



## Scientific drilling and downhole fluid sampling of a natural CO<sub>2</sub> 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 CO<sub>2</sub> through the life of an individual storage site (e.g. Bickle, 2009). Dissolution of the stored CO<sub>2</sub> into reservoir brine will likely form an important mechanism for stabilizing the CO<sub>2</sub> in geological reservoirs (e.g. Gilfillan et al., 2009; see review in Kampman et al., 2013a). Reactions between the acidified CO<sub>2</sub>-charged brine and reservoir minerals might enhance the long-term storage of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> dissolution, and rates of fluid and solute transport (Knauss et al., 2005; White and Brantley, 2003). Investigating natural accumulations of CO<sub>2</sub> can provide insight

into the consequences for geological materials from long-term exposure of supercritical CO<sub>2</sub> and acidic CO<sub>2</sub>-charged brine. Whilst it is expected that a well-sited CO<sub>2</sub> storage facility will not leak, some natural CO<sub>2</sub> reservoirs (such as the Green River site) have conductive features where CO<sub>2</sub> and CO<sub>2</sub>-charged fluids are able to escape from depth to surface. These can provide sampling opportunities and insights into processes that may inhibit CO<sub>2</sub> migration through the overburden, such as dissolution into shallow reservoirs, capillary trapping of CO<sub>2</sub> gas or precipitation of carbonate minerals.

Deep geological storage of anthropogenic CO<sub>2</sub> will involve injection at depths > 800 m up to several kilometres, where the CO<sub>2</sub> is in a supercritical state and formation temperatures can range from ~ 30 to > 80 °C. The geochemical reactions occurring in CO<sub>2</sub> reservoirs, including dissolution into brine, and the subsequent reaction of the CO<sub>2</sub>-charged brine with reservoir minerals are all sensitive to temperature. However, thermodynamic parameters such as the degree of CO<sub>2</sub> and mineral saturation in the fluid, or physical parameters related to flow of the CO<sub>2</sub>, or surface properties of the minerals are equally as important in controlling the rates of these geochemical processes. Observations from shallow reservoirs containing CO<sub>2</sub>-charged brine are thus extremely informative on the fundamental physical and geochemical processes controlling these reactions, and

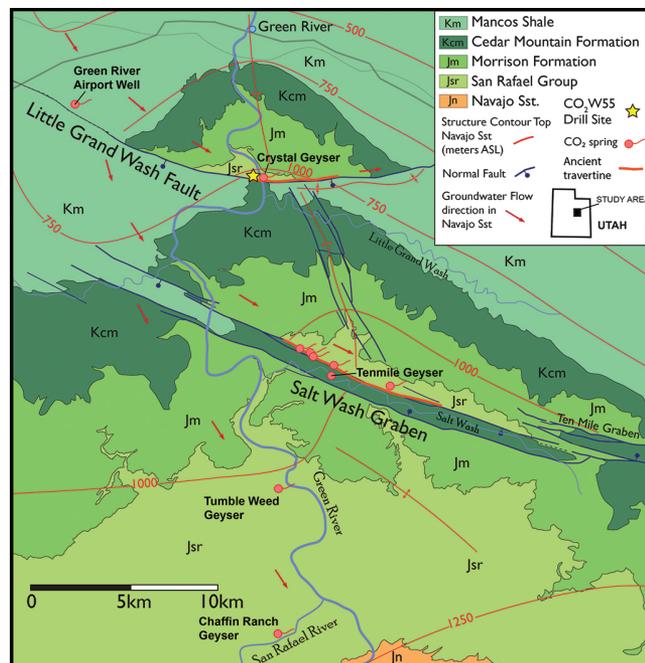
processes that may inhibit CO<sub>2</sub> migration to the surface. The current state of knowledge of fluid flow and geochemical processes occurring during the storage of CO<sub>2</sub> in sedimentary basins is reviewed in Kampman et al. (2013a) and Jun et al. (2012). Natural analogue sites are reviewed in Baines and Worden (2004) and fluid–rock reactions in natural accumulations of CO<sub>2</sub> are reviewed in Bickle et al. (2013). The behaviour of cap rocks is reviewed in Song and Zhang (2012) and geochemical processes occurring during CO<sub>2</sub> 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 CO<sub>2</sub>, CO<sub>2</sub>-gas and CO<sub>2</sub>-charged fluids on reservoir rocks, cap rocks and fault zone materials. This will improve our predictions of the long-term security of anthropogenic CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub> and CO<sub>2</sub>-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 CO<sub>2</sub> System

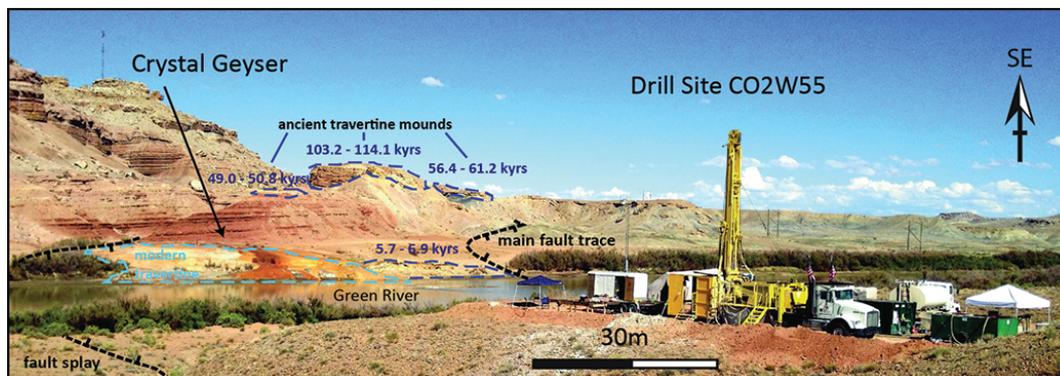
Numerous natural accumulations of supercritical CO<sub>2</sub> and CO<sub>2</sub>-dominant gases occur throughout the greater Colorado Plateau and Southern Rocky Mountains region (Allis et al., 2001; reviewed in Bickle et al., 2013). A small number of



**Figure 1.** Geological map of the Green River anticline showing locations of the Little Grand Wash and Salt Wash Graben normal fault systems, CO<sub>2</sub>-springs and location of drill hole CO<sub>2</sub>W55 (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-CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> and CO<sub>2</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub>-charged brine in the Navajo Sandstone at depths of ~200–340 m; CO<sub>2</sub> gas and CO<sub>2</sub>-charged brine in the Jurassic Wingate sandstones at depths of ~400–500 m; accumulations of supercritical CO<sub>2</sub> and CO<sub>2</sub>-charged brine in the Permian White Rim Sandstone at depths of ~800–900 m; and supercritical CO<sub>2</sub> and CO<sub>2</sub>-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 CO<sub>2</sub> and CO<sub>2</sub>-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). CO<sub>2</sub> and CO<sub>2</sub>-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 CO<sub>2</sub> is thought to accumulate at the anticlinal crest adjacent to the two faults, beneath the south dipping fault seals. The localization of CO<sub>2</sub> leakage to the crest of the anticline reflects this, where open fractures in the fault damage zone allow CO<sub>2</sub> and CO<sub>2</sub>-charged water to escape upwards from the deep supercritical CO<sub>2</sub> 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). CO<sub>2</sub>-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 CO<sub>2</sub> leakage over the past ~ 400 000 yr (Burnside et al., 2013), characterized by successive pulses of CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub>-charged brine within the well bore and expansion of the exsolved CO<sub>2</sub> gas during coring, drilling ceased at 322.5 m b.s. near the base of the Navajo Sandstone.

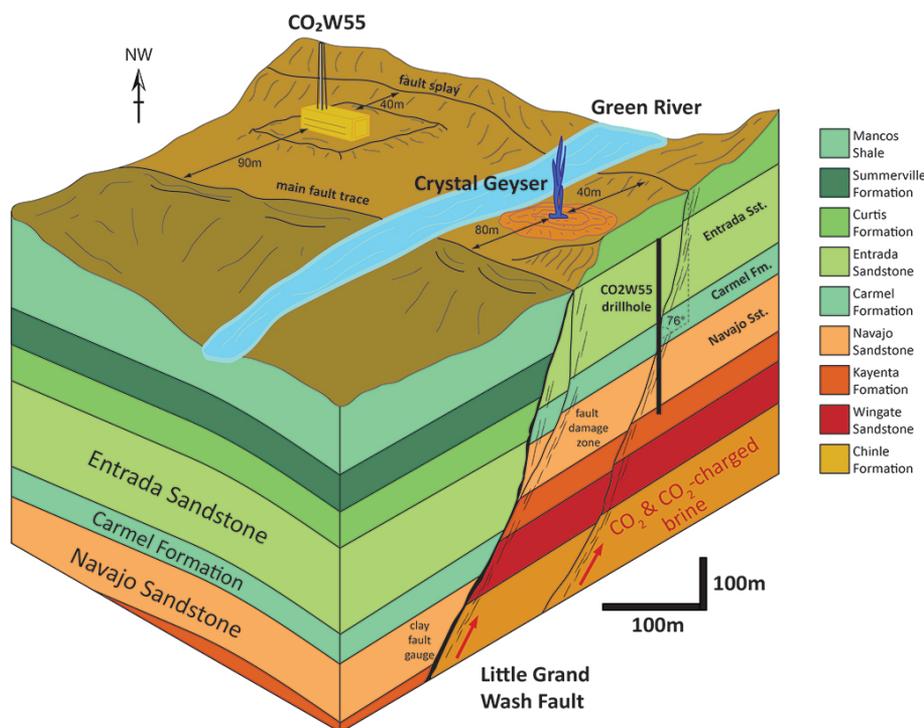
The hole was drilled vertically using DOSECC's hybrid coring system to recover core to a depth of 282 m b.s., with core recovery > 99 %, after which point the drill hole was completed by rotary drilling to a total depth of 322.5 m b.s. On-site processing of the core involved rinsing the core with water 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<sup>-1</sup>, 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 CO<sub>2</sub> gas and CO<sub>2</sub>-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 CO<sub>2</sub> and CO<sub>2</sub>-charged fluids. Zones of CO<sub>2</sub>-bearing fluids were identified based on the presence of CO<sub>2</sub>-degassing and bubbling observed in intervals of core during washing, and CO<sub>2</sub>-charged fluid returns to surface. The CO<sub>2</sub> 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 CO<sub>2</sub> 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<sup>-1</sup>, into the Navajo Sandstone, where the penetration rates increased to around ~ 50 m d<sup>-1</sup>. Within the Navajo Sandstone, the reservoir overpressure and gas lift generated from degassing of the CO<sub>2</sub>-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 CO<sub>2</sub>-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.



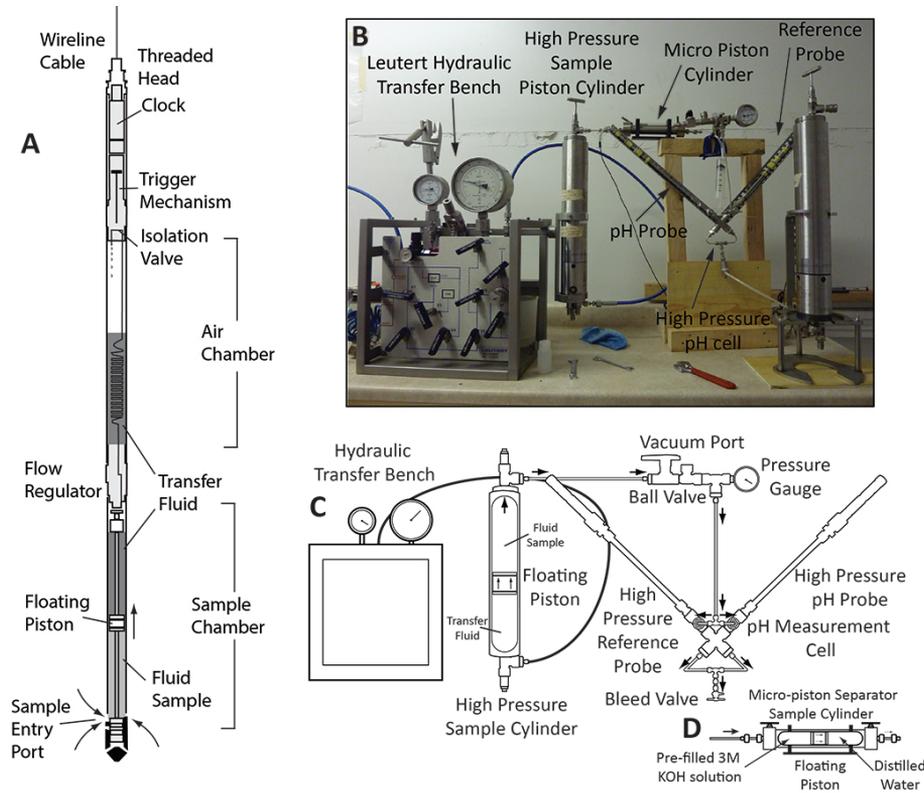
**Figure 3.** Cross section of the region surrounding drill hole CO2W55 showing the location of the Little Grand Wash fault system, including the northerly fault transacted by the drill hole (limited exposure precluded mapping this at surface), and the CO<sub>2</sub>-driven cold water geyser at Crystal 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 CO<sub>2</sub>-rich fluid samples was a key objective of the Green River Drilling project. These CO<sub>2</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub>. 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  $\text{CO}_2$  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  $\text{CO}_2$ .

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  $\text{CO}_2$  in solution by conversion to  $\text{CO}_3^{2-}$  and precipitation as  $\text{K}_2\text{CO}_3$ , from which total  $\text{CO}_2$  concentration could be determined by Gran titration. A sample of the exsolved  $\text{CO}_2$  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  $\text{CO}_2$  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  $\mu\text{m}$  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 $\text{CO}_2\text{W55}$ core stratigraphy

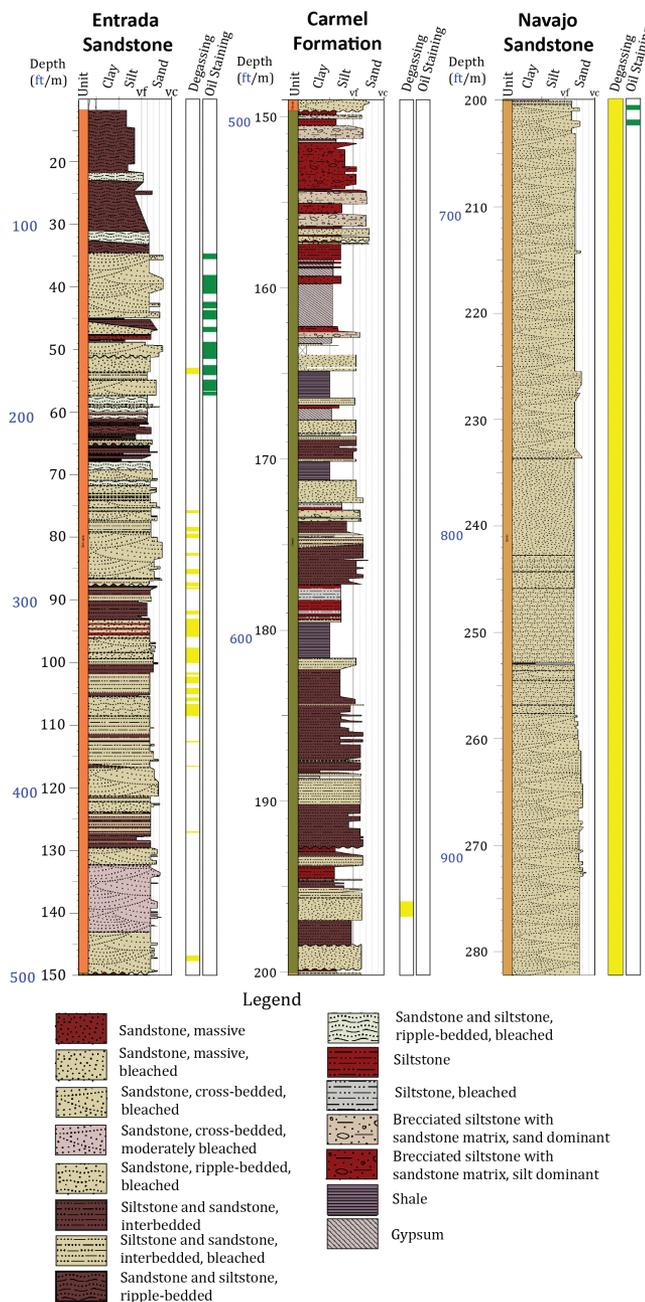
The drill hole from the surface to 25 m.b.s. encountered marine and lacustrine red siltstones facies of the “earthy” Entrada Sandstone member, that grade into the 125 m-thick bleached aeolian dune deposits of the lower Entrada Sandstone, with intercalated marginal marine and sabkha influences throughout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

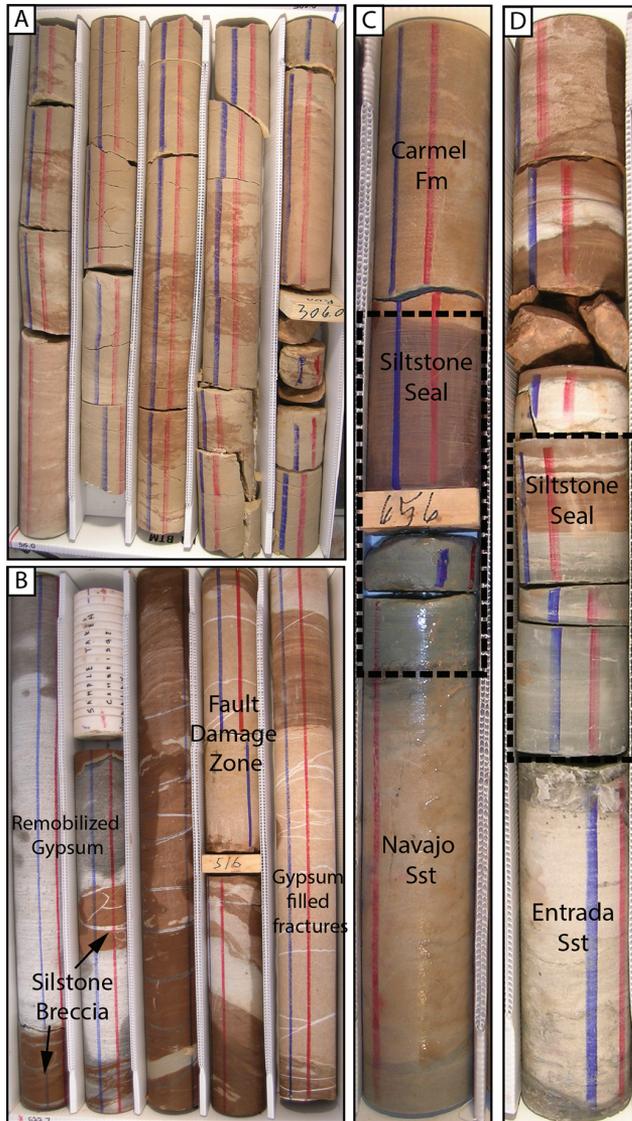
In the CO2W55 core the Navajo Sandstone is comprised of thick sets of high-angle, cross-bedded, well-sorted, fine- to medium-grained sandstones with intercalated inter-dune facies sandstones which are typical of this aeolian deposit (see Verlander, 1995 and references therein). A thin zone of hydrocarbon 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 CO<sub>2</sub>-degassing core and hydrocarbon bearing zones are also shown.

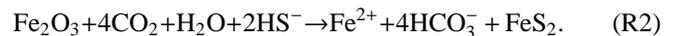
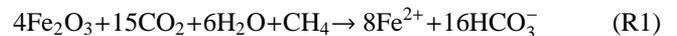
graphic region. This has variously been attributed to bleaching by buoyant hydrocarbons and methane rich brine (Beitler et al., 2003, 2005; Chan et al., 2000; Garden et al., 2001; Parry et al., 2004, 2009) and by dense CO<sub>2</sub>-charged brine containing methane or sulfide reductants (Loope et al., 2010, 2011; Potter-McIntyre et al., 2013; Wigley et al., 2012,



**Figure 6.** (A) Bleached basal sandstones of the Entrada Sandstone hosting CO<sub>2</sub> charged fluids. Fracturing of the core occurs at surface due to exsolution of CO<sub>2</sub> 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 CO<sub>2</sub>-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 Fe<sup>3+</sup> to soluble Fe<sup>2+</sup>. Such acid-reductive disso-

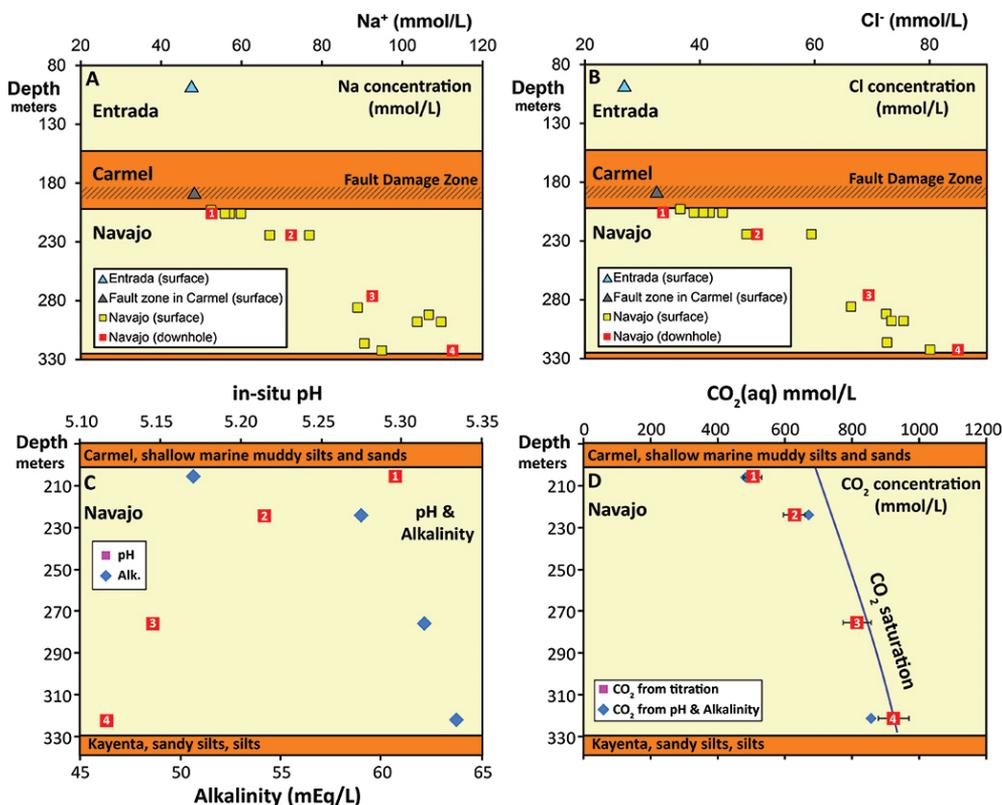
lution is possible with a wide range of naturally occurring sources of acidity (e.g. CO<sub>2</sub>, organic acids, H<sub>2</sub>S) and reductants (e.g. CH<sub>4</sub>, HS<sup>-</sup>, H<sub>2</sub>S) and different combinations most likely act as the bleaching agent in different places. At Green River bleaching of exhumed portions of the Entrada Sandstone has previously been attributed to the passage of CO<sub>2</sub>-charged brine, with minor quantities of dissolved CH<sub>4</sub>. The presence of these CO<sub>2</sub>-rich brine has been inferred from analysis of CO<sub>2</sub>-CH<sub>4</sub> 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 CO<sub>2</sub>W55 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 CO<sub>2</sub>-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<sup>+</sup> and Cl<sup>-</sup> 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<sup>+</sup> and Cl<sup>-</sup> 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 CO<sub>2</sub> 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). CO<sub>2</sub> concentrations are close



**Figure 7.** Preliminary results from the surface and downhole fluid sampling campaign. (A–B) Na<sup>+</sup> and Cl<sup>-</sup> concentrations in downhole and surface sampled fluids. The geochemical profiles illustrate inflow of CO<sub>2</sub>-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<sub>2</sub> concentrations measured directly on titrated samples and recalculated from measured pH and alkalinity. Also shown is the theoretical CO<sub>2</sub> 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<sub>2</sub>-saturated brine and CO<sub>2</sub>-undersaturated meteoric fluid higher in the formation. These results suggest that the Navajo Sandstone is being fed by active inflow of CO<sub>2</sub>-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<sub>2</sub>-charged reservoir have been obtained. Surface and downhole fluid sampling reveals that the sandstone formations are being fed by active inflow of CO<sub>2</sub>-saturated brine through fault fracture networks; with the CO<sub>2</sub>-charged brine being sourced from supercritical reservoirs of CO<sub>2</sub> 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<sub>2</sub>-charged fluids. Narrow zones of mineralogical al-

teration are observed in the cap rock units in contact with the CO<sub>2</sub>-charged reservoir sandstones.

Forthcoming analysis will include mineralogical, petrographic, geochemical and geomechanical studies of the CO<sub>2</sub>-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<sub>2</sub>-promoted fluid–mineral reactions have occurred in the cap rocks and if these reactions either (i) attenuate the CO<sub>2</sub> diffusive distances through the consumption of the CO<sub>2</sub> and the deposition of carbonate minerals or (ii) facilitate CO<sub>2</sub> 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<sub>2</sub>–fluid–mineral reactions. Further drilling is planned at the Green River site to target fault zones that host CO<sub>2</sub> and CO<sub>2</sub>-charged fluid flow. Core samples obtained from this drilling will be studied in order to assess the impacts of CO<sub>2</sub>-promoted fluid–rock interaction on fracture permeability, fault hosted fluid flow and surface leakage of the CO<sub>2</sub>.

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## References

- Allis, R., Chidsey, T., Gwynn, W., Morgan, C., White, S., Adams, M., and Moore, J.: Natural CO<sub>2</sub> Reservoirs on the Colorado Plateau and Southern Rocky Mountains: Candidates for CO<sub>2</sub> Sequestration, Proc. Nat. Conf. On Carbon Sequestration, 2001.
- Allis, R., Bergfeld, D., Moore, J., McClure, K., Morgan, C., Chidsey, T., Heath, J., and McPherson, B.: Implications of results from CO<sub>2</sub> flux surveys over known CO<sub>2</sub> systems for long-term monitoring, United States Geological Survey, 2005.
- Assayag, N., Bickle, M., Kampman, N., and Becker, J.: Carbon isotopic constraints on CO<sub>2</sub> degassing in cold-water Geysers, Green River, Utah, Energy Procedia, 1, 2361–2366, 2009.
- Baer, J. L. and Rigby, J. K.: Geology of the Crystal Geyser and environmental implications of its effluent, Grand County, Utah, Utah Geology, 5, 125–130, 1978.
- Baines, S. J. and Worden, R. H.: The long-term fate of CO<sub>2</sub> in the subsurface: natural analogues for CO<sub>2</sub> storage, Geological Society, London, Special Publications, 233, 59–85, 2004.
- Beitler, B., Chan, M. A., and Parry, W. T.: Bleaching of Jurassic Navajo sandstone on Colorado Plateau Laramide highs: Evidence of exhumed hydrocarbon supergiants?, Geology, 31, 1041–1044, 2003.
- Beitler, B., Parry, W., and Chan, M.: Fingerprints of fluid flow: chemical diagenetic history of the Jurassic Navajo Sandstone, southern Utah, USA, J. Sediment. Res., 75, 547–561, 2005.
- Bickle, M. J.: Geological carbon storage, Nat. Geosci., 2, 815–818, 2009.
- Bickle, M., Kampman, N., and Wigley, M.: Geochemistry of CO<sub>2</sub> sequestration: Natural Analogues, Rev. Mineral. Geochem., 77, doi:10.2138/rmg.2013.77.2, in press, 2013.
- Blakey, R. C., Havholm, K. G., and Jones, L. S.: Stratigraphic analysis of eolian interactions with marine and fluvial deposits, Middle Jurassic Page Sandstone and Carmel Formation, Colorado Plateau, USA, J. Sediment. Res., 66, 324–342, 1996.
- Burnside, N., Shipton, Z., Dockrill, B., and Ellam, R. M.: Man-made versus natural CO<sub>2</sub> leakage: A 400 k.y. history of an analogue for engineered geological storage of CO<sub>2</sub>, Geology, 41, 471–474, 2013.
- Chan, M., Parry, W., and Bowman, J.: Diagenetic hematite and manganese oxides and fault-related fluid flow in Jurassic sandstones, southeastern Utah, AAPG Bull., 84, 1281–1310, 2000.
- Crabaugh, M. and Kocurek, G.: Entrada Sandstone: an example of a wet aeolian system, Geological Society, London, Special Publications, 72, 103–126, 1993.
- Dockrill, B. and Shipton, Z. K.: Structural controls on leakage from a natural CO<sub>2</sub> geologic storage site: Central Utah, USA, J. Struct. Geol., 32, 1768–1782, 2010.
- Doelling, H. H.: Geologic map of the Moab and Eastern Part of the San Rafael Desert 30' × 60' quadrangles, Grand and Emery counties, Utah and Mesa county, Colorado, Geologic map 180: Utah Geological Survey Geologic Map, 180, scale 1:100,000, 2001.
- Duan, Z., Sun, R., Zhu, C., and Chou, I.: An improved model for the calculation of CO<sub>2</sub> solubility in aqueous solutions containing Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, Mar. Chem., 98, 131–139, 2006.
- Evans, J. P., Heath, J., Shipton, Z. K., Kolesar, P. T., Dockrill, B., Williams, A., Kirchner, D., Lachmar, T. E., and Nelson, S. T.: Natural Leaking CO<sub>2</sub>-charged Systems as Analogs for Geologic Sequestration Sites, in: Third Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, 2004.
- Garden, I. R., Guscott, S. C., Burley, S. D., Foxford, K. A., Walsh, J. J., and Marshall, J.: An exhumed palaeo-hydrocarbon migration fairway in a faulted carrier system, Entrada Sandstone of SE Utah, USA, Geofluids, 1, 195–213, 2001.
- Gilfillan, S. M. V., Lollar, B. S., Holland, G., Blagburn, D., Stevens, S., Schoell, M., Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G., and Ballentine, C. J.: Solubility trapping in formation water as dominant CO<sub>2</sub> sink in natural gas fields, Nature, 458, 614–618, 2009.
- Gilfillan, S., Wilkinson, M., Haszeldine, R. S., Shipton, Z. K., Nelson, S. T., and Poreda, R. J.: He and Ne as tracers of natural CO<sub>2</sub> migration up a fault from a deep reservoir, Int. J. Greenh. Gas Con., 5, 1507–1516, 2011.
- Gouveia, F. and Friedmann, S.: Timing and prediction of CO<sub>2</sub> eruptions from Crystal Geyser, UT, United States. Dept. of Energy, 2006.
- Gouveia, F., Johnson, M., Leif, R., and Friedmann, S.: Aerometric measurement and modeling of the mass of CO<sub>2</sub> emissions from Crystal Geyser, Utah, UCRL-TR-211870, Lawrence Livermore National Lab., Livermore, CA (USA), 2005.
- Han, W. S., Lu, M., McPherson, B. J., Keating, E. H., Moore, J., Park, E., Watson, Z. T., and Jung, N.-H.: Characteristics of CO<sub>2</sub>-driven cold-water geyser, Crystal Geyser in Utah: experimental observation and mechanism analyses, Geofluids, 13, 283–297, 2013.
- Harvey, O. R., Qafoku, N. P., Cantrell, K. J., Lee, G., Amonette, J. E., and Brown, C. F.: Geochemical Implications of Gas Leakage associated with Geologic CO<sub>2</sub> Storage – A Qualitative Review, Environ. Sci. Technol., 47, 23–36, 2012.
- Heath, J.: Hydrogeochemical Characterization of Leaking Carbon Dioxide-Charged Fault Zones in East-Central Utah, Masters thesis, Utah State University, USA, 2004.
- Hood, J. and Patterson, D.: Bedrock aquifers in the northern San Rafael Swell area. Utah, with special emphasis on the Navajo

- Sandstone, State of Utah Department of Natural Resources Technical Publication, 78, p. 139, 1984.
- Jun, Y.-S., Giammar, D. E., and Werth, C. J.: Impacts of Geochemical Reactions on Geologic Carbon Sequestration, *Environ. Sci. Technol.*, 47, 3–8, 2012.
- Kampman, N., Bickle, M., Becker, J., Assayag, N., and Chapman, H.: Feldspar dissolution kinetics and Gibbs free energy dependence in a CO<sub>2</sub>-enriched groundwater system, Green River, Utah, *Earth Planet. Sc. Lett.*, 284, 473–488, 2009.
- Kampman, N., Burnside, N. M., Shipton, Z. K., Chapman, H. J., Nicholl, J. A., Ellam, R. M., and Bickle, M. J.: Pulses of carbon dioxide emissions from intracrustal faults following climatic warming, *Nat. Geosci.*, 5, 352–358, 2012.
- Kampman, N., Bickle, M., Wigley, M., and Dubacq, B.: Fluid flow and CO<sub>2</sub>-fluid-mineral interactions during CO<sub>2</sub>-storage in sedimentary basins, *Chem. Geol. Rev.*, in press, 2013a.
- Kampman, N., Maskell, A., Chapman, H. J., Bickle, M. J., Evans, J. P., Purser, G., Zhou, Z., Gattacceca, J., Schaller, M., Bertier, P., Chen, F., Turchyn, A. V., Assayag, N., Rochelle, C., Ballentine, C., and Busch, A.: Drilling and fluid sampling a natural CO<sub>2</sub> reservoir: implications for fluid flow and fluid-rock reaction during CO<sub>2</sub> migration through the overburden, *Chemi. Geol.*, in press, 2013b.
- Kietäväinen, R., Ahonen, L., Kukkonen, I. T., Hendriksson, N., Nyssönen, M., and Itävaara, M.: Characterisation and isotopic evolution of saline waters of the Outokumpu Deep Drill Hole, Finland – Implications for water origin and deep terrestrial biosphere, *Appl. Geochem.*, 32, 37–51, 2013.
- Knauss, K., Johnson, J., and Steefel, C.: Evaluation of the impact of CO<sub>2</sub>, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO<sub>2</sub>, *Chem. Geol.*, 217, 339–350, 2005.
- Loope, D. B., Kettler, R. M., and Weber, K. A.: Follow the water: Connecting a CO<sub>2</sub> reservoir and bleached sandstone to iron-rich concretions in the Navajo Sandstone of south-central Utah, USA, *Geology*, 38, 999–1002, 2010.
- Loope, D. B., Kettler, R. M., and Weber, K. A.: Morphologic Clues to the Origins of Iron Oxide–Cemented Spheroids, Boxworks, and Pipelike Concretions, Navajo Sandstone of South-Central Utah, USA, *J. Geol.*, 119, 505–520, 2011.
- O’Sullivan, R. B.: The Middle Jurassic San Rafael Group and related rocks in east-central Utah. *New Mexico Geological Society Guidebook*, 32, 89–95, 1981.
- Parry, W. T., Chan, M. A., and Beitler, B.: Chemical bleaching indicates episodes of fluid flow in deformation bands in sandstone, *AAPG Bull.*, 88, 175–191, 2004.
- Parry, W. T., Chan, M. A., and Nash, B. P.: Diagenetic characteristics of the Jurassic Navajo Sandstone in the Covenant oil field, central Utah thrust belt, *AAPG Bull.*, 93, 1039–1061, 2009.
- Pasala, S. M., Forster, C. B., Deo, M., and Evans, J. P.: Simulation of the impact of faults on CO<sub>2</sub> injection into sandstone reservoirs, *Geofluids*, 13, 344–358, 2013.
- Peterson, F. and Turner-Peterson, C.: *Geology of the Colorado Plateau: Grand Junction to Denver, Colorado June 30–July 7, 1989*, 130, American Geophysical Union, 1989.
- Potter-McIntyre, S., Allen, J., Chan, M., Shik Han, W., Lee, S.-Y., and McPherson, B.: Iron precipitation in a natural CO<sub>2</sub> reservoir: Jurassic Navajo Sandstone in the northern San Rafael Swell, UT, USA, *Geofluids*, 2013.
- Regensburg, S., Wiersberg, T., Brandt, W., Huenges, E., Saadat, A., Schmidt, K., and Zimmermann, G.: Geochemical properties of saline geothermal fluids from the in-situ geothermal laboratory Groß Schönebeck (Germany), *Chemie der Erde – Geochemistry*, 70, Suppl. 3, 3–12, 2010.
- Shipton, Z. K., Evans, J. P., Kirschner, D., Kolesar, P. T., Williams, A. P., and Heath, J.: Analysis of CO<sub>2</sub> leakage through “low-permeability” faults from natural reservoirs in the Colorado Plateau, east-central Utah, *Geological Society London Special Publications*, 233, 43–58, 2004.
- Shipton, Z. K., Evans, J. P., Dockrill, B., Heath, J., Williams, A., Kirchner, D., and Kolesar, P. T.: Natural leaking CO<sub>2</sub>-charged systems as analogues for failed geologic storage reservoirs Carbon dioxide capture for storage in deep geologic formations: results from the CO<sub>2</sub> capture project, 2, 699–712, 2005.
- Song, J. and Zhang, D.: Comprehensive Review of Caprock-Sealing Mechanisms for Geologic Carbon Sequestration, *Environ. Sci. Technol.*, 47, 9–22, 2012.
- Verlander, J. E.: The Navajo Sandstone, *Geology Today*, 11, 143–146, 1995.
- White, A. and Brantley, S.: The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field?, *Chem. Geol.*, 202, 479–506, 2003.
- Wigley, M., Kampman, N., Dubacq, B., and Bickle, M.: Fluid-mineral reactions and trace metal mobilization in an exhumed natural CO<sub>2</sub> reservoir, Green River, Utah, *Geology*, 40, 555–558, 2012.
- Wigley, M., Dubacq, B., Kampman, N., and Bickle, M.: Controls of sluggish, CO<sub>2</sub>-promoted, hematite and K-feldspar dissolution kinetics in sandstones, *Earth Planet. Sc. Lett.*, 362, 76–87, 2013a.
- Wigley, M., Kampman, N., Chapman, H., Dubacq, B., and Bickle, M.: In-situ re-deposition of trace metals mobilized by CO<sub>2</sub>-charged fluids, *Geochem. Geophys. Geosys.*, 12, 1321–1332, 2013b.
- Wilkinson, M., Gilfillan, S. V. M., Haszeldine, R. S., and Ballentine, C. J.: Plumbing the depths: Testing natural tracers of subsurface CO<sub>2</sub> origin and migration, Utah, in: *Carbon dioxide sequestration in geological media – State of the science*, AAPG Stud. Geol., edited by: Grobe, M., Pashin, J. C., and Dodge, R. L., 619–634, 2009.