

Quarterly Technical Report

Reactive Multiphase Behavior of CO₂ in Saline Aquifers Beneath the Colorado Plateau

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ABSTRACT

Soil gas surveys have been carried out on the Colorado Plateau over areas with natural occurrences of CO₂. At Farnham Dome, Utah, and Springerville-St. Johns, Arizona, proven CO₂ reservoirs occur at 600 - 800 m depth, but no anomalous soil gas CO₂ flux was detected. Background CO₂ fluxes of up to about 5 g m⁻² day⁻¹ were common in arid, poorly vegetated areas, and fluxes up to about 20 g m⁻² day⁻¹ were found at Springerville-St. Johns in heavily vegetated, wet ground adjacent to springs. These elevated fluxes are attributed to shallow root zone activity rather than to a deep upflow of CO₂. Localized areas of anomalously high CO₂ gas flux (~ 100 g m⁻² day⁻¹) were documented along the Little Grand Wash Fault Zone near Crystal Geyser, Utah and nearby in Ten Mile Graben, but those in Ten Mile Graben are not directly associated with the major faults. In both areas, features with a visible gas flux are present. Isotopic measurements on the CO₂ gas confirm that it originated at depth. Evidence of widespread vein calcite at the surface at Farnham Dome and travertine deposits in the other areas suggests that there has been an outflow of CO₂-rich fluids in the past. ¹⁴C ages of pollen trapped in the travertine at Springerville-St. Johns record a period of CO₂ leakage to the atmosphere between 887 ± 35 and 3219 ± 30 years BP. No travertine deposits appear to be currently forming. At Springerville-St. Johns, Crystal Geyser and Ten Mile Graben, there are significant outflows of high-bicarbonate water. Movement of CO₂-rich groundwaters may be the dominant mechanism controlling the mobility of CO₂ today. The very localized nature of the soil gas anomalies, evidence of large scale discharge of CO₂ over a very short period of time and the outflow of ground water containing dissolved CO₂ will present challenges for effective, long term monitoring of CO₂ leakage.

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EXECUTIVE SUMMARY

During this reporting period, CO₂ flux measurements were made along the Little Grand Wash Fault Zone and within the Ten Mile Graben near Green River in central Utah. In contrast to our previous soil gas surveys at Farnham Dome, Utah, and Springerville-St Johns Arizona-New Mexico CO₂ fields, where no anomalous CO₂ flux was observed, anomalously high CO₂ gas flux ($\sim 100 \text{ g m}^{-2} \text{ day}^{-1}$) were observed along the Little Grand Wash Fault Zone and within the Ten Mile Graben

¹⁴C dating of pollen from seven travertine samples from the Springerville-St Johns CO₂ field has been completed. The travertine domes occur over a wide range of elevations from the banks of Little Colorado River to the hilltops over 1000 feet above the river. Despite the broad range of elevations, all of the dates ranged from 887 ± 35 to 3219 ± 30 BP. These ages document a recent, short lived period of CO₂ discharge to the atmosphere

The results of the dating at Springerville-St Johns field are being used to modify the existing numerical model of the reservoir's evolution. The results will be presented at the 2005 Carbon Sequestration Conference in Alexandria. Improvements include a better representation of the geology/permeability regime, inclusion of a 30 bar (1000 feet) head decline inferred from the travertine distribution with elevation and a CO₂ flux that better matches the observations.

A paper was presented at the Fall Meeting of the American Geophysical Union in a session organized by NETL (Advancements in CO₂ Geologic Sequestration Measurement, Mitigation, and Verification Technologies Applied to Field Studies II). The paper describes the results of the soil gas flux surveys.

An invited poster was presented at the 2005 Gordon Conference on Hydrocarbon Resources held in January in Ventura Ca. The poster describes the geologic setting of the Springerville-St. Johns CO₂ field and presents the results of the ¹⁴C dating of the travertine deposits, gas flux measurements and numerical modeling on the migration and mineral sequestration of CO₂.

EXPERIMENTAL

Not applicable.

RESULTS AND DISCUSSION

The most critical issue confronting acceptance of geologic sequestration of anthropogenic CO₂ is the assurance that most of the CO₂ will stay in the subsurface. Natural CO₂ systems on the Colorado Plateau provide insights into the characteristics of CO₂ reservoirs and their overlying sealing rocks (Allis et al. 2001; White et al. 2004). The existence of these reservoirs appears to confirm that favorable structures can trap CO₂ on a geologic time scale. However, there has been little work on how effectively sealed the reservoirs are, and the nature, if any, of CO₂ leakage to the surface. We have completed soil gas flux surveys over areas of known CO₂ accumulation on the Colorado Plateau. These data have important implications with respect to long term monitoring of sequestered CO₂.

Although considerable work has been published on leakage of hydrocarbons from reservoirs (e.g. Schumacher and Abrams, 1996), most of the scientific literature referring to anomalous diffuse soil CO₂ flux has been in volcanic and geothermal settings (Cardellini et al., 2003 (and references within)). There does not appear to be any published literature on the anomalous soil gas emissions from natural CO₂ systems within sedimentary settings. Klusman (2003a, b) carried out CH₄ and CO₂ soil gas flux measurements over Rangely Oil field, Colorado where there has been CO₂ injection for enhanced oil recovery since 1986. Here a low level of CH₄ and CO₂ “microseepage” was detected, and most of the CO₂ was attributed to methanotropic oxidation of CH₄ in the unsaturated zone. CO₂ soil fluxes locally ranged up to 1 – 3 g m⁻² day⁻¹ at the Rangely oil field. At another oil field, the Teapot Dome

in Wyoming, average fluxes during winter at a time of low soil bacterial activity, were an order of magnitude lower (Klusman, 2004).

Soil gas flux measurements were made at Farnham Dome, (Utah), Springerville-St. Johns (Arizona-New Mexico), along the Little Grand Wash Fault Zone near Crystal Geysers and at Ten Mile Graben (Utah, Fig. 1). In these areas, CO₂ has accumulated in the Mesozoic to Paleozoic sedimentary section that is common on the Colorado Plateau. Nearly 5 BCF of CO₂ was produced from Farnham Dome between 1931 and 1979, when the wells were shut-in because of the lack of a market. The main reservoir is Jurassic Navajo sandstone at about 600 m depth. CO₂ has also been tested in deeper formations, and has been found in several wells over 4 km apart on the east flank of the anticlinal structure. (Morgan and Chidsey, 1991; White et al., 2004). The CO₂ reserves have been estimated at 1.5 TCF (D. Davis, pers. comm., cited in White et al., 2004).

At Springerville-St Johns, the proven CO₂ field covers > 1000 km² and contains approximately 14 TCF of CO₂ (S. Melzer, pers. comm., in White et al., 2004). The CO₂ mostly occurs at about 500 m depth in clastic and carbonate units of the Permian Supai group sediments in an anticlinal structure, with overlying anhydrite and mudstone units acting as sealing units (Rauzi, 1999). Some CO₂ has also been found in alluvium deposited on fractured Precambrian granite beneath the Supai Group sediments. There are large volumes of travertine at the surface, natural bicarbonate-rich springs and groundwater, and nearby Quaternary volcanics (0.3 – 3 Ma) suggestive of a possible recent deep CO₂ source (Moore et al., 2004).

At Crystal Geysers and Ten Mile Graben, east-west trending faults cut two north-dipping anticlines (Doelling, 2001). Several natural CO₂ features (bubbling pools) and abandoned oil wells that discharge CO₂-rich waters (e.g. Crystal Geysers) occur along the fault zones near the axis of the structural highs (Doelling, 1994). Travertine is actively precipitating, and significant amounts of ancient travertine occur near these features and cap adjacent terraces and buttes. Recent work has characterized the geology and geochemistry of the area (Heath 2004, Williams 2004, Dockrill et al. 2004).

Soil Gas Flux Measurements

Method

The purpose of the CO₂ soil gas flux measurements was to carry out reconnaissance-scale surveys over areas of subsurface CO₂ accumulation to identify areas of anomalous flux. The potential areas of CO₂ accumulation are large (100 – 1000 km²), so a systematic grid survey across each area was not feasible. Instead, measurement sites were chosen based on geologic and hydrologic factors with sites preferentially located in areas of possible leakage. These sites included fault zones, structural highs, calcite veins or thick travertine accumulations, and springs or pools. It was recognized that results from such survey patterns could not be used to assess total soil gas CO₂ emissions, but it was hoped that the results would confirm or deny CO₂ leakage from the reservoirs and provide qualitative estimates of the scale of CO₂ soil gas fluxes.

Measurements were made using a Westsystems flux meter containing a LI-COR 820 infrared gas analyzer (IRGA) connected to a palm computer. The IRGA was calibrated at the start of each field survey using CO₂-free air and 1000 ppm CO₂ standards. CO₂ measurements are made by placing an accumulation chamber (AC) on the soil surface and pressing it into the soil to obtain a seal. AC gases are pumped through a desiccant to the IRGA and are returned to the AC in a closed loop. During the measurement CO₂ concentration data and elapsed time are displayed on the computer. Data were collected for a minimum of 2 minutes at each site. Atmospheric pressure (P) and temperature (T) were recorded at each grid node. The CO₂ flux (F_{CO2}) in units of grams of CO₂ per m² per day (g m⁻² d⁻¹) is calculated from the rate of change of CO₂ concentration (dc/dt) using equation 1, where R is the gas constant, V is the system volume, A is the area of the AC footprint, and k is a constant for unit conversion.

$$F = k \left[\frac{P}{RT} \times \frac{V}{A} \times \frac{dc}{dt} \right] \quad 1$$

An example of the increase in AC CO₂ concentration with time at a site with a flux of 120 g m⁻² day⁻¹ is shown in Figure 2.

Because our goal was to measure anomalous fluxes, if the CO₂ concentration in the AC did not increase sufficiently to produce a good correlation coefficient for dc/dt in two minutes

then the flux was defined as “zero”. For the chosen sampling time constraint, the minimum flux value we recorded was $1.3 \text{ g m}^{-2} \text{ d}^{-1}$. Low flux values in this range are similar to what has been described from basin-fill sediments at Dixie Valley, Nevada, and are likely related to biogenic CO_2 emissions (Bergfeld et al., 2001).

Expected variability

The variation in replicate flux measurements at an individual site is a function of the amount of soil-disturbance, meteorological conditions, operator skill, instrument stability and natural variations in CO_2 emissions (Lewicki et al., 2005). Expected measurement errors are reported from laboratory experiments as under-representing actual values by 12% (Evans et al., 2001), or varying by $\pm 10\%$ (Chiodini et al., 1998). A recent field-based comparative study of diffuse CO_2 emissions on the flanks of Comalito Volcano, Nicaragua showed that consecutive flux measurements by five teams of researchers at thirty-six grid points over very high-flux thermal ground (F_{CO_2} from 218 to $14,719 \text{ g m}^{-2} \text{ d}^{-1}$) varied between 5 and 167% (Lewicki et. al., 2005).

Results from replicate flux measurements from thirty-four moderate to high-flux thermal sites (F_{CO_2} from 6 to $1,368 \text{ g m}^{-2} \text{ d}^{-1}$) over geothermal systems in Long Valley caldera, California, and Dixie Valley, Nevada, indicate that measurement variations over the more moderate flux sites in this study will be lower than what is reported above (Fig. 3). The geothermal data exhibit a positive exponential relation between increasing flux and the standard deviation of replicate measurements. The coefficient of variation for replicate measurement at these sites was between 0.2 and 29%. Since most fluxes at the Green River sites are $\leq 50 \text{ g m}^{-2} \text{ d}^{-1}$, and assuming the field sites will be properly sited and sufficiently prepared, we expect replicate measurements will vary at or below what was found in the geothermal locations.

Field Survey Techniques

The measurement technique varied for each of the three survey areas. At Farnham Dome, the first of the areas to be surveyed, we began by having 40 soil gas measurement nodes on a 25 m grid at the first measurement site in order to increase the accuracy of the average gas flux for the site. This took several hours, and once it was realized that the gas flux was uniformly low, the number of measurements per site was decreased. The average number of measurement nodes per site at Farnham Dome after the first measurement site was 18, and in

most cases, these were still on a grid spacing of 25 m. This enabled sampling 5 to 8 measurement sites a day, depending on ease of access and distance between sites. At Springerville-St. Johns, the number of measurements per site was further reduced to about 10 after the first day of measurements also showed uniformly low values. It was decided that the priority should be to survey as many prospective sites as possible rather than concentrate on acquiring more accurate values at fewer sites. Along the Little Grand Wash Fault Zone and at Ten Mile Graben, the obvious fault control to the visible CO₂ outflow areas, and in places limited access through washes at right angles to the faults, meant that long traverses were often made with measurements at a 25 m spacing. In the areas where gas anomalies were detected, additional measurements were usually made to improve delineation of the anomaly.

Results

Farnham Dome

Soil gas flux results were first presented in White et al. (2004). Measurements were made at 14 sites during April 2004 (Fig. 4). The average soil CO₂ fluxes and the 95% confidence intervals for the grid means were between 0.5 (0.2-0.9) and 3.7 (2.6-4.7) g m⁻² d⁻¹. Lower fluxes were measured at grids containing soils derived from shale as compared with grids that were sited on sandstone-derived soils.

These are very low CO₂ soil fluxes and are consistent with a low level of shallow biogenic CO₂ production in arid terrains, indicating negligible input of CO₂ gas from reservoir depths. Klusman (2004a) reports similar values at the Rangely oil field, Colorado. In similar arid sagebrush terrain, background fluxes of 1 to 5 g m⁻² d⁻¹ have been observed adjacent to the Dixie Valley geothermal field, Nevada (Bergfeld et al., 2001), and at Long Valley, California (Bergfeld, in prep.). In comparison, soil CO₂ respiration rates of 10 to 20 g m⁻² d⁻¹ are characteristic of temperate grasslands, croplands and tropical savannas (Raich and Schlesinger, 1992).

Although it is possible that seepage, and therefore leakage, of CO₂ derived from the Farnham Dome reservoir may be occurring at locations that we did not capture with our measurements, we suggest that because we surveyed the most likely sites for CO₂ seepage, it is unlikely that

seepage is occurring in this area. The low result for all 14 sites suggests that Farnham Dome may be sealed.

During reconnaissance mapping of the faults and structural trends for site selection for the soil gas measurements at Farnham Dome, widespread calcite veins were noted in joints in sandstone units of the Cedar Mountain Formation, and linear calcite debris mounds were found in some of the shale. Because the mapping was not comprehensive, other areas are likely to exist. We believe that these calcite veins reflect past leakage of CO₂ from the Farnham Dome reservoir. Soil gas measurements indicate these zones are now tightly sealed and not leaking at the resolution of our measurements.

Springerville-St. Johns, Arizona-New Mexico

Soil gas measurements were made at 27 sites around the known extent of the CO₂ field during May, 2004 (Fig. 5). Although the sites were widely spaced, sites were located in areas where geologic or hydrologic factors enhanced the possibility of a soil gas flux. We sampled areas adjacent to travertine domes, inside the dome craters, on basalt cinder cones, areas adjacent to high-bicarbonate springs, next to ground water and deep wells that reportedly encountered CO₂ at depth and over more deeply eroded structural highs where some of the lower permeability seal rocks may have been thin or absent.

For 22 sites, the average flux is $4 \pm 4 \text{ g m}^{-2} \text{ d}^{-1}$, and is similar in magnitude to the values at Farnham Dome. At five sites, the soil gas flux ranged between 10 and 25 $\text{g m}^{-2} \text{ d}^{-1}$. In all these cases the sites were on wet, vegetated ground adjacent to springs, the Little Colorado River, or a lake. Disturbance of the soil often released visible bubbles of CO₂-rich gas, occasionally with an H₂S smell. These higher soil fluxes are interpreted as due to shallow root zone activity in the permanently saturated soil, and not to an upflow of CO₂ from greater depth.

Little Grand Wash Fault Zone (Crystal Geyser) and -Ten Mile Graben, Utah

Soil gas measurements were concentrated along the Little Grand Wash Fault Zone (LGSFZ, on which Crystal Geyser is located), and along Ten Mile Graben about 8 km to the south of LGWFZ. Figure 6 shows the 10 profiles along the LGWFZ in relation to the fault zone traces

as mapped by Doelling (2001). Each data point represents one soil gas measurement, in contrast to the data for Farnham Dome and Springerville-St Johns which were averages of several soil gas measurements. On five of the profiles (#1, 2, 5, 6, and 8), anomalous soil gas fluxes appear to coincide with the southern trace of the LGWFZ. On two of the profiles closest to Crystal Geysers (#1, 2), a second spike of anomalous soil gas flux occurs approximately 100 m north of the main spike. This appears to coincide with the dual fault trace comprising this part of the LGWFZ.

The highest soil gas fluxes occurred close to Crystal Geysers (profile 1), with the highest flux site ($> 700 \text{ g m}^{-2} \text{ day}^{-1}$) being on an outcrop of pre-geyser travertine close to the Green River. This outcrop appears to be the original spring outflow site prior to the drilling of the now-abandoned oil exploration well in 1935, which has subsequently become known as Crystal Geysers. Zones of gas bubbles were seen in a 50 m stretch of the Green River adjacent to the travertine apron below the geysers, and adjacent to the opposite shore where travertine also outcropped. During the soil gas measurements, an H_2S gas odor was noticed on profile 3 between the two fault zones, and near the north end of profile 8 (Figure 6). Shipton et al. (2004) also note a gas seep in about the same position as our profile 3.

In Ten Mile Graben, (Fig. 7), one profile straddled the entire graben (#13), whereas all other profiles were close to the northern fault zone, because all the bubbling pools and springs occur close to or immediately north of this fault zone. On profile 13, the measurements suggested no anomalous soil flux on the mapped fault zones defining either side of the graben. However, at the north end of this profile, approximately 400 m from the northern fault trace, one site was found where the soil gas flux was $23 \text{ g m}^{-2} \text{ d}^{-1}$. Three other measurements within about 10 m of this site were not anomalous. The one anomalous site was on top of a subtle ridge ($< 0.5 \text{ m}$ elevation) of travertine debris suggesting a fracture at depth. On profile 14 a similar pattern was observed. At the northern end of the profile, close to a bubbling spring surrounded by a travertine apron and about 400 m north of the fault trace, three soil gas fluxes of $3 - 5 \text{ g m}^{-2} \text{ d}^{-1}$ were measured. Elsewhere the flux was less than $1 \text{ g m}^{-2} \text{ d}^{-1}$. Some significant soil gas anomalies were also detected in profile 12, where at one location, the soil gas flux ranged to over $100 \text{ g/m}^2/\text{day}^{-1}$. At this location, several measurement sites within about a 50 m radius gave anomalous fluxes. Most of the sites in profile 12 were in a broad wash that was covered with broken sheets of recent but inactive travertine. The two active features, overflowing pools with gas bubbles, were precipitating

travertine, which was cementing the sands in the wash. This type of spring activity had probably moved around the wash in recent geologic time.

In contrast to the soil gas measurements at LGWFZ, the sites with anomalous gas fluxes at Ten Mile Graben were, with one exception, not directly associated with the mapped fault zone traces. There was one site near the eastern end of profile 12 (Figure 9) where a flux of $21 \text{ g m}^{-2} \text{ d}^{-1}$ did coincide with a fault trace. The soil gas flux anomalies typically appeared to be localized leakage points within the Entrada Sandstone that outcrops on the north side of the graben. Occasionally there was evidence that joints in the sandstone may be influencing the location of the gas leakage, but there were also many sites located on joint trends that showed no anomalous soil gas flux.

AGU Meeting Presentation

The results of the soil gas surveys were presented at the Fall Meeting of the American Geophysical Union in a session organized by NETL (Advancements in CO₂ Geologic Sequestration Measurement, Mitigation, and Verification Technologies Applied to Field Studies II). The slides used in the presentation follow.

Implications of soil gas survey results over known carbon dioxide systems for long-term monitoring

Rick Allis (Utah Geological Survey)

Deborah Bergfeld (U.S.G.S.)

Joe Moore (EGI. Univ. of Utah)

Jason Heath (NMIMT)

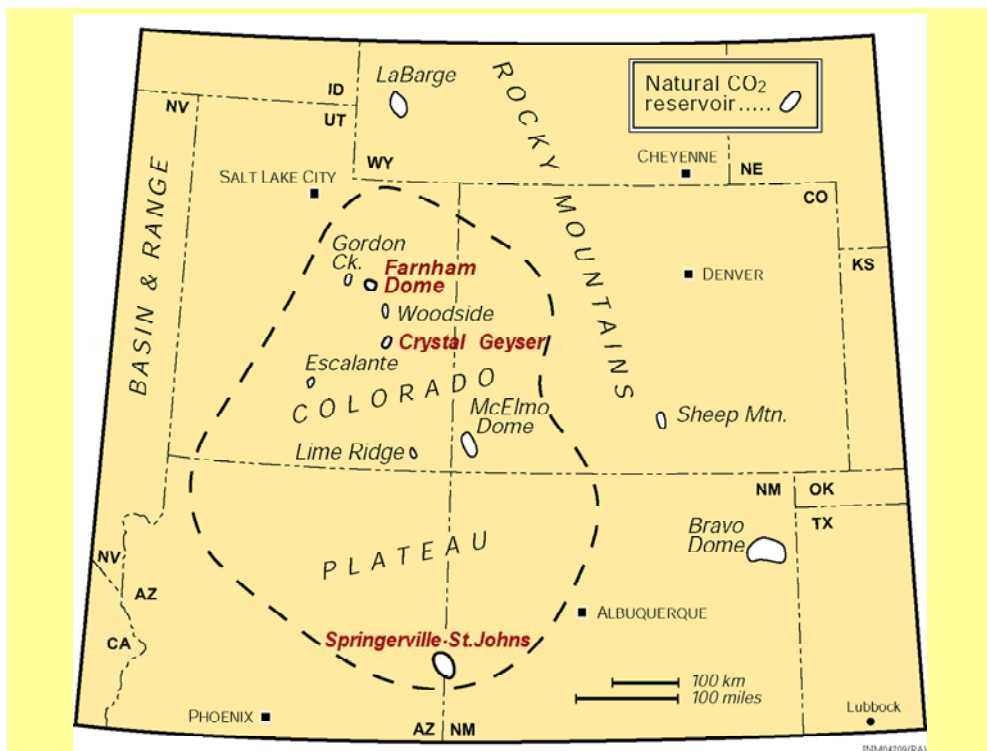
Brian McPherson (NMIMT)

Supported by grant from DOE NETL

GCA54A-07, AGU Fall meeting, Dec. 17 2004

We carried out soil gas surveys over three natural CO₂ areas on the Colorado Plateau as part of a study of reservoir analogues for CO₂ sequestration

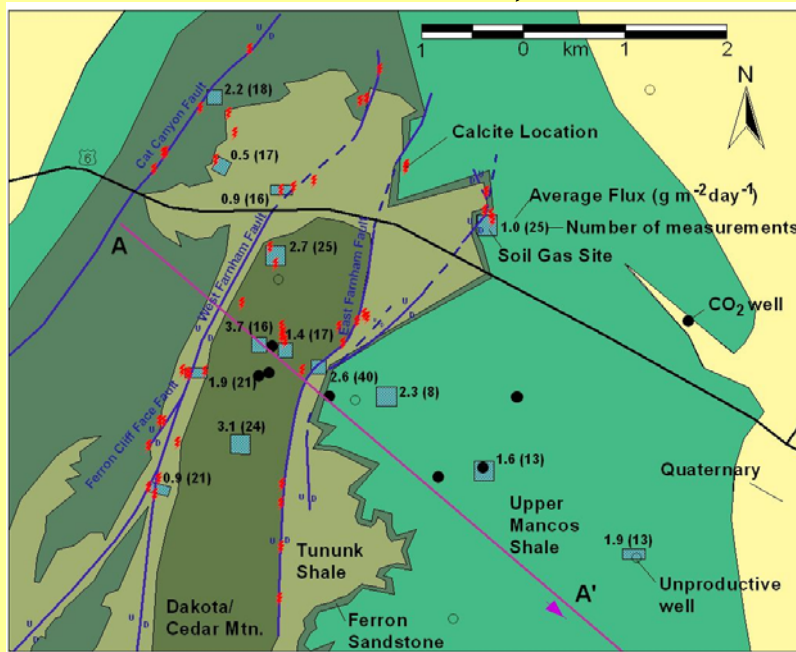
- Farnham Dome, UT (~ 1 tcf CO₂ at 600 m depth in Navajo sandstone reservoir; no evidence of CO₂ discharge at surface)
- Springerville – St Johns, AZ-NM (> 1 tcf CO₂ in domal Permian reservoir; no CO₂ gas features, but bicarbonate-rich springs and travertine)
- Crystal Geysers-Ten Mile Graben, UT (faulted, structural highs containing active CO₂-charged features and travertine along the fault zones)



Flux measurements were made using a Westsystems flux meter containing an infrared gas analyzer, calibrated with CO₂-free air and 1000 ppm CO₂ standards. At most grids 10 measurements on grid per site yielded an average flux



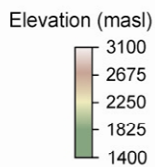
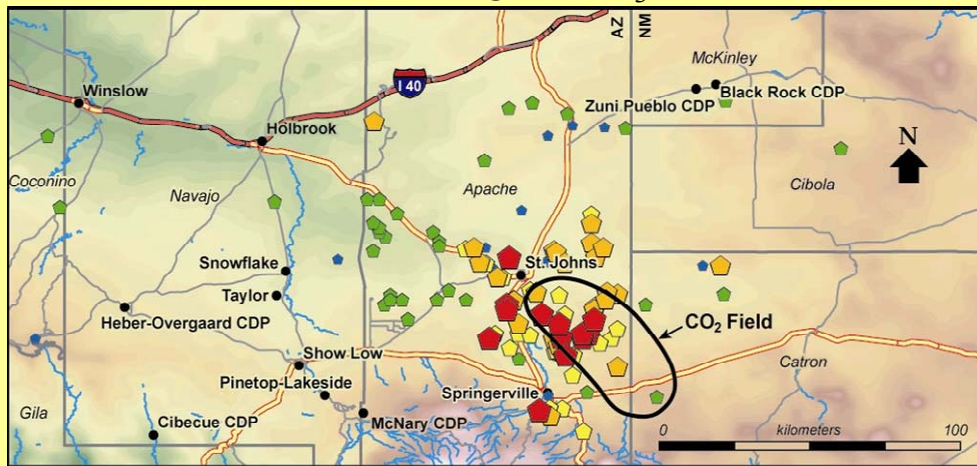
Farnham Dome, UT



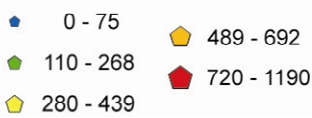


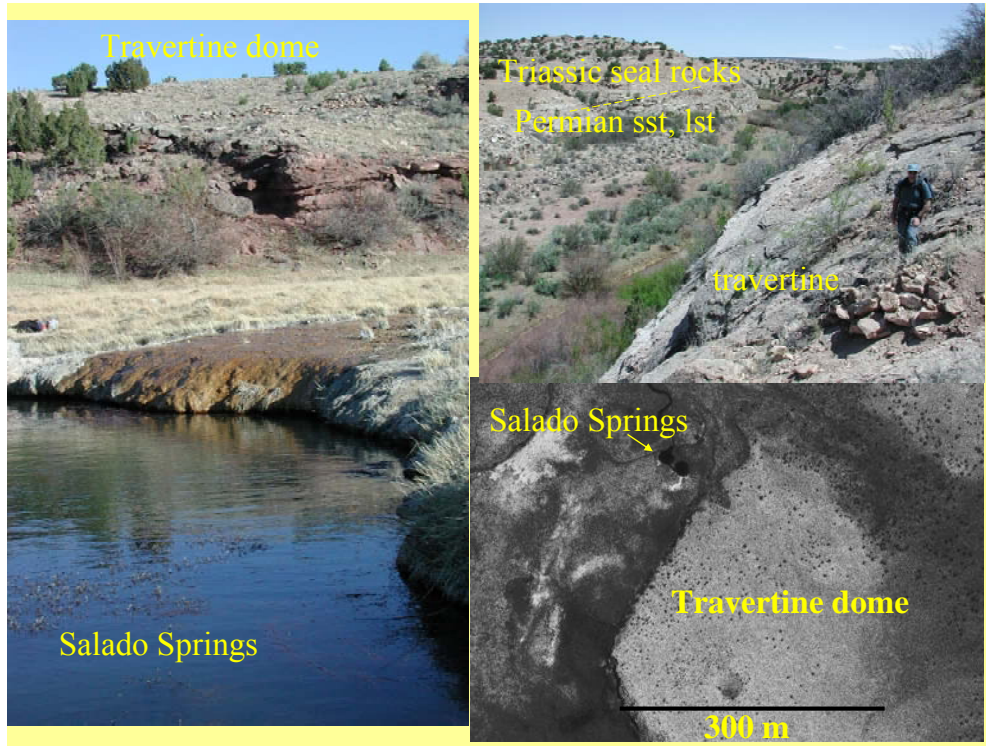
Although no anomalous soil-gas flux was detected, vein calcite debris-fields suggest past episodes of CO₂-saturated fluid flow, perhaps sealing the present day reservoir

Springerville-St Johns CO₂ field: groundwater wells in the area show high HCO₃ concentrations



HCO₃ (ppm)

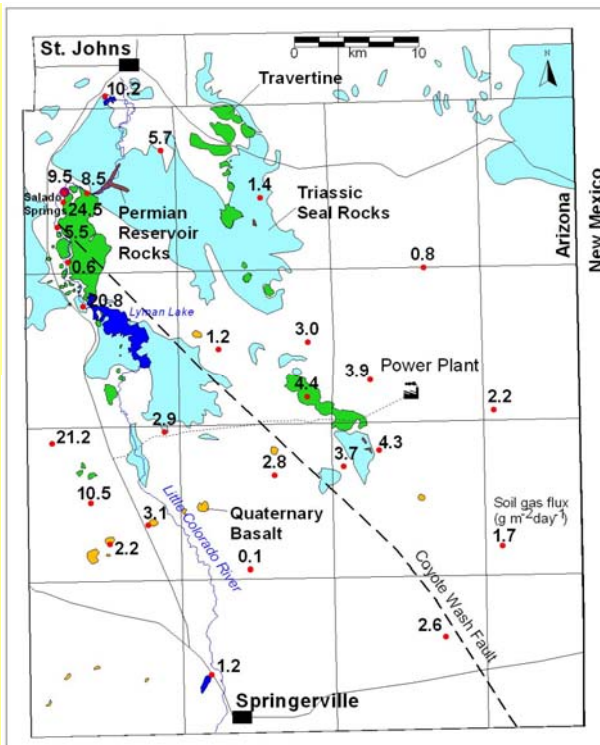


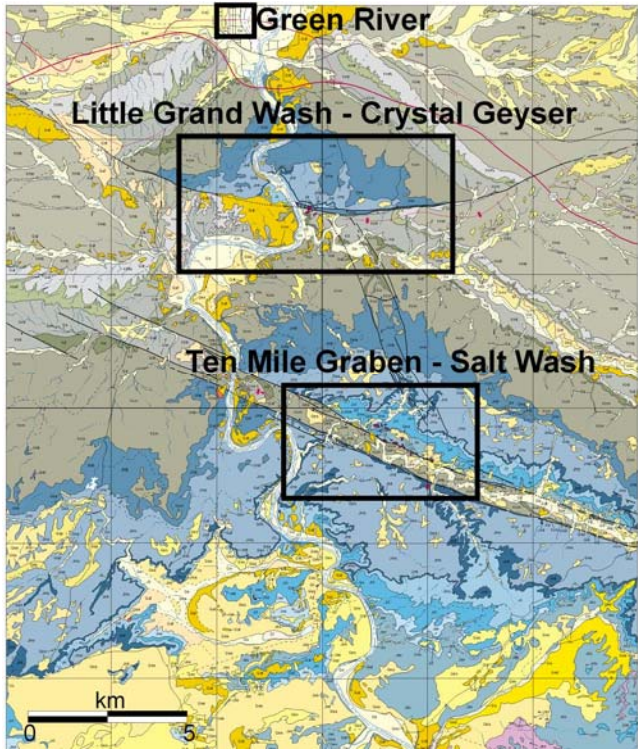


Soil-gas CO₂ flux results, Springerville-St Johns (g m⁻² day⁻¹)

Higher fluxes occur at heavily vegetated sites in wet ground adjacent to spring outflows

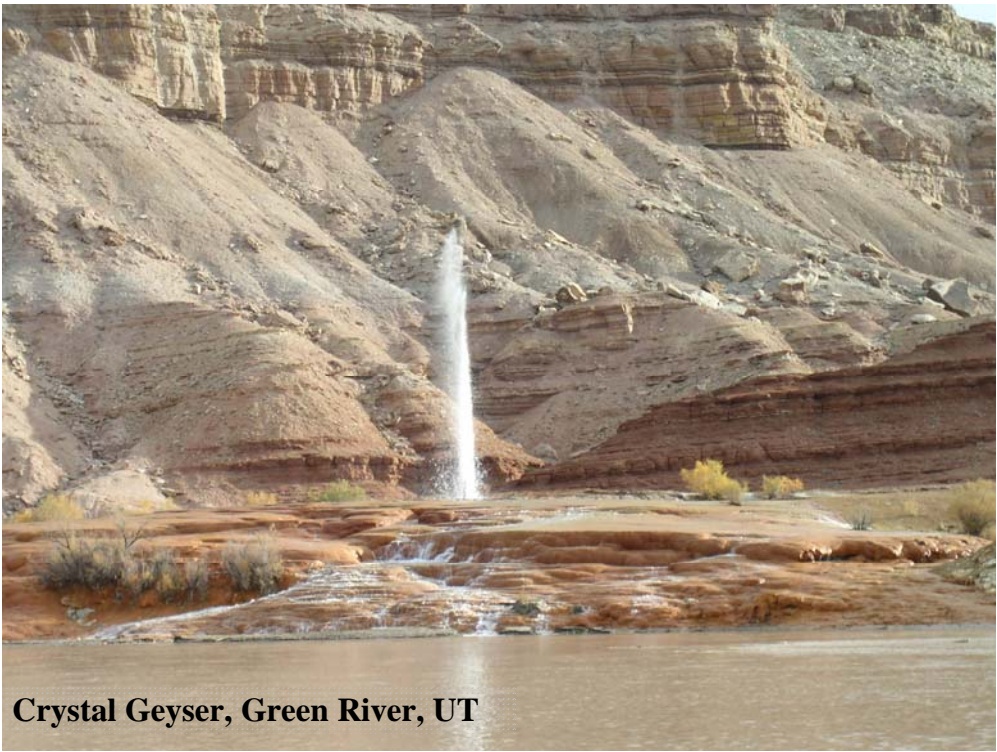
Higher fluxes are due to shallow root zone activity, not to deep upflow of CO₂ gas



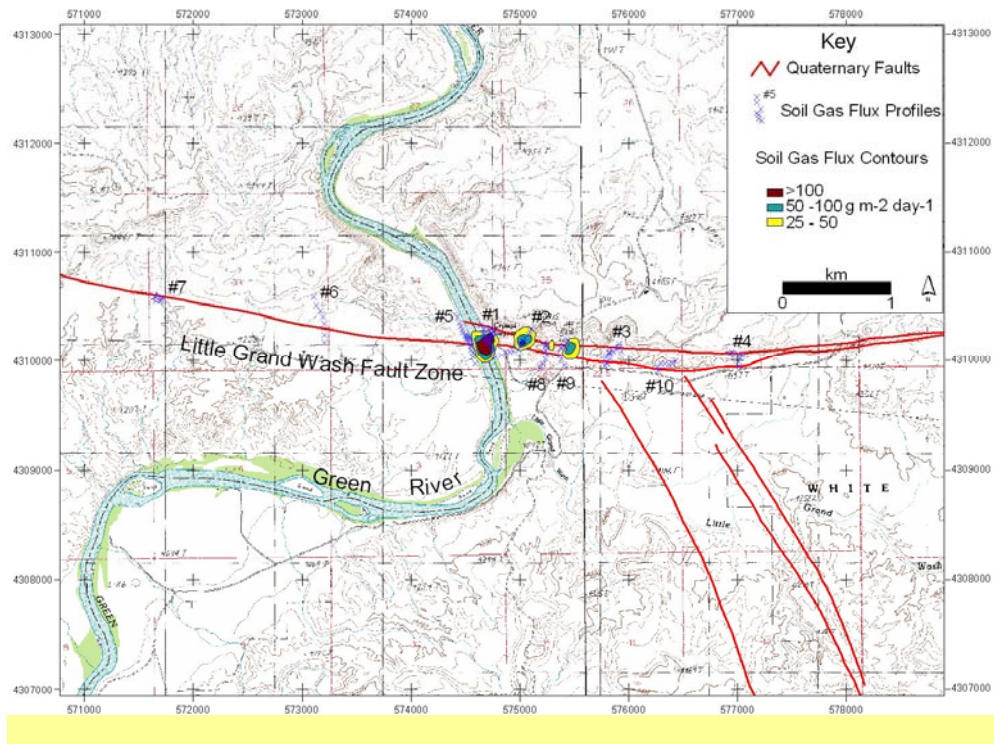


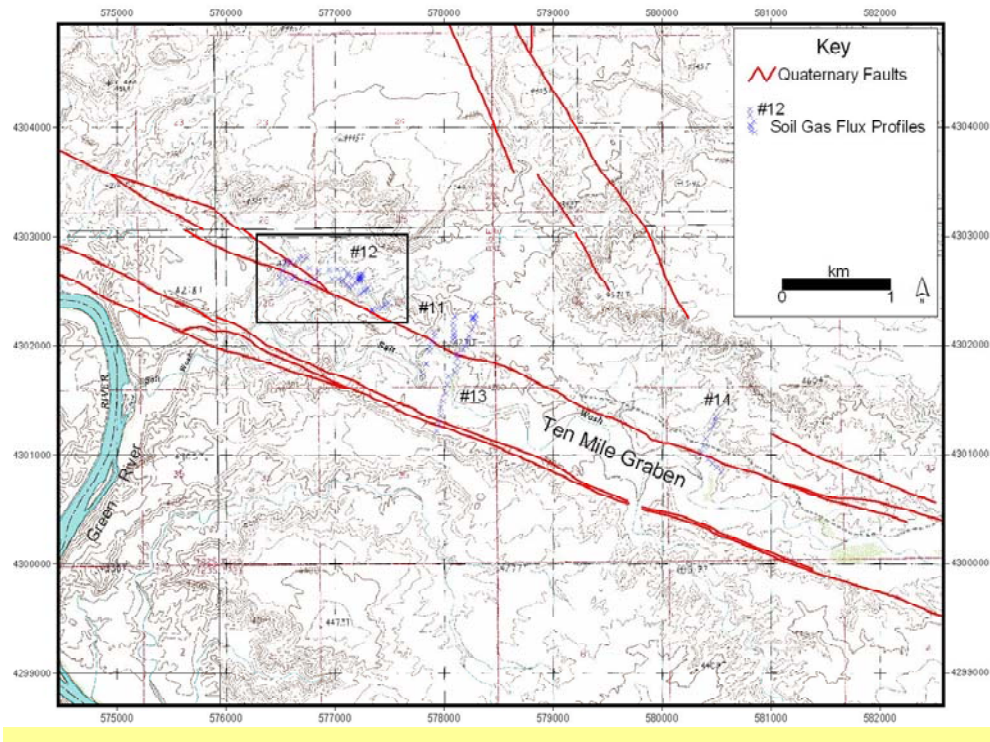
CO₂ soil-gas measurements were carried out adjacent to the fault zones highlighted in the boxes, south of Green River, Utah.

In both areas, an anticlinal structure dips to the north, and CO₂-charged features occur on the faults near the crest of the anticlines



Crystal Geyser, Green River, UT





Implications (1)

- We find the results encouraging (and surprising) – no obvious leakage to the surface of CO₂ gas at two areas (Farnham Dome, Springerville) despite known CO₂ reservoirs at 600 m depth, which is a positive result for the sequestration industry
- At the third site (Crystal Geyser - Ten Mile Graben), soil gas measurements confirmed the observed CO₂ leakage; however even here, the leakage is not widespread, but may be localized as almost point sources along the fault zones

Implications (2)

- At Springerville and Crystal Geysir-Ten Mile Graben areas, major outflows of high-HCO₃ ground water and recent, extensive travertine deposits, imply a significant loss of *dissolved* CO₂. This could be the main source of CO₂ leakage, and must be included in any monitoring program
- At Farnham Dome, widespread vein calcite debris at the surface implies a past episode of CO₂-saturated flux through now-eroded cover rocks. This CO₂ reservoir may have self-sealed itself
- More work is needed on all these systems to better understand the both the fluid flow and fluid-rock interactions that may occur over CO₂ reservoirs

Gordon Conference Presentation

An invited poster was presented at the 2005 Gordon Conference on Hydrocarbon Resources held in January in Ventura Ca. The poster highlights the geology, hydrology, ages of travertine deposits and the results of preliminary numerical modeling on the migration and mineral sequestration of CO₂ at Springerville-St. Johns.

One of the most significant features of the Springerville-St. Johns area is the presence of travertine deposits that cover an area of more than 250 km². These deposits provide unequivocal evidence of CO₂ leakage to the atmosphere. ¹⁴C ages of pollen from 7 travertine deposits have been obtained. These travertine domes occur over a wide range of elevations from the banks of Little Colorado River to over 1000 feet above the river. Despite the broad range of elevations, all of the dates ranged from 887 ± 35 to 3219 ± 30 BP (refer to panel 1 of the poster below). No deposits appear to be forming today. This narrow range of dates was unexpected. The dates indicate that the reservoir was at higher pressures in the recent past, and that significant leakage of CO₂ from natural reservoirs may occur episodically and over relatively short time periods. Additional samples from travertine deposits at higher elevations, which may be older, have been collected and submitted for ¹⁴C AMS dating at the New Zealand Institute for Geological and Nuclear Sciences.

In our initial numerical models we assumed that the travertine had been deposited over a much longer time periods, on the order of 10⁵ years. We are in the process of modifying these calculations to reflect the new data and their implications regarding pressures within the reservoir and fault permeabilities. The results of the models will be presented at the 2005 Carbon Sequestration Conference.

CO₂ Sequestration and Migration in a Natural CO₂ Field at Springerville-St. Johns, USA

Joseph Moore¹
 Stephen White²
 Richard Allis³
 Michael Adams⁴
 Deborah Bergfeld⁴

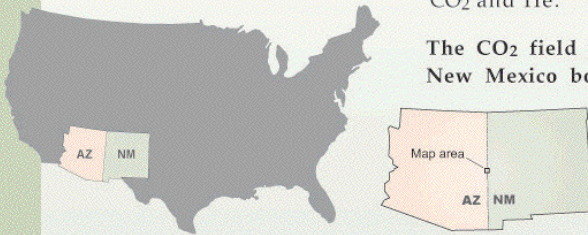
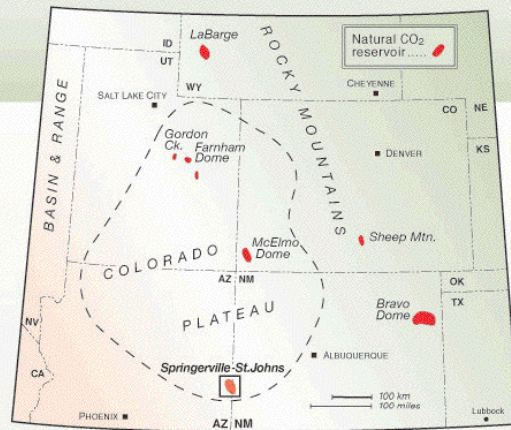
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⁴ USGS, Menlo Park, 345 Middlefield Rd., MS434, California 94025

Theme

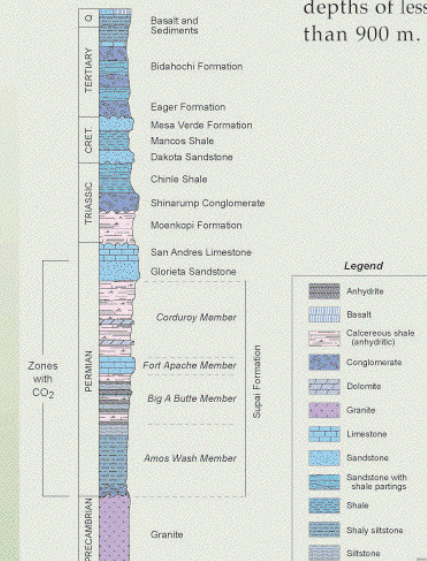
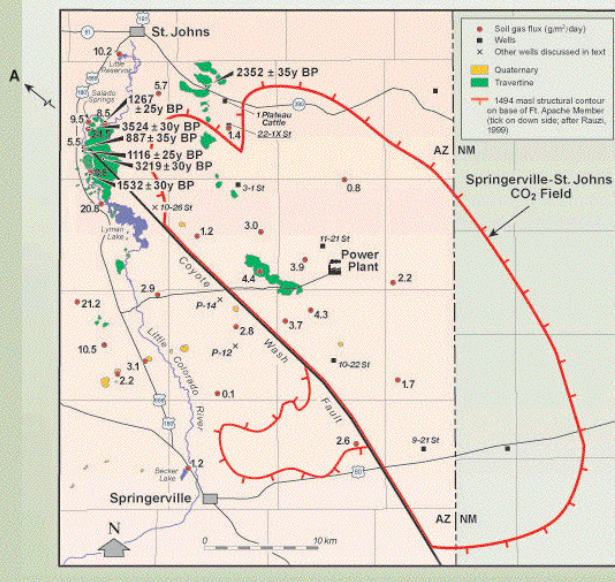
Increasing global interest in the geologic sequestration of CO₂ has raised important questions about its long-term fate. Geochemical models suggest that substantial amounts of CO₂ injected into deep reservoirs can be removed through fluid-fluid and fluid-mineral reactions, particularly those that produce carbonates. However, few studies of natural CO₂ reservoirs are currently available to determine the efficiency of mineral sequestration and the effects of fluid-mineral reactions. In this poster, the results of geochemical and hydrologic investigations conducted on the Springerville-St. Johns CO₂ field in eastern Arizona and western New Mexico are described. The study documents the effects of both water-rock interactions and leakage of CO₂ to the atmosphere.

Geologic Setting

Springerville-St. Johns is one of more than a dozen generally similar CO₂ reservoirs developed in domed Mesozoic and Paleozoic sedimentary rocks of the Colorado Plateau and Southern Rocky Mountain region of the western U.S (Allis et al., 2001). Within these reservoirs, siliciclastic rocks and to a lesser extent carbonates serve as the primary aquifers, whereas anhydrite beds and mudstones act as local seals. The Ridgeway Arizona Oil Corp. is presently developing the Springerville-St. Johns field for CO₂ and He.



The CO₂ field covers approximately 1813 km² on the Arizona-New Mexico border adjacent to the Plio-Pleistocene Springerville volcanic field. The Permian Supai Formation, which forms a broad, northwest-trending asymmetrical anticline with steeper dips on the faulted southwest flank of the structure, hosts the reservoir. Most of the production is from red siltstones at depths of less than 900 m.



Travertine Deposits

The Springerville-St. Johns area contains one of the greatest concentrations of travertine (CaCO_3) spring deposits in the U.S. These deposits cover an area of approximately 250 km² (Sirrinc, 1956). They are prevalent adjacent to a 10 km length of the Little Colorado River between Lyman Lake and Salado Springs, where numerous springs and seeps occur today.

Many deposits are unusually large and symmetric. Travertine sheets up to 6.4 by 3.2 km in extent and circular domes up to 610 m in diameter were deposited.

Travertine occurs adjacent to seepage areas and on terraces up to nearly 300 m above the valley floor. Domes have thicknesses ranging from less than 3 to about 60 m.

The size and extent of the deposits points to a long

history of CO_2 migration and leakage to the atmosphere. ¹⁴C ages have been obtained on plant material from seven deposits. The large dome southeast of Salado Springs (Figure D) has yielded the oldest age of 3524 ± 35 y BP; the youngest deposit an age of 887 ± 35 y BP (see map on preceding panel). Travertine deposition today is relatively insignificant and no dome structures are currently forming. Measured CO_2 gas fluxes over the reservoir are also low (refer to map), and can be attributed to organic processes occurring in the soil.



A Travertine sheets and pool adjacent to Salado Springs.

B A small well preserved travertine dome on the valley floor.

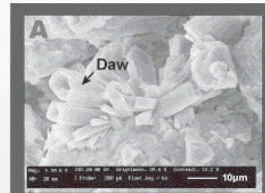
C Interior of the large travertine dome located southeast of Salado Springs (see next figure).

D Aerial view of the Salado Springs area showing travertine sheets north of the springs and the large dome to the southeast.

E Travertine sheets on the bluff above the Little Colorado River (lower left and center of photo).

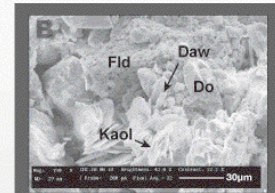
Mineralogy of the CO_2 Reservoir Rocks

Core samples of the productive Supai Formation were studied petrographically and by X-ray diffraction analysis. Only samples from 462 to 472 m in well 22-1X State yielded evidence of reactions that could be related to interactions with CO_2 -rich fluids. These samples are characterized by the dissolution of authigenic cements and detrital feldspar grains and by the formation of dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) and kaolinite. Dawsonite is thought to be an important mineral sink for CO_2 in deep continental aquifers (e.g. Knauss et al., 2001).



Dawsonite (Daw) prisms showing characteristic hollow interiors.

Scanning electron microscope backscattered electron images.



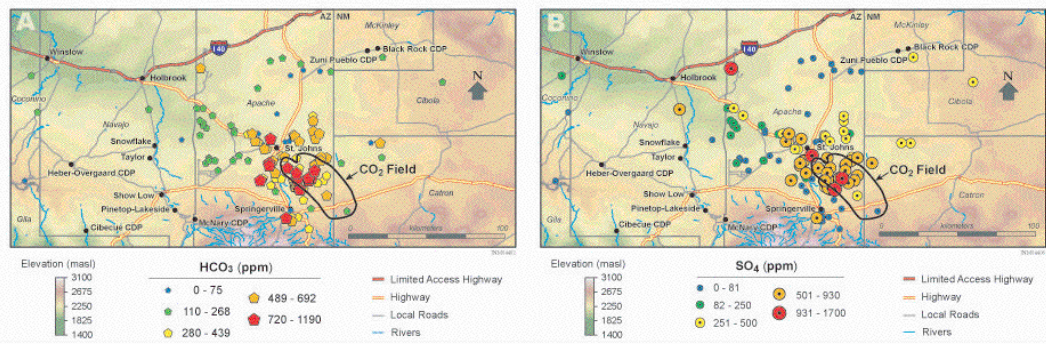
Pore-filling kaolinite (Kaol) and dawsonite. A partially dissolved grain of detrital feldspar (Fld) projects into the pore space which is lined with early authigenic dolomite (Do). The kaolinite appears younger than the dawsonite.

Groundwater Chemistry

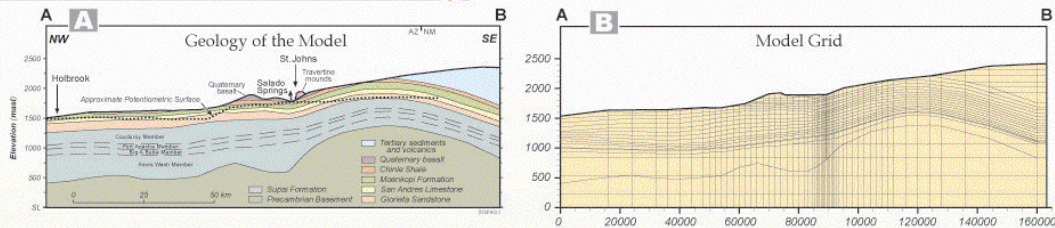
The waters in the Springerville-St. Johns area range continuously in chemical character from Ca-Mg HCO_3 to Ca-Mg Cl- SO_4 . Waters in the immediate vicinity of the CO_2 field show the greatest

enrichments in HCO_3 and SO_4 . All of the waters are supersaturated with respect to calcite and dolomite but undersaturated with respect to anhydrite and gypsum. The

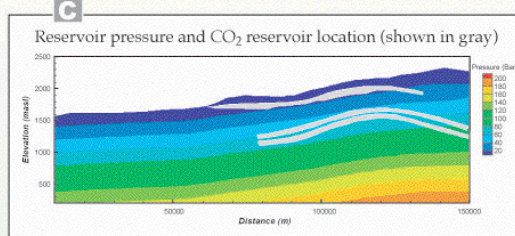
degree of supersaturation of dolomite is highest in the immediate vicinity of the CO_2 field. Similarly, saturation indices for gypsum are highest in the vicinity of the CO_2 field.



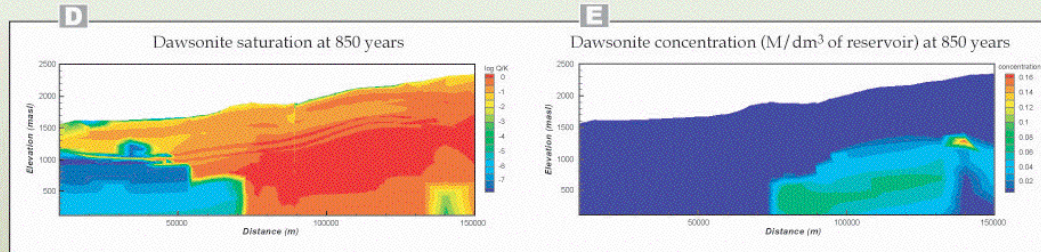
Groundwater Chemistry *continued*



In order to understand the changes suggested by the geologic evidence we have begun to model the hydrology of the system, including the reactive chemistry of the water-rock interactions on a broad scale. Two TOUGH2/ChemTOUGH2 integrated finite difference models of the cross section shown in A have been developed. The cross section has been divided into a number of elements to match the geological layer interfaces (B). A high permeability fault has been incorporated into the model. Figure C shows the locations of the CO₂ reservoirs that form beneath seal rocks when CO₂ is added to the base of the model for 10⁵ years. Flow from the fault is about 80 kg/s, compared to the present-day flow at Salado Springs of 20 kg/s.



Figures D and E show dawsonite saturations and regions of precipitation. Dawsonite is undersaturated throughout most of the field. Precipitation occurs largely in the deep area of the reservoir with a high concentration of CO₂.



Conclusions

- The Springerville-St. Johns CO₂ field is a shallow gas reservoir that shows evidence of both CO₂ leakage to the atmosphere and low temperature interactions between CO₂ charged fluids and rocks typical of other Colorado Plateau gas reservoirs.
- Interactions between the CO₂-charged fluids and reservoir rocks has resulted in dissolution of detrital feldspars and carbonate cements and the formation of dawsonite (NaAlCO₃OH)₂ and kaolinite. Only minor amounts of dawsonite are predicted to precipitate, primarily within the deep parts of the reservoir where CO₂ pressures are high.
- Leakage of CO₂-charged waters at the surface has produced spectacular symmetrical domes ranging up to 610 m in diameter and extensive sheets of travertine up to 6.4 by 3.2 km in extent. ¹⁴C dates on seven deposits have yielded ages ranging from 3524 ± 35 y BP to 887 ± 35 y BP.
- Travertine deposition appears to be relatively insignificant today, although bicarbonate-rich groundwaters document a continued flux of CO₂ from depth. No anomalous flux of CO₂ was observed at the surface. The present conditions may reflect the effects of a declining water table, a significantly diminished outflow of CO₂-charged waters due to a drier climate and a reduced flux of CO₂ at depth.
- The results of this study suggest that CO₂ is stored primarily as dissolved carbonate species in groundwater and as gas accumulations. Only a small percentage of the CO₂ was sequestered in secondary minerals.

Acknowledgements

We thank Tom White at Ridgeway Arizona Oil Corp. for discussions about the Springerville-St. Johns CO₂ field and for help in obtaining chemical analyses of the groundwaters. Jeff Hammond at Tucson Electric Power Co. was also very helpful in sharing information about the groundwater characteristics of the area. Doug Jensen drafted the figures. Support for this project was provided by a grant from the Department of Energy (DE-FC25-00NT4096, Program Manager David Hyman), the Utah Energy Office, and by the Utah Geological Survey.

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Conclusions

Soil gas surveys conducted over three areas with natural occurrences of CO₂ on the Colorado Plateau. The results indicate that the gas reservoirs at Farnham Dome, Utah, and Springerville-St. Johns, Arizona, are sealed. In contrast, significant gas flux ($\sim 100 \text{ g m}^{-2} \text{ day}^{-1}$) was observed at the Crystal Geyser-Ten Mile Graben area near Green River, Utah. Areas of high flux are localized along faults near features with a visible gas flux. Isotopic measurements on the CO₂ gas confirm that it has originated from depth. However, evidence of widespread vein calcite at the surface (Farnham Dome) and travertine deposits in the other two areas suggests that there has been an outflow of CO₂-rich fluids in the past. ¹⁴C ages obtained on pollen from 7 travertine deposits at Springerville-St. Johns indicate that substantial leakage of CO₂ occurred in the recent past between 887 ± 35 and 3219 ± 30 years BP. Thus leakage to the atmosphere may occur episodically, over relatively short time periods. Movement of bicarbonate-rich groundwaters may be the dominant mechanism controlling the mobility of CO₂ today in these reservoirs. The very localized nature of the soil gas anomalies, evidence of episodic leakage, and the outflow of ground water containing dissolved CO₂ will present challenges for effective, long term monitoring of CO₂ leakage.

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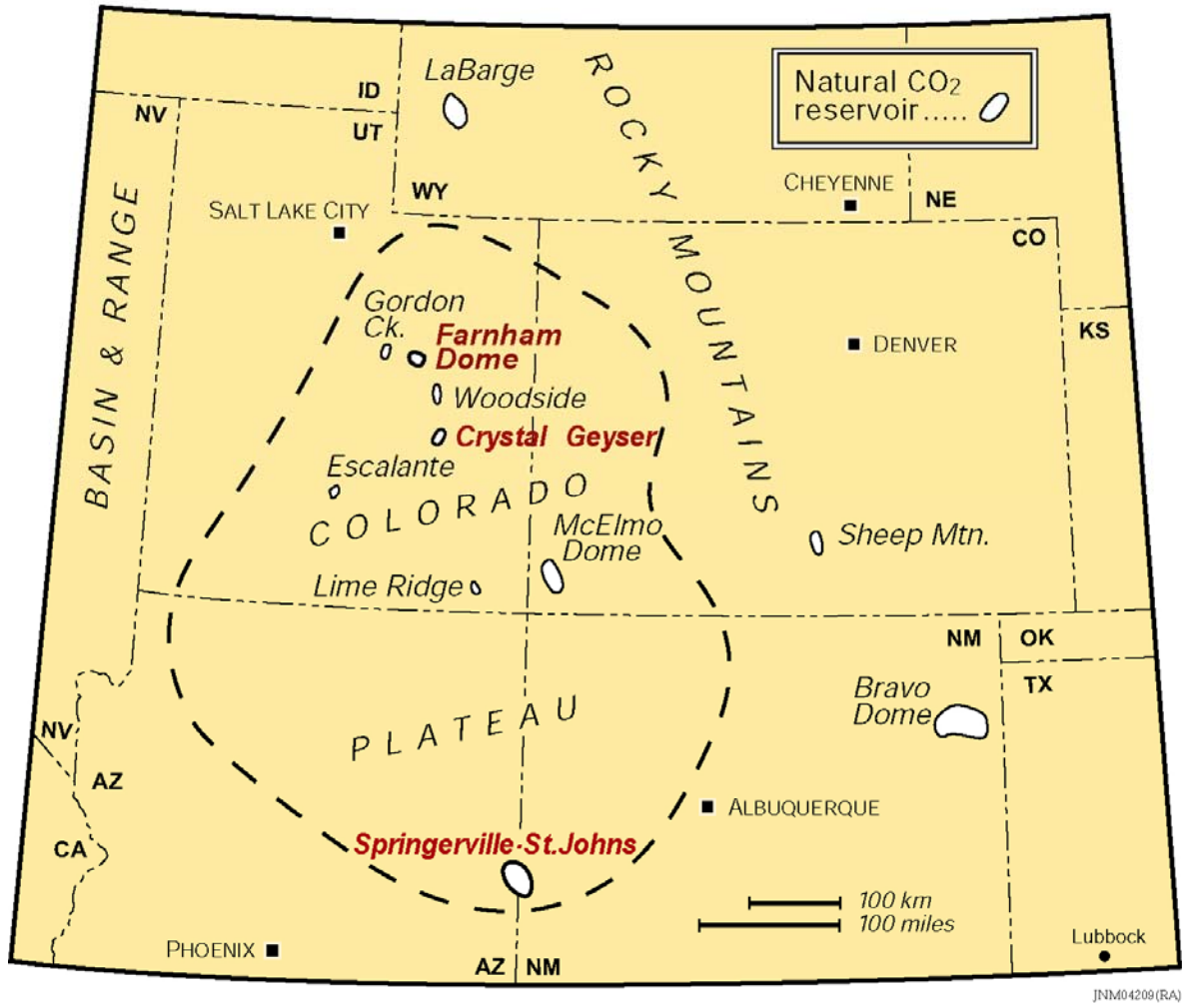


Figure 1. Natural CO₂ occurrences on the Colorado Plateau, with the occurrences discussed highlighted in red.

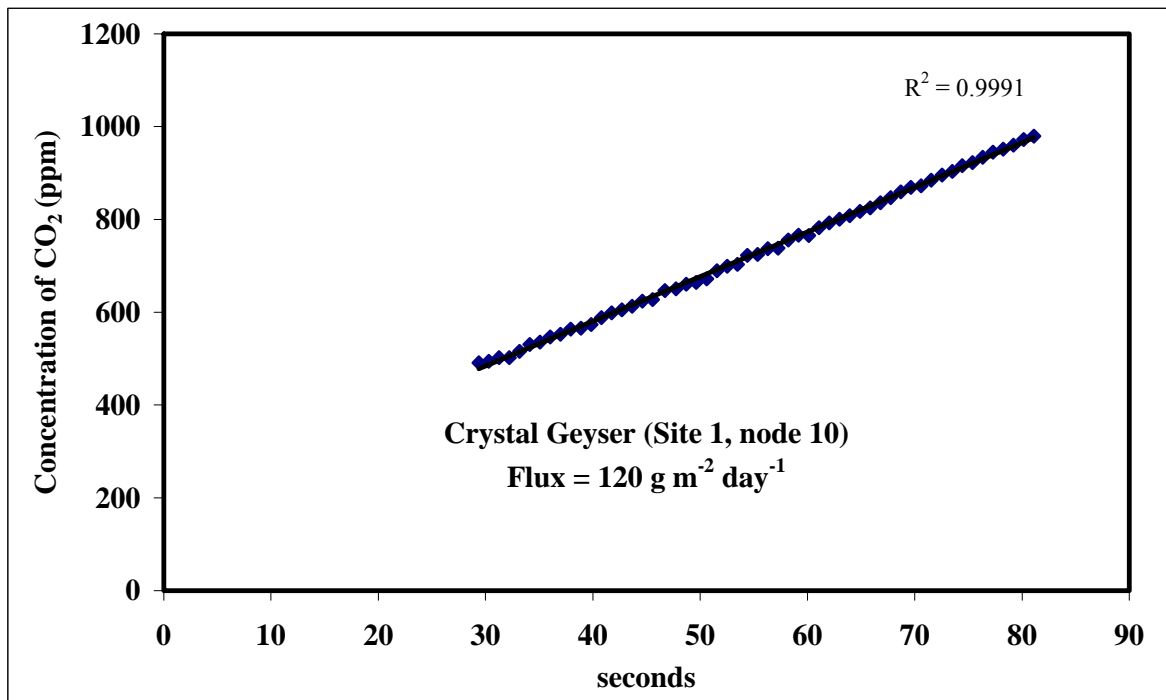


Figure 2. Example of the CO₂ concentration change with time in the accumulation chamber. The flux is calculated from the slope of the line and the other factors defined in Equation 1.

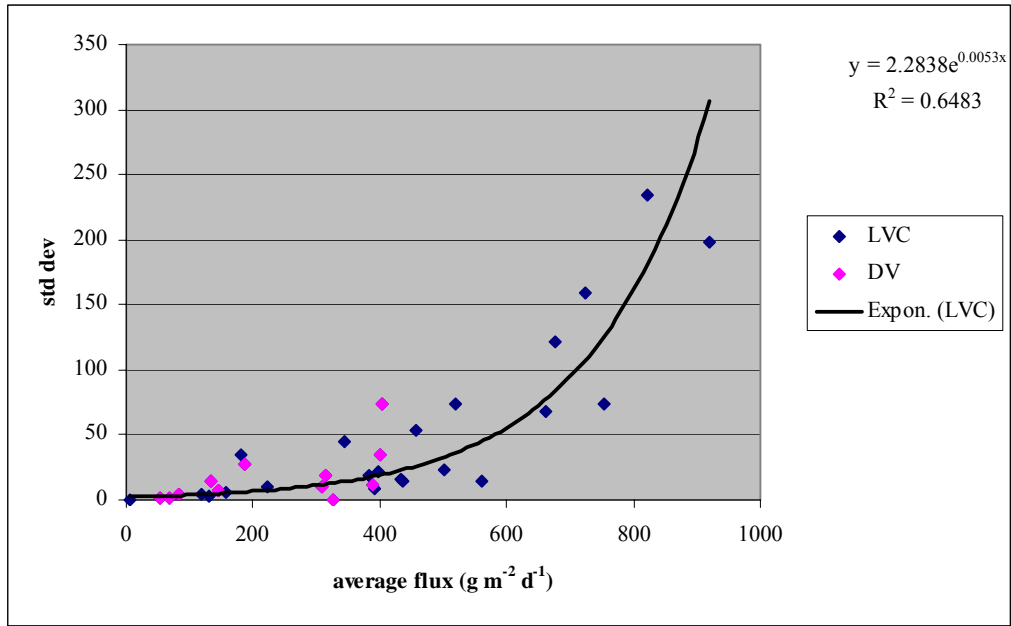


Fig. 3. Plot of the average flux vs standard deviation for 34 geothermal sites at Long Valley caldera, CA and Dixie Valley, NV. A minimum of 3 replicate measurements were taken at each site. This pattern of increasing standard deviation with increasing flux is assumed to be similar to the measurements on natural CO₂ systems.

Farnham Dome, UT

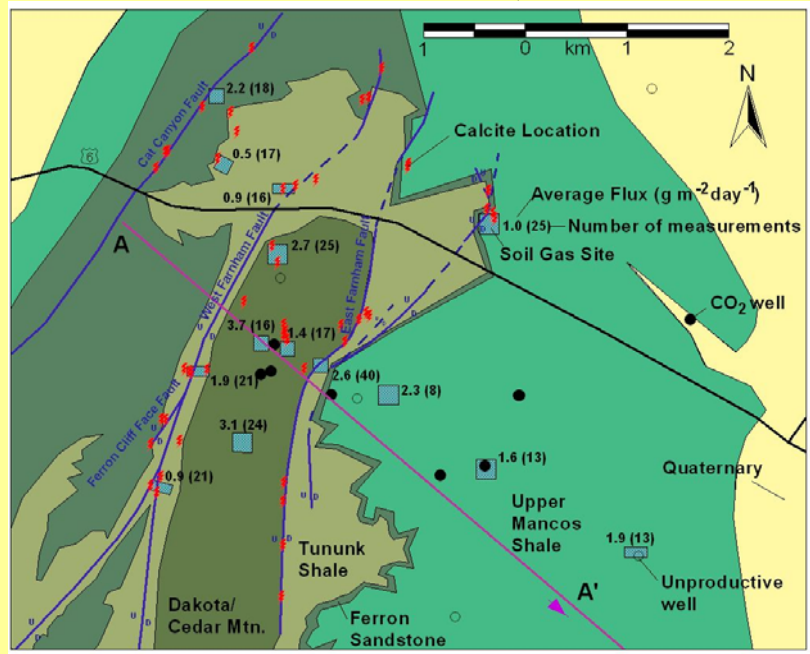


Fig. 4. Soil gas flux measurements at Farnham Dome, Utah.

Soil-gas CO₂ flux results, Springerville-St Johns (g m⁻² day⁻¹)

Higher fluxes occur at heavily vegetated sites in wet ground adjacent to spring outflows

Higher fluxes are due to shallow root zone activity, not to deep upflow of CO₂ gas

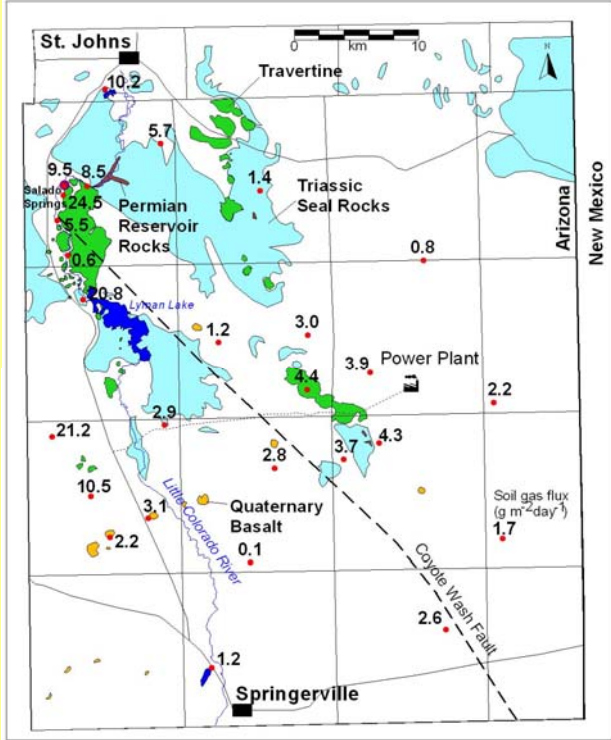


Fig. 5. Soil gas flux measurements at Springerville-St. Johns, Arizona-New Mexico.

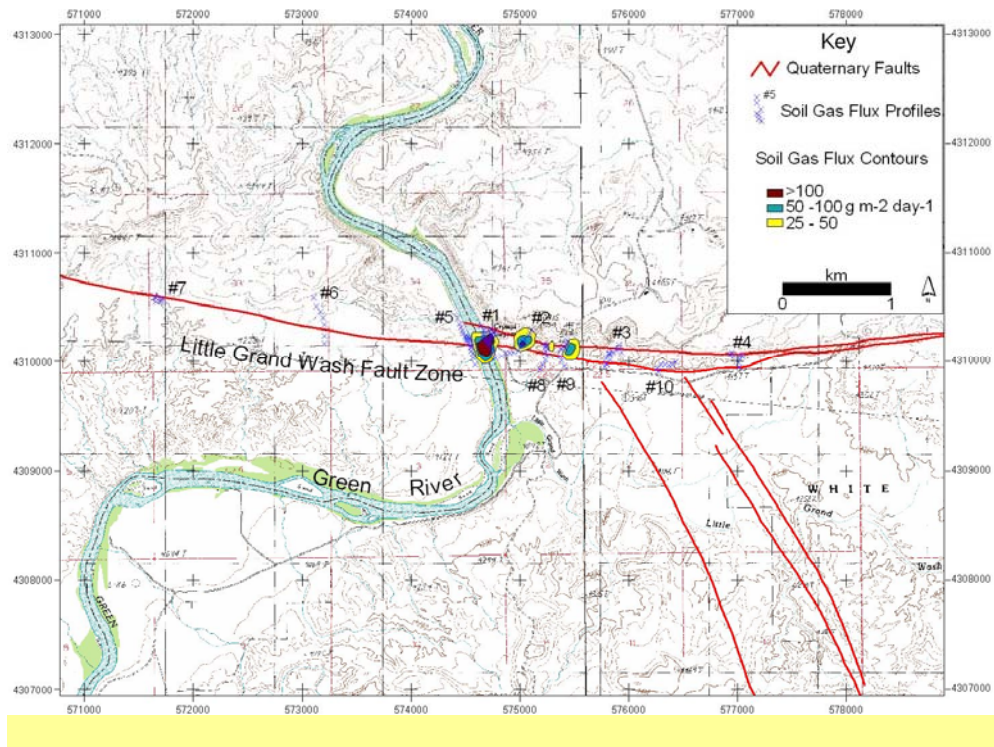


Fig. 6. Soil gas flux measurements along the Little Grand Wash Fault Zone, Utah..

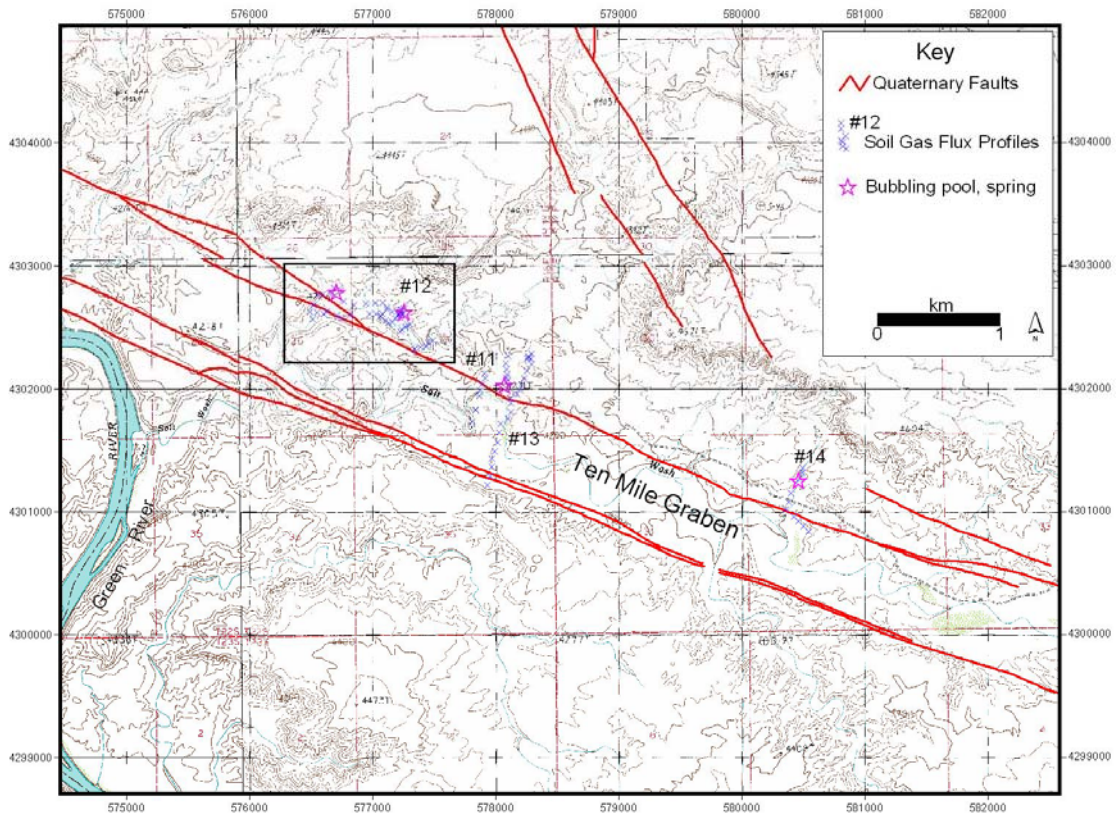


Fig. 7. Soil gas flux measurements in Ten Mile Graben.