geochemical, mineralogical and petrophysical profiles through the cap rocks will be combined with diffusive modelling to constrain the velocity of the mineral reaction fronts. This work aims to establish whether CO_2 -promoted fluid–mineral reactions have occurred in the cap rocks and if these reactions either (i) attenuate the CO_2 diffusive distances through the consumption of the CO_2 and the deposition of carbonate minerals or (ii) facilitate CO_2 escape by generating porosity and permeability pathways. The results of this analytical work will be compared to, and used to calibrate, numerical models of coupled CO_2 –fluid–mineral reactions. Further drilling is planned at the Green River site to target fault zones that host CO_2 and CO_2 -charged fluid flow. Core samples obtained from this drilling will be studied in order to assess the impacts of CO_2 -promoted fluid–rock interaction on fracture permeability, fault hosted fluid flow and surface leakage of the CO_2 .

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