Surface and Near-surface Geochemical Detection of Gas Microseepage from CO_2 Sequestration and CO_2-EOR Projects*

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Descriptive Statement

Comparison of various methodologies and various gaseous components in the detection and quantification of gas microseepage from overpressured injection reservoirs.

Problems with CO2 and Gas Monitoring in Natural Systems

- Large open systems,
- Dynamic, where "equilibrium" is only occasionally approximated,
- Systematic surface variation on at least two time scales (seasonal and diurnal) and possibly two spatial scales (cm-m range, km range),
- Searching for a small, deep-sourced signal in the presence of substantial near-surface noise,
- An understanding of the noise is essential if the deep signal is to be discovered.

Conclusions

- Monitoring protocols will need to be developed for each project that reflects climate, geology, and accommodates cultural interferences,
- A tracer that has low atmospheric concentration and low variability offers the best chance for early detection of gas microseepage,
- No single method is likely to be completely satisfactory for most sites,

- Measurement of carbon-containing gases will require liberal use of isotopes,
- The promotion of tower methods only measuring CO_2 as the answer to monitoring has been excessive; indeed, probability of early seepage detection may be limited.

References

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Trotter, J., I. Williams, C. Barnes, C. Lecuyer, and R. Nicoll, 2008, Did cooling oceans trigger Ordovician biodiversification? Evidence from conodont thermometry: Science, v. 321/5888, p. 550-554.

Wells, A.W., J.R. Diehl, G.S. Bromhal, B.R. Strazisar, T.H. Wilson, and C.M. White, 2007, The use of tracers to assess leakage from the sequestration of CO_2 in a depleted oil reservoir, New Mexico, USA: Applied Geochemistry, v. 22/5, p. 996-1016.

SURFACE AND NEAR-SURFACE GEOCHEMICAL DETECTION OF GAS MICROSEEPAGE FROM CO_2 SEQUESTRATION AND CO_2-EOR PROJECTS

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PROBLEMS WITH CO_2 AND GAS MONITORING IN NATURAL SYSTEMS

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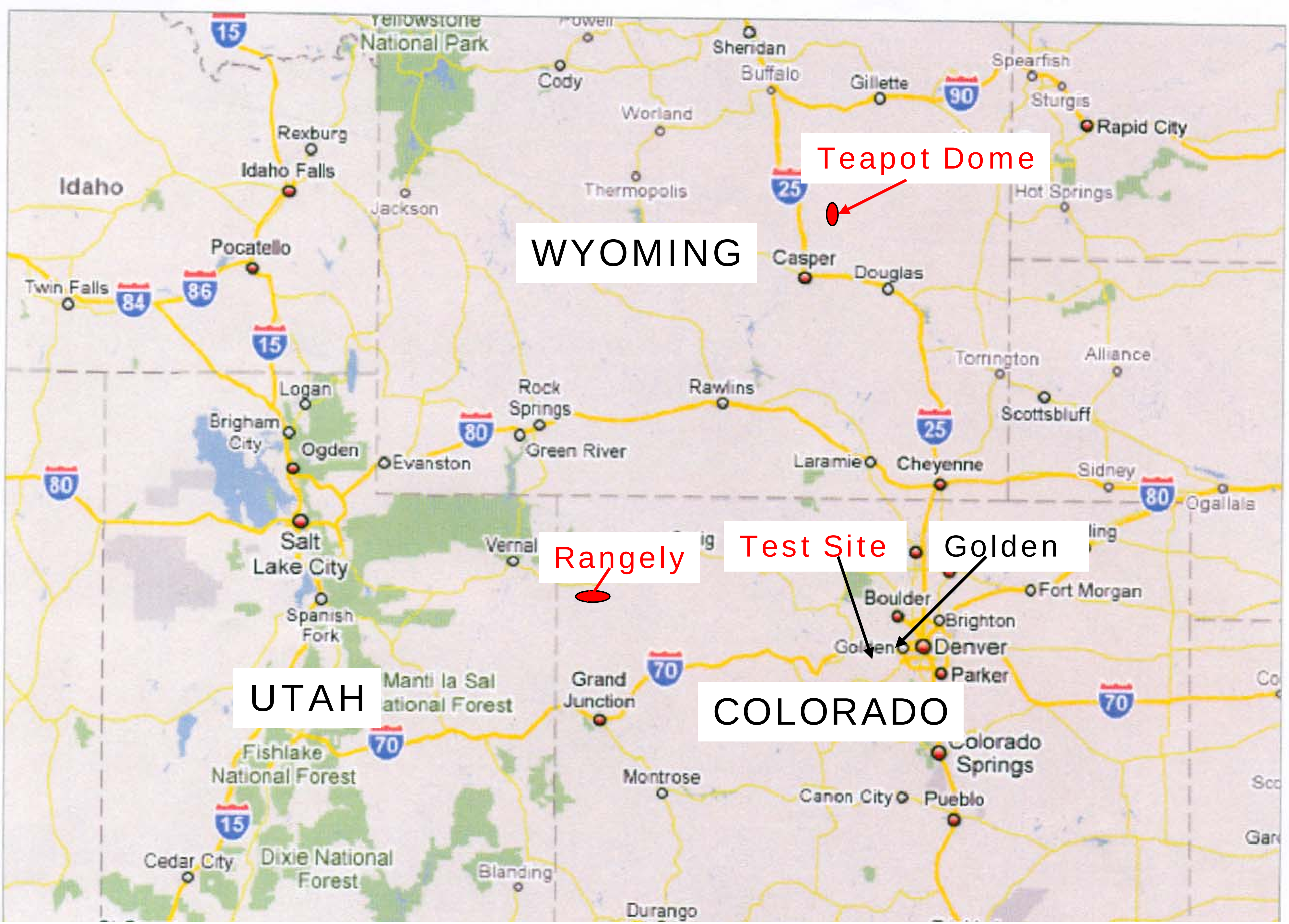
TRI-STATE REGION



RANGELY OIL FIELD
(bigger and better than Weyburn)

- Production from Pennsylvanian Weber formation with a miscible CO_2 flood since 1986 with injection at a depth of 6500 ft (2000 m); porosity approximately 12% with permeability 2-200 md, averaging 8 md,
- 426 producers and 281 injectors, producing 12-13,000 BOPD (2010) plus 1300 barrels of NGL; OOIP was 1.9-2.4 billion barrels with cumulative production of 881 million barrels,
- Injection rate is 160,000,000 scf/day (4,500,000 m^3/day) with about 80% currently returning to surface via producers for separation, compression and reinjection; make-up gas from the LaBarge field in Wyoming; eleven 4000 hp compressors pressurize to 2100 psi at surface, consuming 50 Mw of power,
- Reservoir pressure is approximately 3600 psi (21 Mpa); slightly overpressured,
- 27.3 million metric tonnes have been sequestered as of May, 2010.

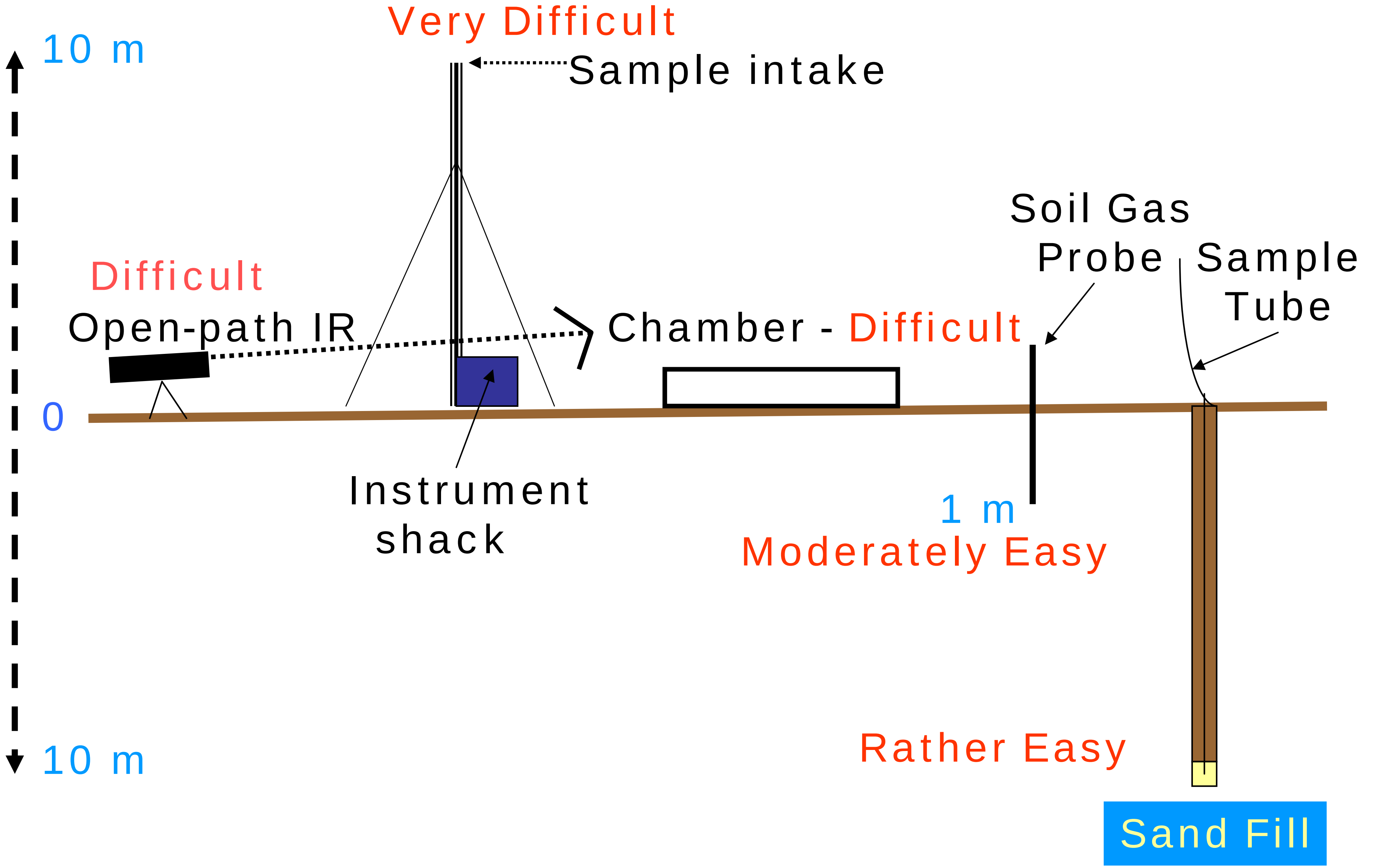
TEAPOT DOME OIL FIELD (Naval Petroleum Reserve #3)

- Production from three stacked reservoirs , ranging from Pennsylvanian Tensleep formation (5200 ft), with bulk of production from Cretaceous 2nd Wall Creek (2500 ft) and Cretaceous Shannon formation (400-600 ft); porosity approximately 15% with permeability 2-10 md,
- Several hundred inactive or low production wells are in the field, producing in aggregate only about 200 BOPD, with cumulative production of 200 million barrels; the field is significantly underpressured,
- CO_2-EOR is not occurring at Teapot, but the Tensleep has been proposed for large-scale CO_2 experimentation, but has not occurred as of 2010.
- Teapot surface and subsurface is owned by the U.S. Dept. of Energy; the Rocky Mountain Oilfield Testing Center (RMOTC) manages experimentation on the field,
- The field was originally owned by the U.S. Navy, was taken over by the U.S. Dept. of Interior, and significant corruption occurred during the leasing process in the 1920s with the Secretary of Interior serving prison time; older locals still refer to the NPR as “Navy.”

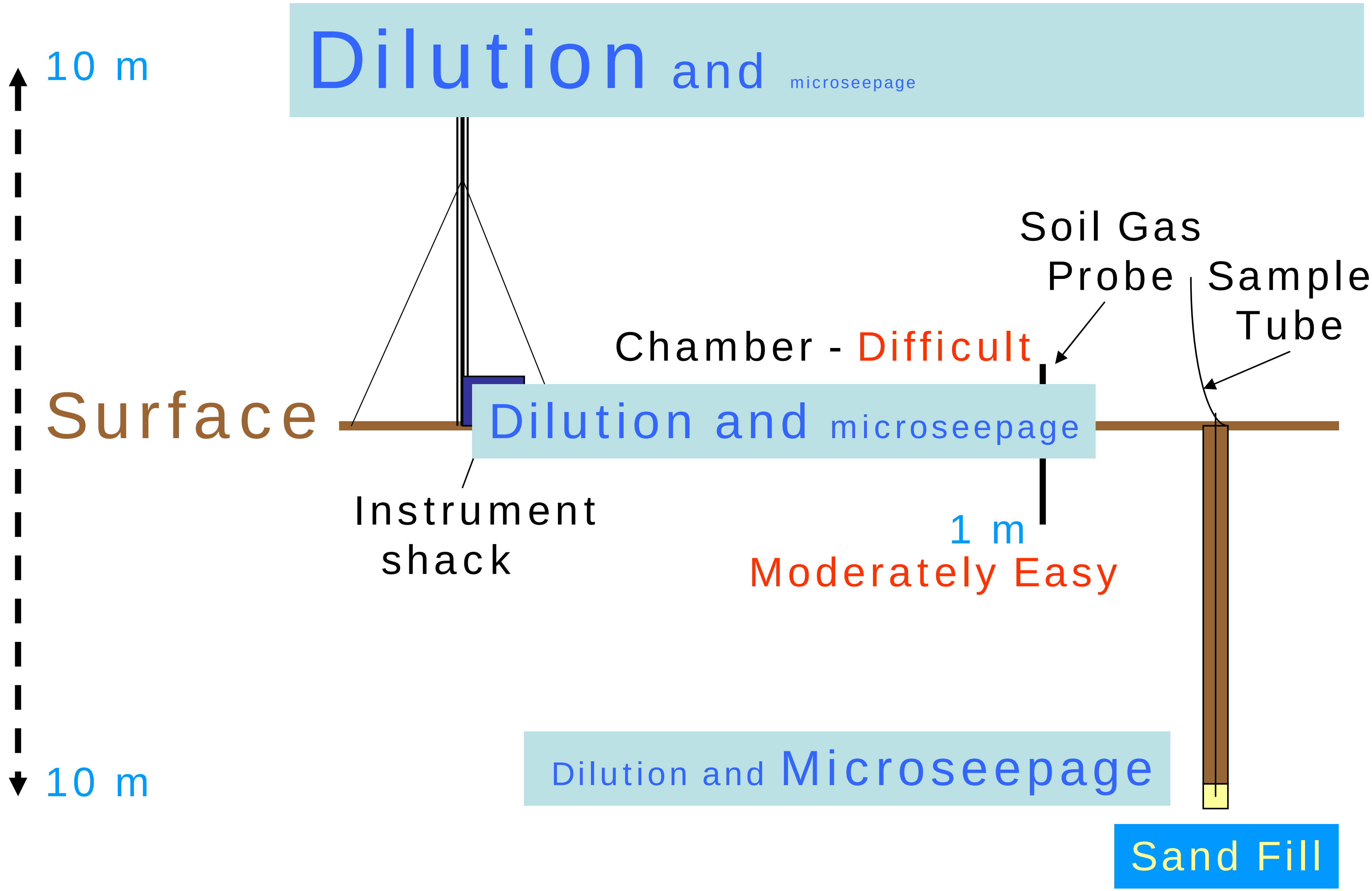
OBJECTIVES

- The primary objective of the completed Rangely and Teapot Dome studies was to determine if gas microseepage could be detected and quantified over the overpressured Rangely where CO_2-EOR had been operational for a substantial period of time, and the underpressured Teapot Dome field where no CO_2 injection had previously occurred.
- The climate of these study areas is “severe” with relatively hot summers and very cold winters; the study areas are semiarid to arid allowing for a high contrast in biological activity which was expected to complicate the measurements, as well as the detection and quantification of the gas microseepage to the atmosphere.
- The objective of this presentation is to present “pros and cons” of various geochemical methodologies for the detection of gas microseepage; the discussion is backed with selected data from a “test site,” and both the Rangely and Teapot Dome studies.
- A wide variety of techniques has been proposed for Monitoring, fewer for Verification, with the Rangely study providing direct gas flow measurements into the atmosphere as an Accounting for purposes of carbon credits (MVA).

DETECTION OF MICROSEEPAGE

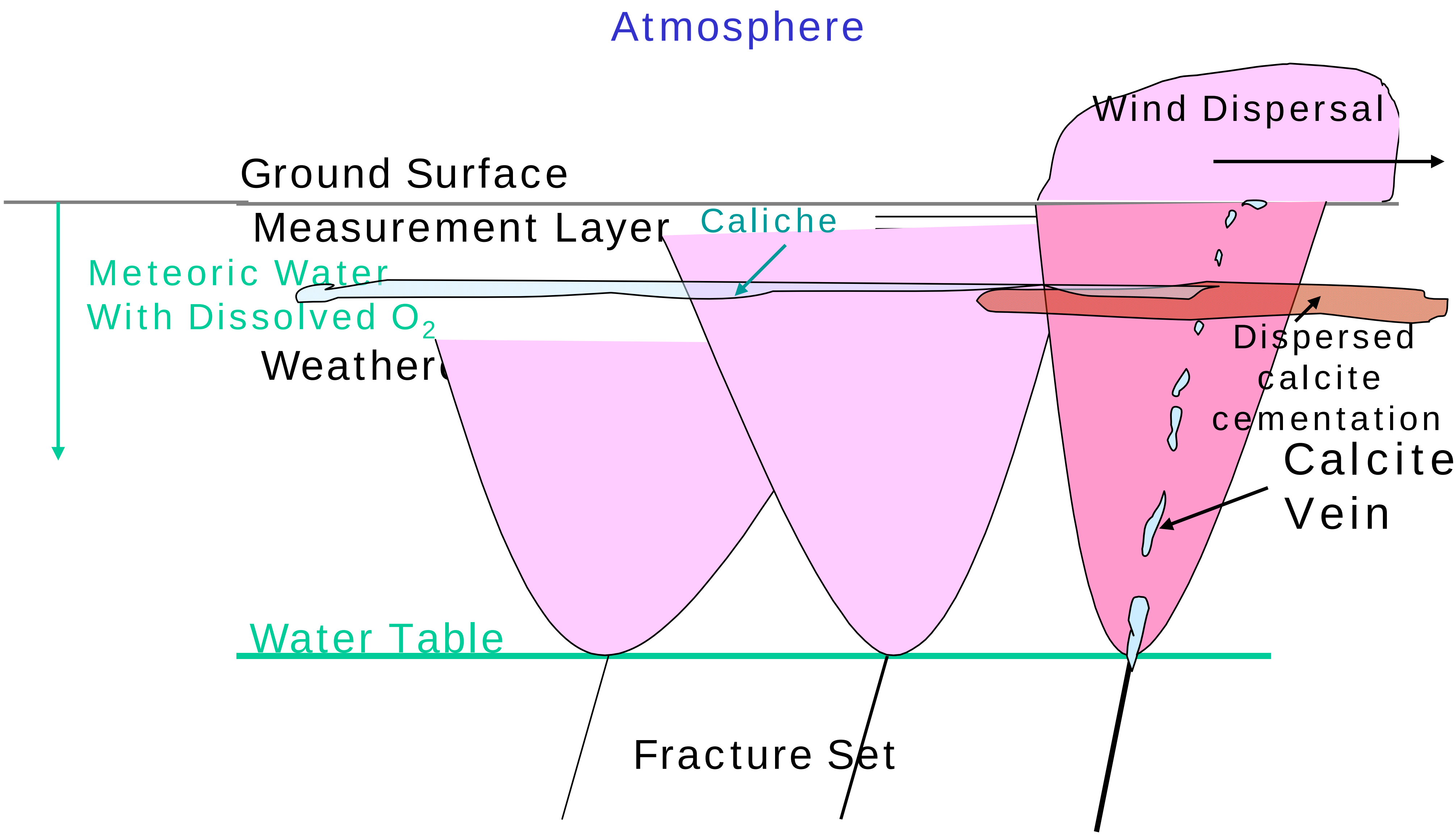


DETECTION OF MICROSEEPAGE



SAMPLING AND ANALYTICAL

- Triplicate measurement of CO_2 and CH_4 fluxes from the surface into the atmosphere using three 1.00 m^2 chambers set 10 m apart,
- CO_2, CH_4, light hydrocarbons, and $\delta^{13}C$ of CO_2 determined in soil gas at 30-, 60-, 100-cm depths,
- Flux and soil gas measurements at 41 locations over the Rangely field, 16 in a control area, and 10 over the Mellen Hill fault; 40 locations over the Teapot Dome field,
- Summer and winter flux and soil gas measurements at Rangely, winter only flux and soil gas measurements at Teapot Dome,
- Five 10-m deep holes with nested sampling at five depths for all of above parameters, plus $\delta^{13}C$ of CH_4 and C-14 content of CO_2 at both Rangely and Teapot Dome; O_2 at Teapot Dome,
- Field measurement of CO_2 fluxes by IR spectrometer, soil gas CO_2 , CH_4, and light hydrocarbons by laboratory gas chromatography, isotope ratios by mass spectrometry, carbon-14 by accelerator mass spectrometry (AMS),
- Determination of $\delta^{13}C$ and $\delta^{18}O$ in solid carbonate materials,
- Inert gas isotopes in 10-m holes at Teapot Dome determined by Sarah Mackintosh and Chris Ballentine of Manchester University,
- Miscellaneous field measurements including barometric pressure, soil temperature gradient, soil air permeability.



Atmosphere
Wind Dispersal
Ground Surface
Measurement Layer
Caliche
Meteoric Water
With Dissolved O_2
Weathere
Dispersed
calcite
cementation
Calcite
Vein
Water Table
Fracture Set

TEAPOT DOME

Calcite vein at anomalous location 17

SOURCES OF CO_2 IN SURFACE ENVIRONMENT

- Three sources are always present;
- a) atmospheric,
- b) biological,
- c) near-surface inorganic.
- 4th - Methanotrophic oxidation of CH_4,
- 5th – CO_2 from injection reservoir,
- 6th – Sampler's breath for surface samples,
- Photosynthesis is a sink for CO_2,
- Measurement of stable isotopes of carbon and carbon-14 can help differentiate sources.

MEASUREMENT ABOVE THE LAND SURFACE (1-10 METERS)

- Pros – a) Mixing with the atmosphere allows detection of a point or linear source in an upwind direction, b) coverage of an area approximately 10+ times the elevation of measurement, c) Open-path horizontal measurements change the point measurement of a tower to a one-dimensional measurement.

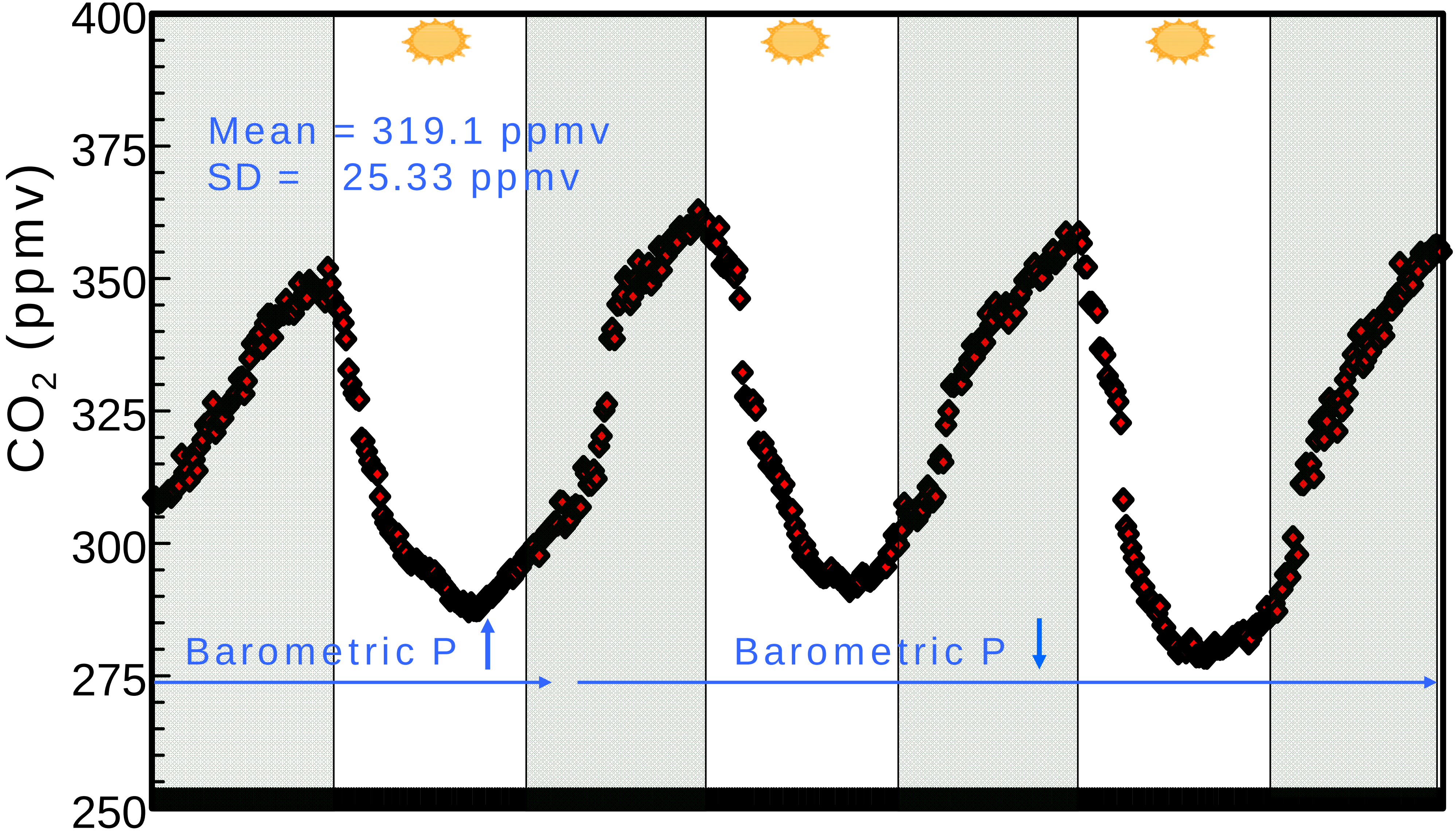
- Cons – a) considerable dilution of deep source with background atmosphere makes detection of a subsurface source difficult, particularly when superimposed on the natural variability, b) gas dispersion is a complex function of atmospheric stability and mixing, complicating the calculation of flux and doing the “accounting.”

PARAMETER TO MEASURE: Atmospheric CO_2(?)

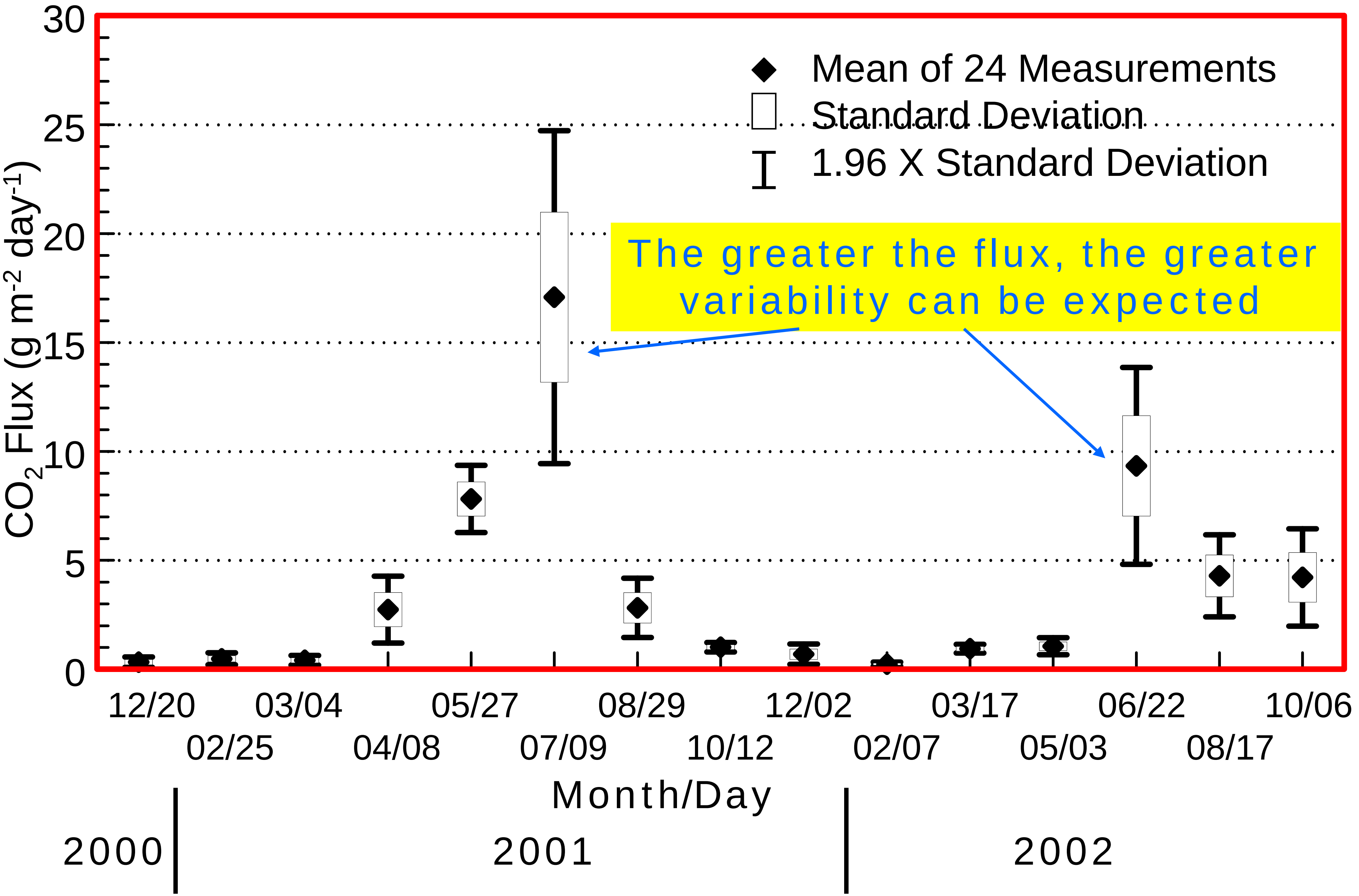
- Pros – a) Easy in open atmosphere with IR techniques, b) atmospheric mixing allows assessment in upwind direction, c) “continuous” measurement (monitoring) possible, d) large footprint for tower methods.

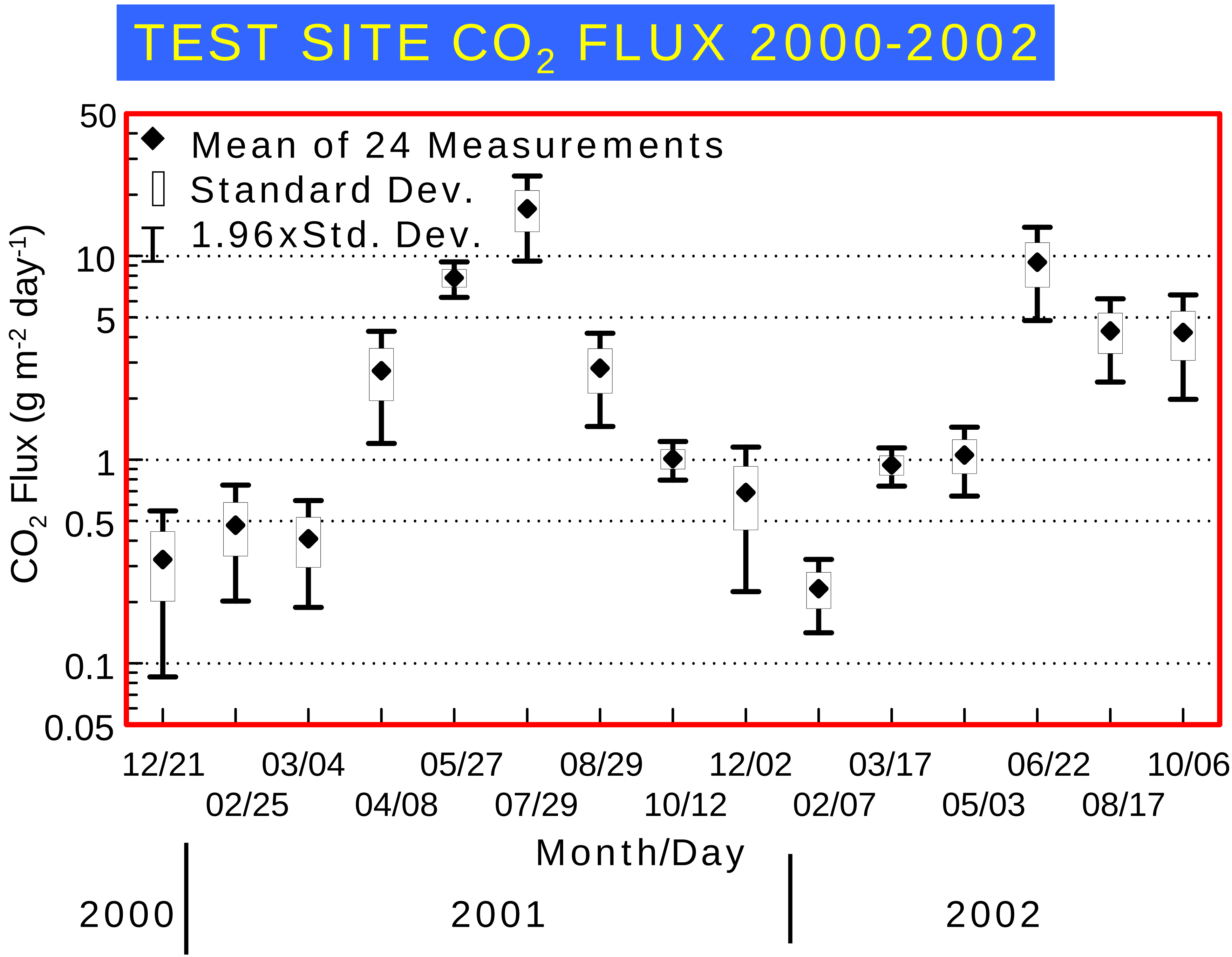
- Cons – a) high atmospheric concentration and highly variable concentration on two time scales, (low signal/noise), b) CO_2 soluble in, and reactive with, water which will attenuate and delay subsurface migration, c) biological production/consumption, d) other influences; soil moisture, temperature, solar insolation, agricultural practices and fertilization, e) vertical gradient due to photosynthesis in forested environments, f) multiple sources of CO_2, g) traffic interferences, h) a commercial scale project will require a large number of towers with high capital, operation and frequent instrument calibration costs, i) surface and visual impacts are high due to roads and power lines, j) coal is a strong adsorber of seeping CO_2 which is a benefit in terms of attenuation, but a negative in terms of early detection of migration outside the reservoir.

ATMOSPHERIC CO_2 –TEST SITE- 6/26-30 ILLUSTRATING PHOTOSYNTHESIS

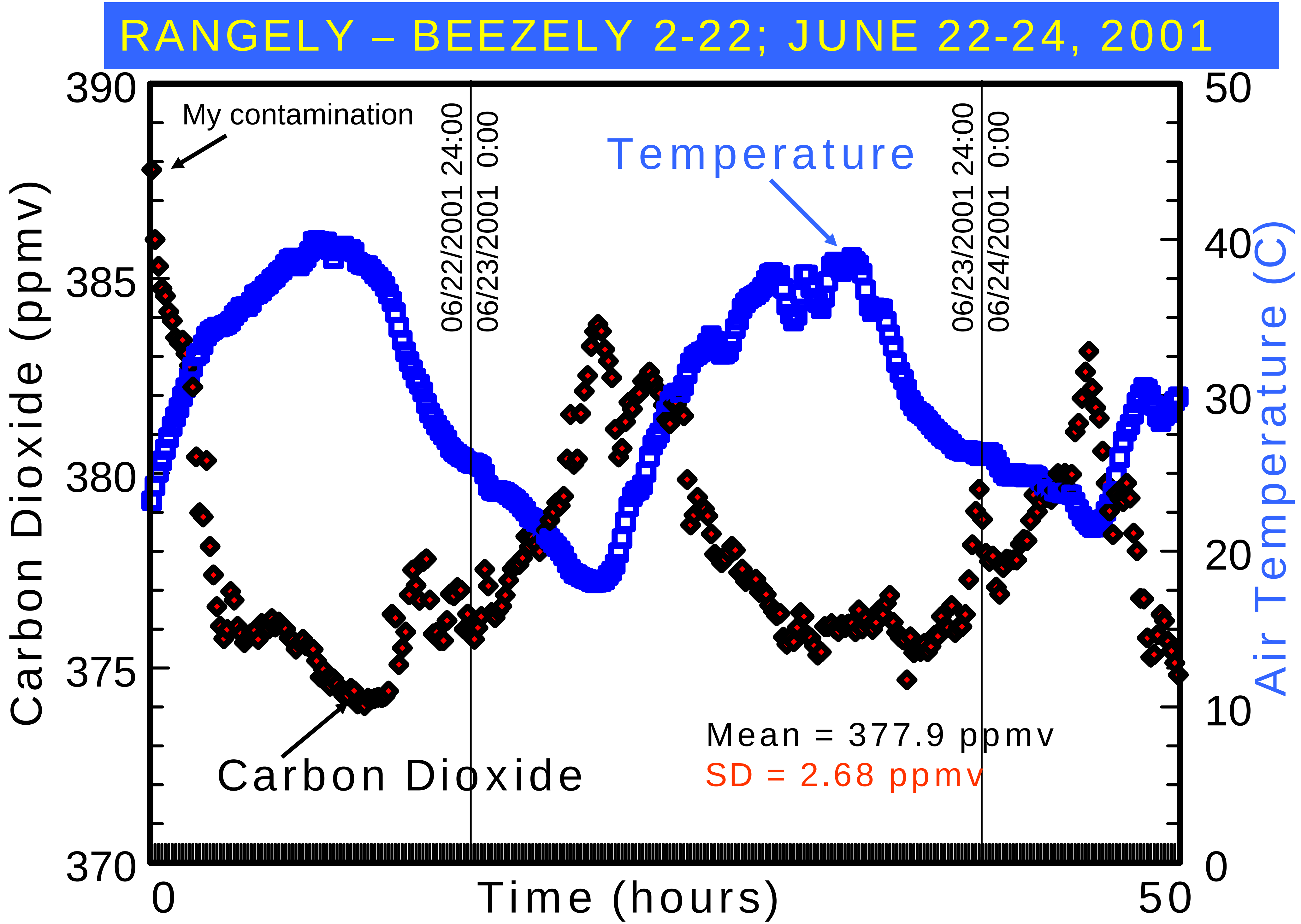


TEST SITE CO_2 FLUX 2000-2002



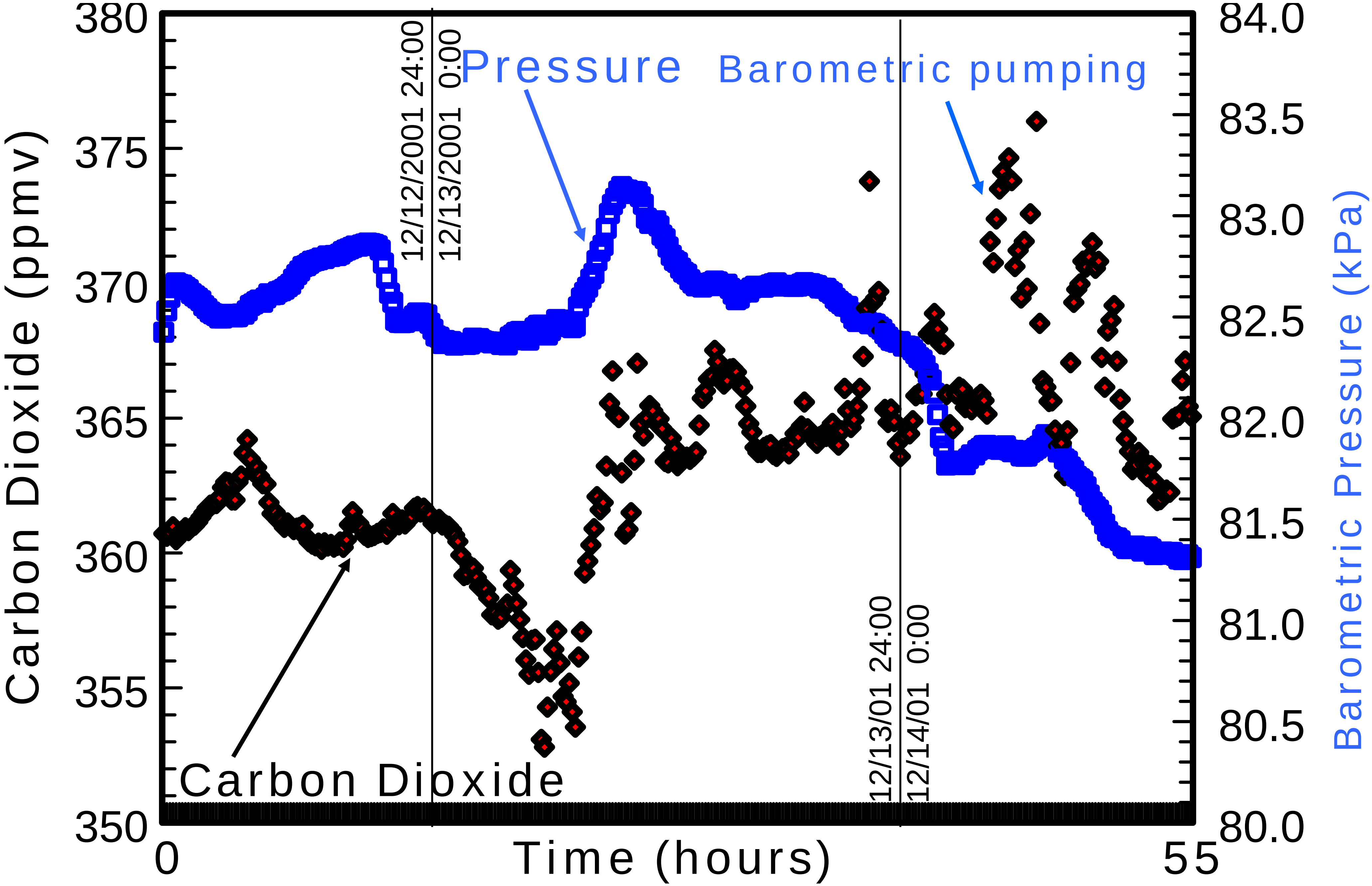


TEST SITE CO2 FLUX 2000-2002
Mean of 24 Measurements
Standard Dev.
1.96xStd. Dev.
CO2 Flux (g m-2 day-1)
50
10
5
1
0.5
0.1
0.05
12/21
02/25
03/04
04/08
05/27
07/29
08/29
10/12
12/02
02/07
03/17
05/03
06/22
08/17
10/06
Month/Day
2000
2001
2002



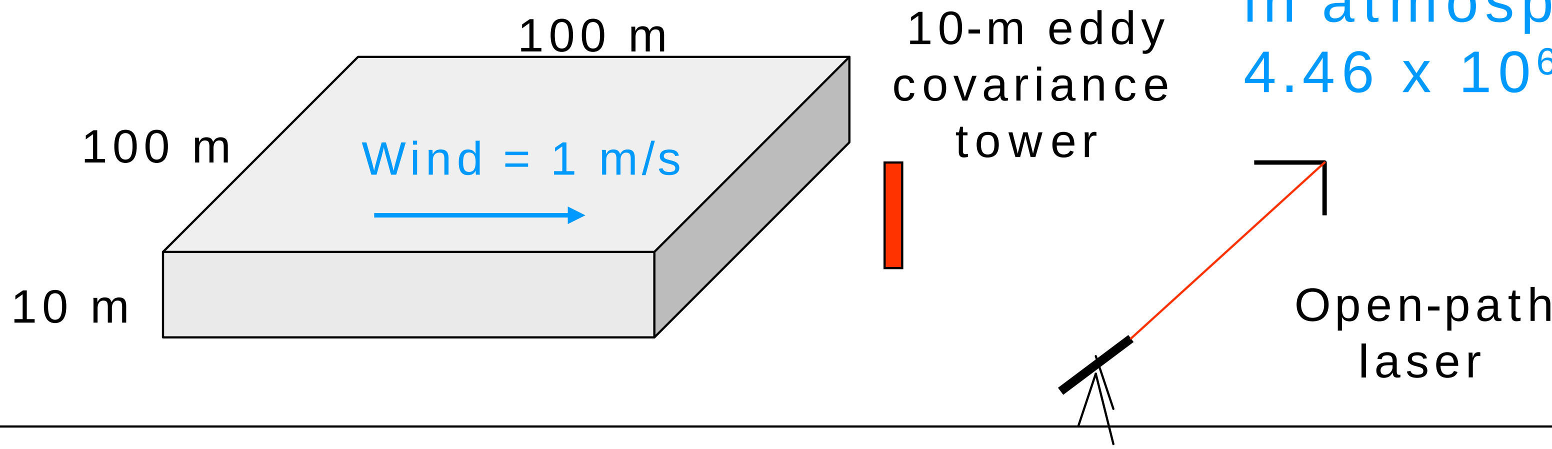
RANGELY – BEEZELY 2-22; JUNE 22-24, 2001
Carbon Dioxide (ppmv)
Air Temperature (C)
Time (hours)
My contamination
Temperature
Carbon Dioxide
06/22/2001 24:00
06/23/2001 0:00
06/23/2001 24:00
06/24/2001 0:00
Mean = 377.9 ppmv
SD = 2.68 ppmv
390
385
380
375
370
50
40
30
20
10
0
0
50

RANGELY – BEEZELY 2-22; DECEMBER 12-14, 2001



Diffuse or point leakage anywhere in block becomes mixed in atmosphere block

4.46×10^6 moles (STP)



<u>CO_2 at Rangely during 2 days of maximum photosynthesis.</u>

To increase atmospheric concentration from 377.9 ppmv by one SD (2.7 ppmv) to 380.6 ppmv would require 526 g of CO_2. A leakage rate of 5.26 g/sec is required.

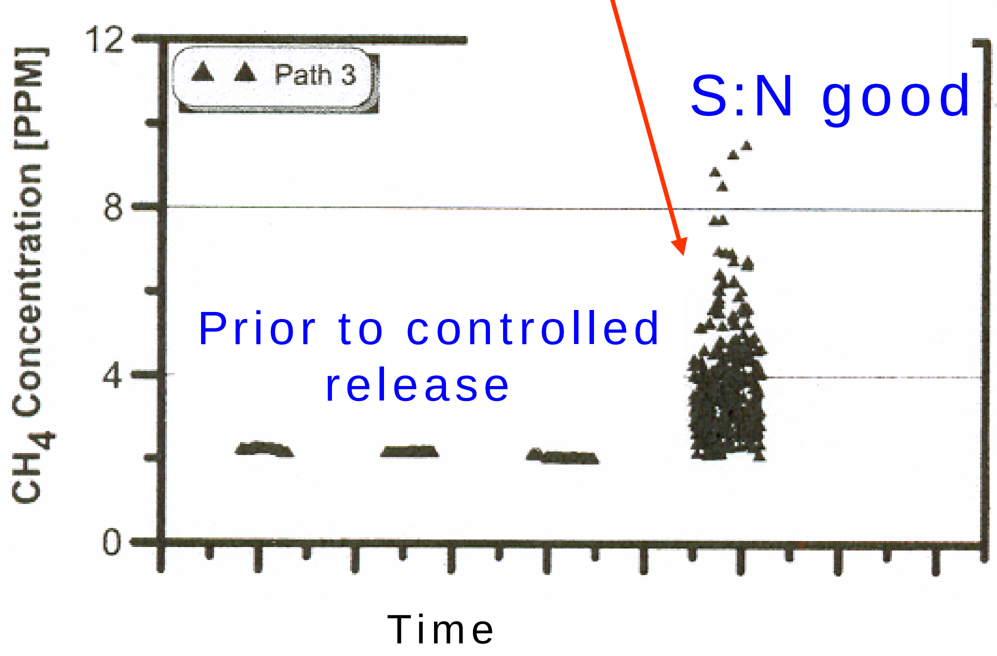
<u>CH_4 at Rangely during 6 weeks of winter 2001/02.</u>

To increase atmospheric concentration from 1.8ppmv by one SD to 1.95 ppmv would require 10.74 g. A leakage rate of 0.11 g/sec is required.

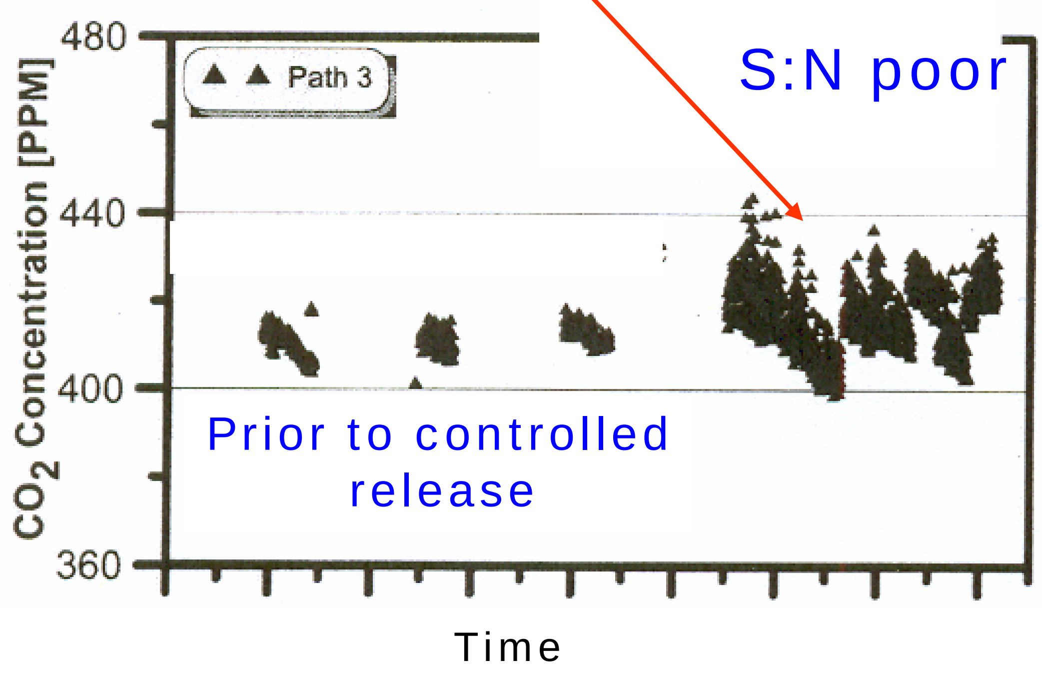
<u>Conclusion:</u> The atmospheric gas concentration and variability sets limits for the above-ground detection of microseepage (need a high signal:noise ratio).

MEASUREMENT OF CONTROLLED RELEASE OF GASES UPWIND WITH MEASUREMENT BY OPEN-PATH IR (FROM TROTTIER ET AL. 2008)

CH_4 controlled release of 8 SLPM (0.095 g/sec)



CO_2 controlled release of 40 SLPM (1.31 g/sec)

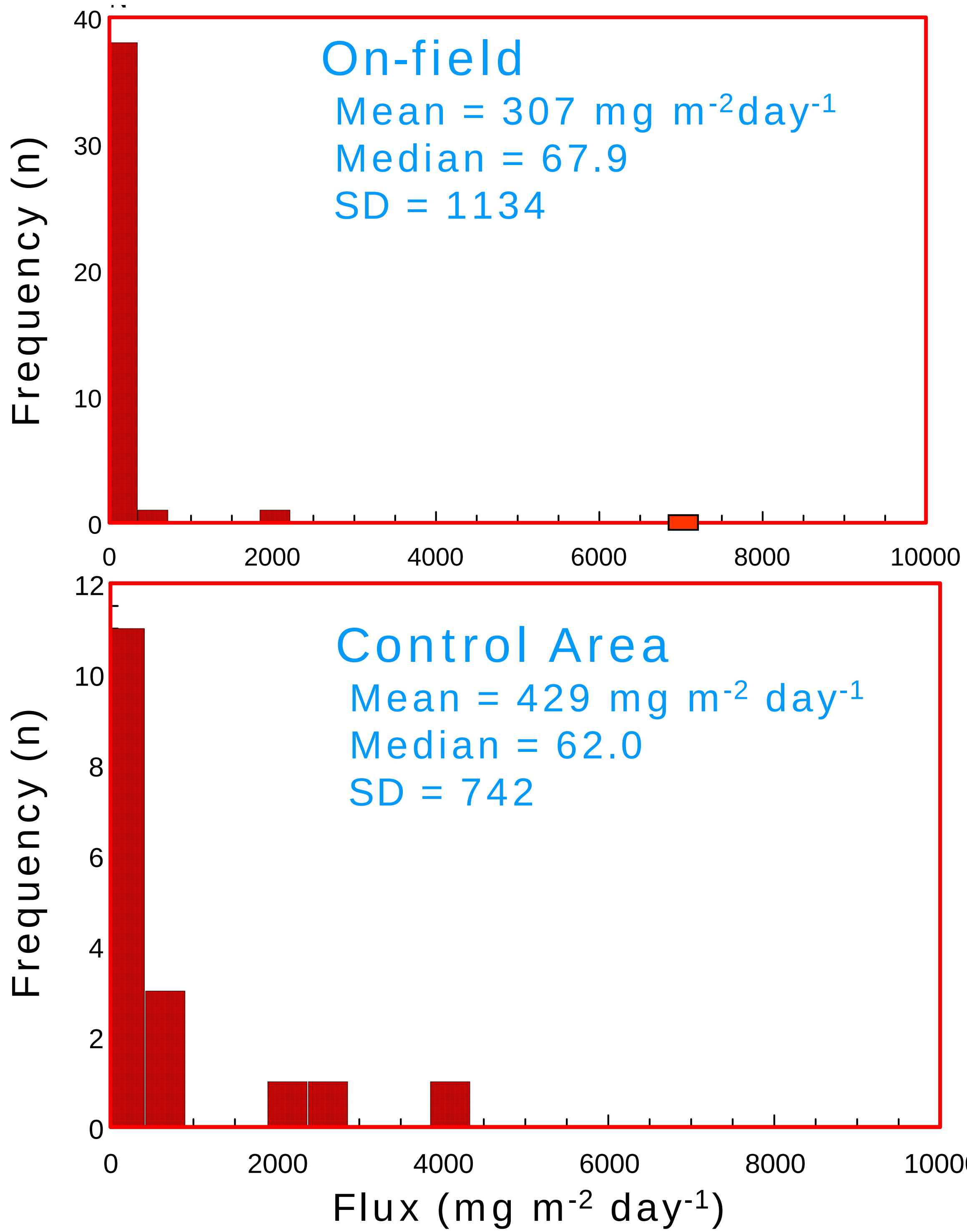


CHAMBER MEASUREMENT AT THE LAND SURFACE

- Pros – a) Substantial portability depending on the size of the chamber, b) provide a baseline measurement of gas exchange with the atmosphere, or periodic evaluation during the injection and operation phase, c) CO_2 can be directly measured in the field by IR methods, d) less atmospheric dilution, e) other lower concentration gases can be measured, f) low rates of exchange can be measured if "flux limit of detection" has been determined, g) direct measurement, not involving complex mathematics of dispersion and mixing, h) known faults can be directly measured, i) vegetation has less interference if chamber will fit between.

- Cons – a) the measurement is limited to the area of the collar, b) the method has limited monitoring capability except for periods of days, and with current technology only CO_2 can be measured "continuously," c) measurements of CO_2 on grass can yield false negative fluxes due to photosynthesis.

RANGELY – CO_2 FLUX; WINTER 2001/2002 (monitoring)



MEASUREMENT BELOW THE LAND SURFACE (1-10 METERS)

- Pros – a) diurnal and seasonal variability is much less than the atmosphere, particularly at 10 m, b) sampling at 1 m is fast, portable, and very low cost, c) appropriate measurements of flux and 1 m soil gas allow selection of locations for 10-m holes is reliable in dry/cold climates and allows an initial baseline characterization of soil gas, d) anomalous soil gas perfuses through a substantial volume surrounding a fault/fracture.

- Cons – a) limited sample volume withdrawal rate will prevent continuous measurement or “monitoring”, b) discrete sampling and laboratory analysis may be required, c) subsurface volume represented by a discrete sample is quite small.

CORRELATIONS OF SURFACE CO_2 FLUX VS. SOIL GAS CO_2 (Summer)

	Teapot s04	Rangely s01
CO_2 Flux and 30 cm soil gas CO_2	-	0.266*
CO_2 Flux and 60 cm soil gas CO_2	-	0.252*
CO_2 Flux and 100 cm soil gas CO_2	-	0.093

* $\alpha < 0.05$, ** $\alpha < 0.01$

CORRELATIONS OF SURFACE CO_2 FLUX VS. SOIL GAS CO_2 (Winter)

	Teapot W04	Rangely w01/02
CO_2 Flux and 30 cm soil gas CO_2	0.151	0.135
CO_2 Flux and 60 cm soil gas CO_2	0.231	0.268*
CO_2 Flux and 100 cm soil gas CO_2	0.446**	0.339**

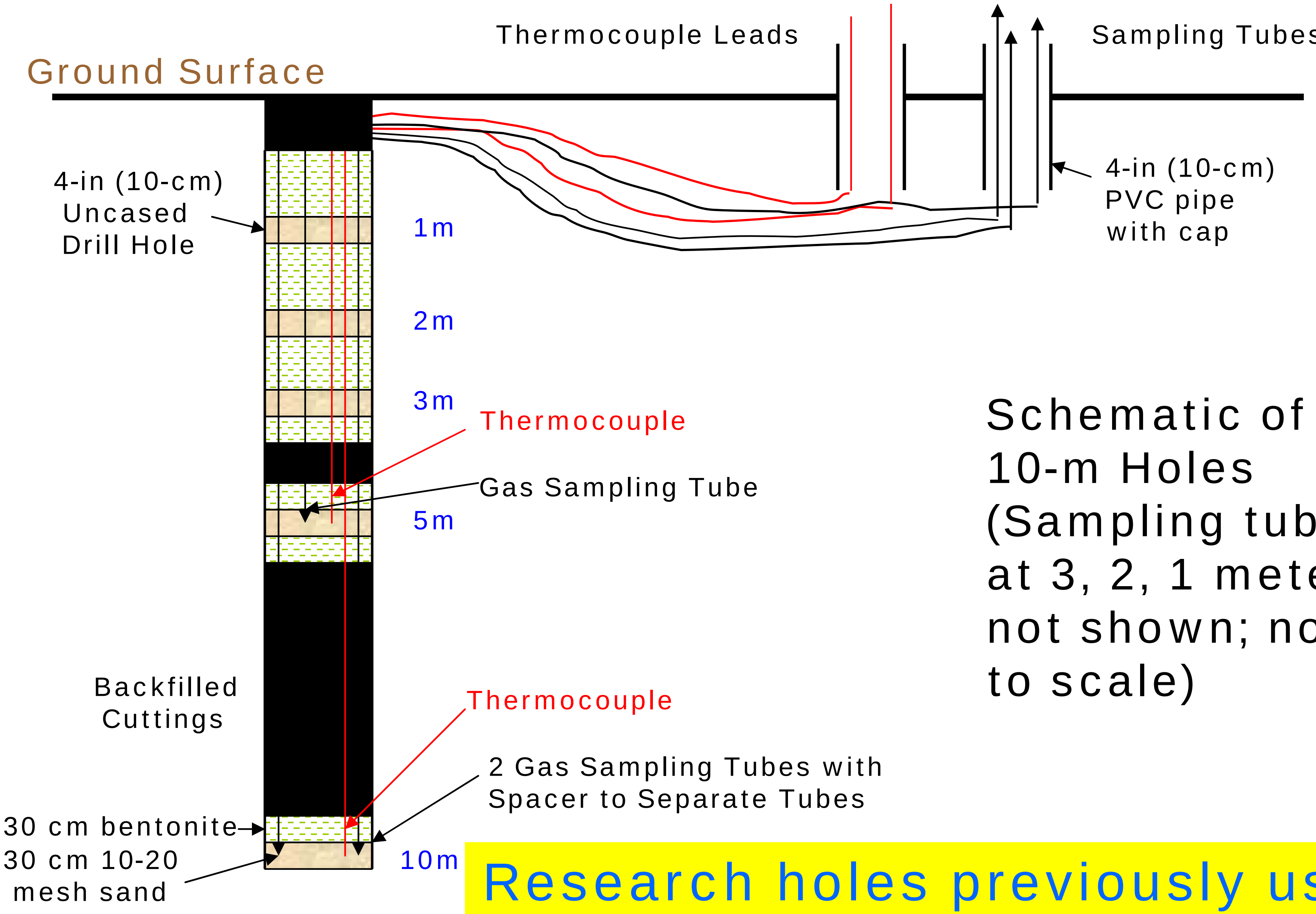
* $\alpha < 0.05$, ** $\alpha < 0.01$

CONCLUSIONS ABOUT ELEVATION OF SAMPLING AND MEASUREMENT

- Shallow soil gas (1 m) is rapid, low cost, and can determine whether the area of interest has a propensity for seepage,
- Pre-development baseline can be established in two seasons with chambers, if appropriate for climate,
- A single pass in the proper (low-noise) season can allow selection of locations for 10-m holes,
- Not all potential microseepage locations will be found; but sampling is guided by previously available data on faulting and fracturing which was developed by 3-D seismic, remote sensing, surface mapping,
- Only large-scale seepages will be found by atmospheric measurements of CO_2, and likely delayed in time relative to other tracers,
- Horizontal spectroscopic measurement between a source and reflector has promise for detection and measurement of moderate-scale seepages along the path of the beam or a short distance upwind (finding old improperly P&A wells?).

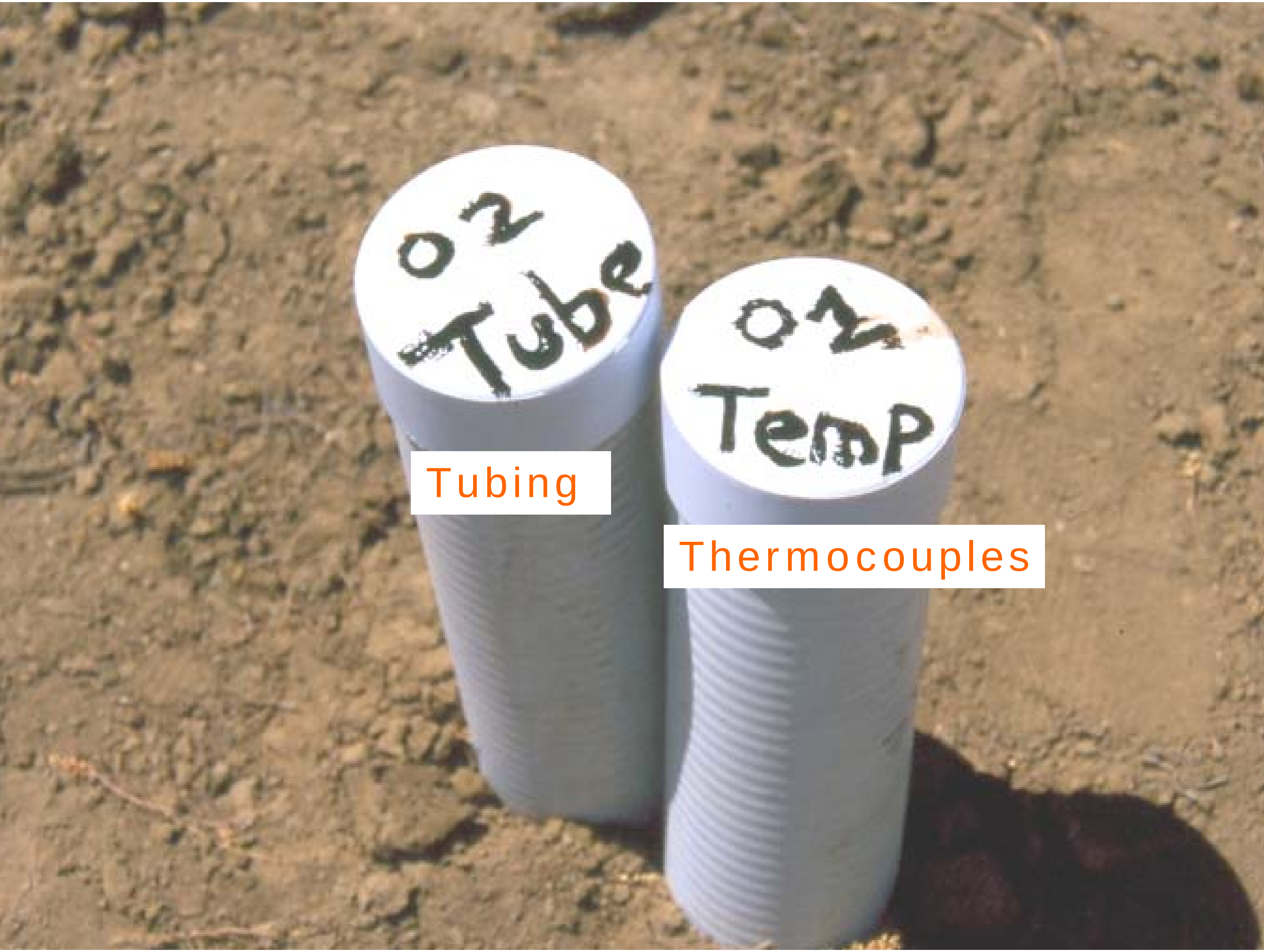
SELECTION OF "INTERESTING" LOCATIONS FOR 10-M HOLES

- Magnitude <u>and</u> direction of <u>both</u> CO_2 and CH_4 fluxes,
- Magnitude and gradient of both CO_2 and CH_4 soil gas profiles,
- Isotopic shift of $\delta^{13}C$ of CO_2 in 60- and 100-cm soil gas, relative to the atmosphere,
- Presence of C_2H_6 (ethane) and C_3H_8 (propane), and/or anomalous amounts of C_2H_4 (ethene) and C_3H_6 (propene) in soil gas. If we see the latter, it is an indication of the first stage of microbial oxidation of thermogenic ethane and propane, respectively.



Schematic of 10-m Holes (Sampling tubes at 3, 2, 1 meters not shown; not to scale)

Research holes previously used at Rangely and Teapot Dome had five sampling intervals; Future “monitoring” holes may only be completed at 1- and 10-meters.

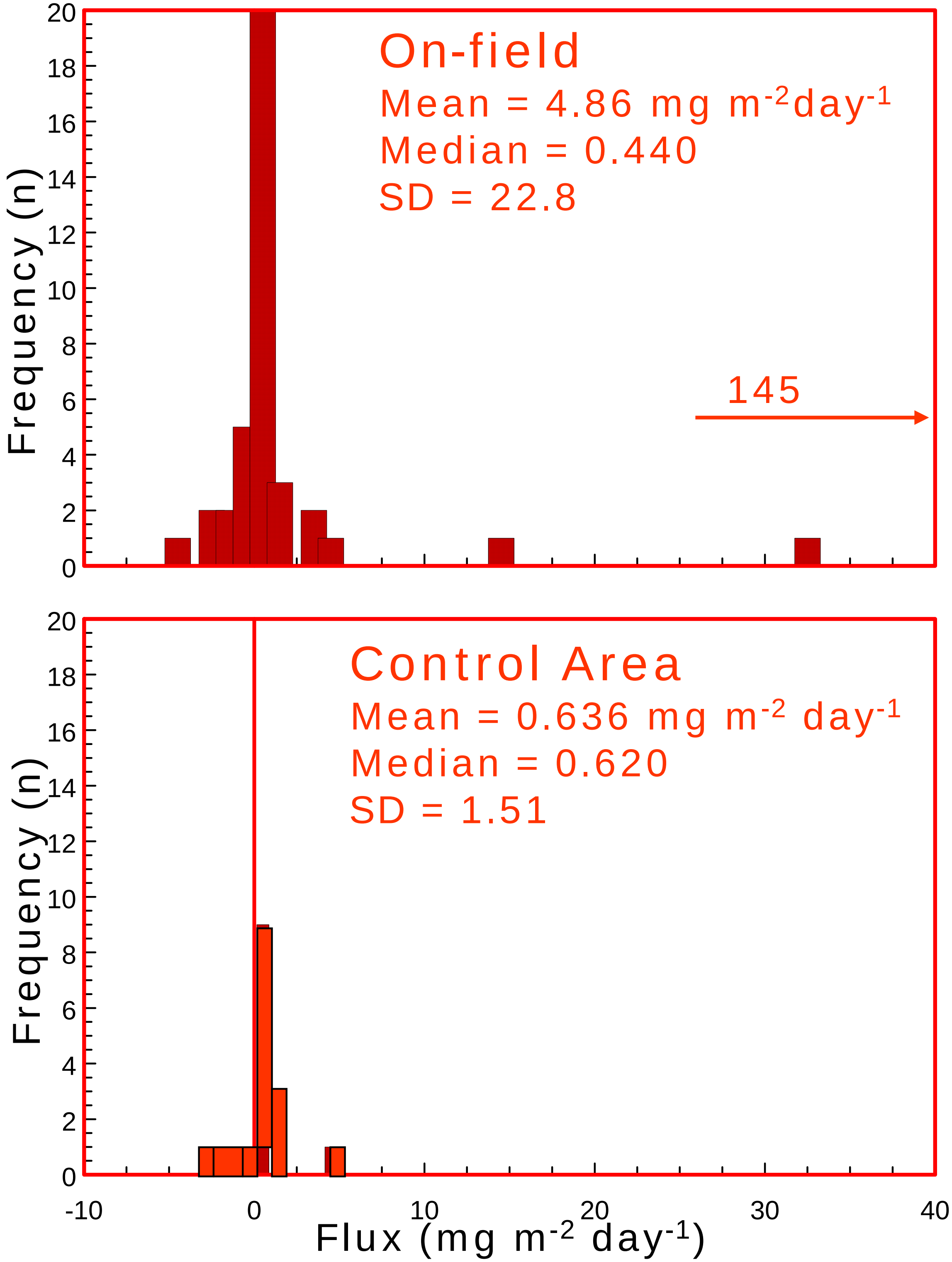

O2
Tube
O2
Temp
Tubing
Thermocouples

OTHER GASEOUS SPECIES-METHANE

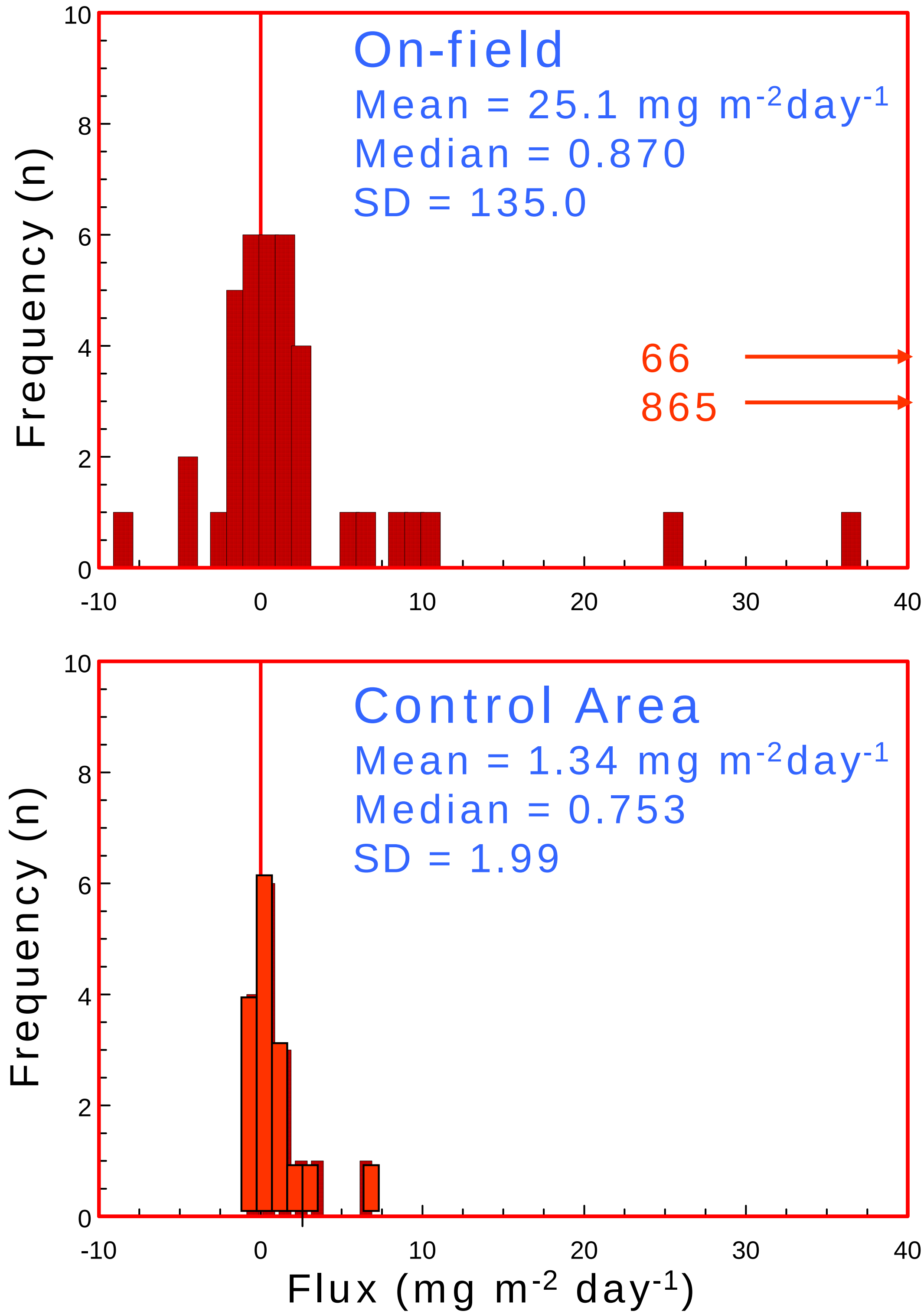
- Pros – a) Present in oil and gas fields being considered for CO_2-EOR, but only in minor amounts in deep, saline aquifers, b) natural atmospheric concentrations are low and vary by only small amounts, primarily seasonally, c) open-path spectroscopic measurements may be possible to detect small differences in concentration allowing “monitoring,” d) EPA-approved open-path methodology appears to work at estimating flux over landfills.

- Cons – a) Measurements of sufficient precision and accuracy may require laboratory measurements, b) possibly inadequate CH_4 concentrations in most deep, saline aquifers to use as an indigenous tracer, c) not suitable for wet climates because of methanogenesis in shallow soils and wet areas.

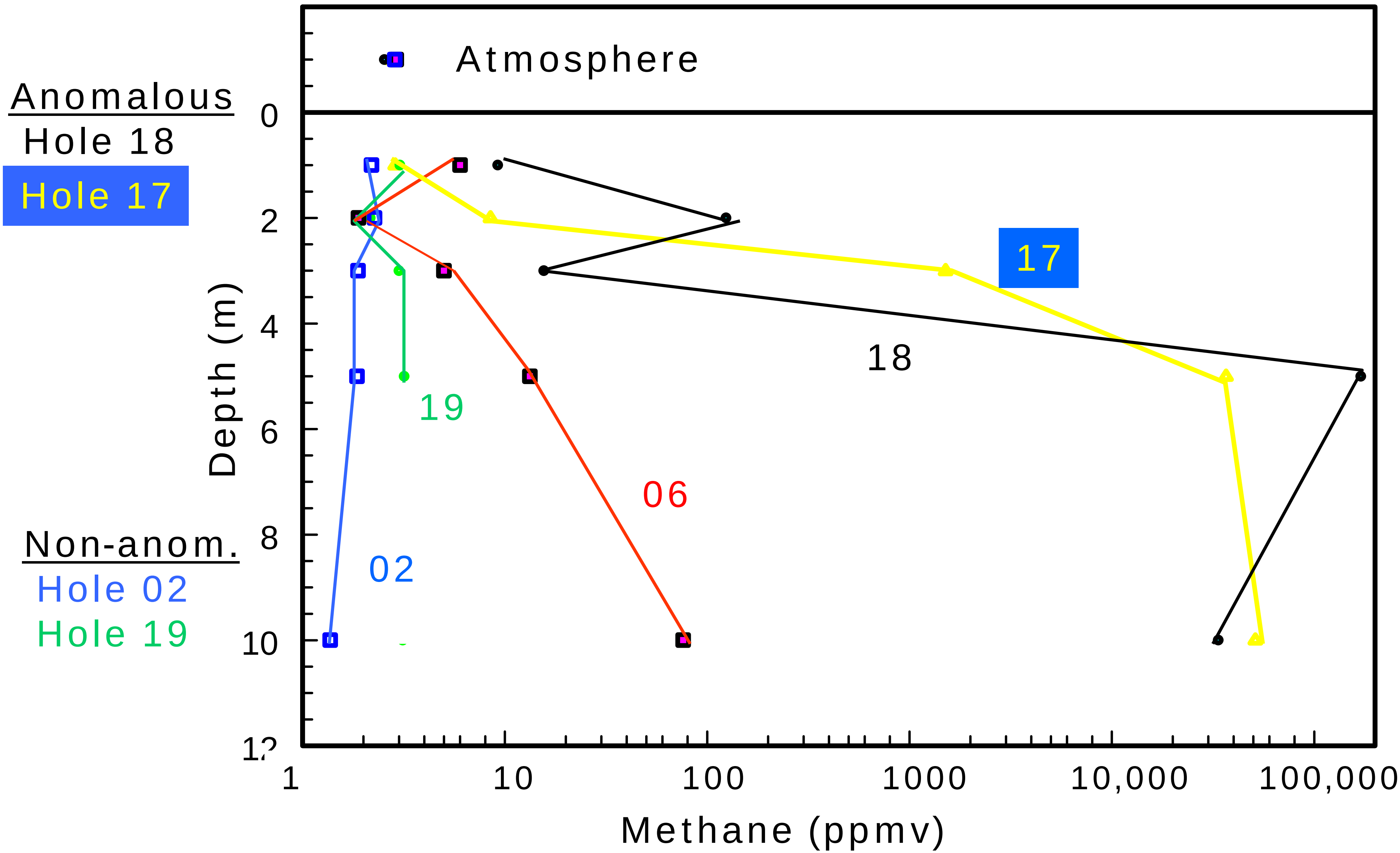
Rangely – CH_4 Flux; Summer 2001 (monitoring)



Rangely – CH_4 Flux; Winter 2001/2002 (monitoring)



TEAPOT DOME – METHANE IN 10-m HOLES; JANUARY, 2005 (monitoring)



Soil Gas Methane Process Types: 2004 Teapot Dome Baseline Survey

"Bad"

"Good"

5 – Upward seepage but methanotrophic oxidation not evident or minor,

7 – Upward seepage and methanotrophic oxidation evident,

7 – Low rates of seepage both directions and methanotrophic oxidation evident,

16 – Noise, or no process evident,

5 – Downward seepage of atmospheric methane and oxidation evident,

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40 – Total locations in baseline survey.

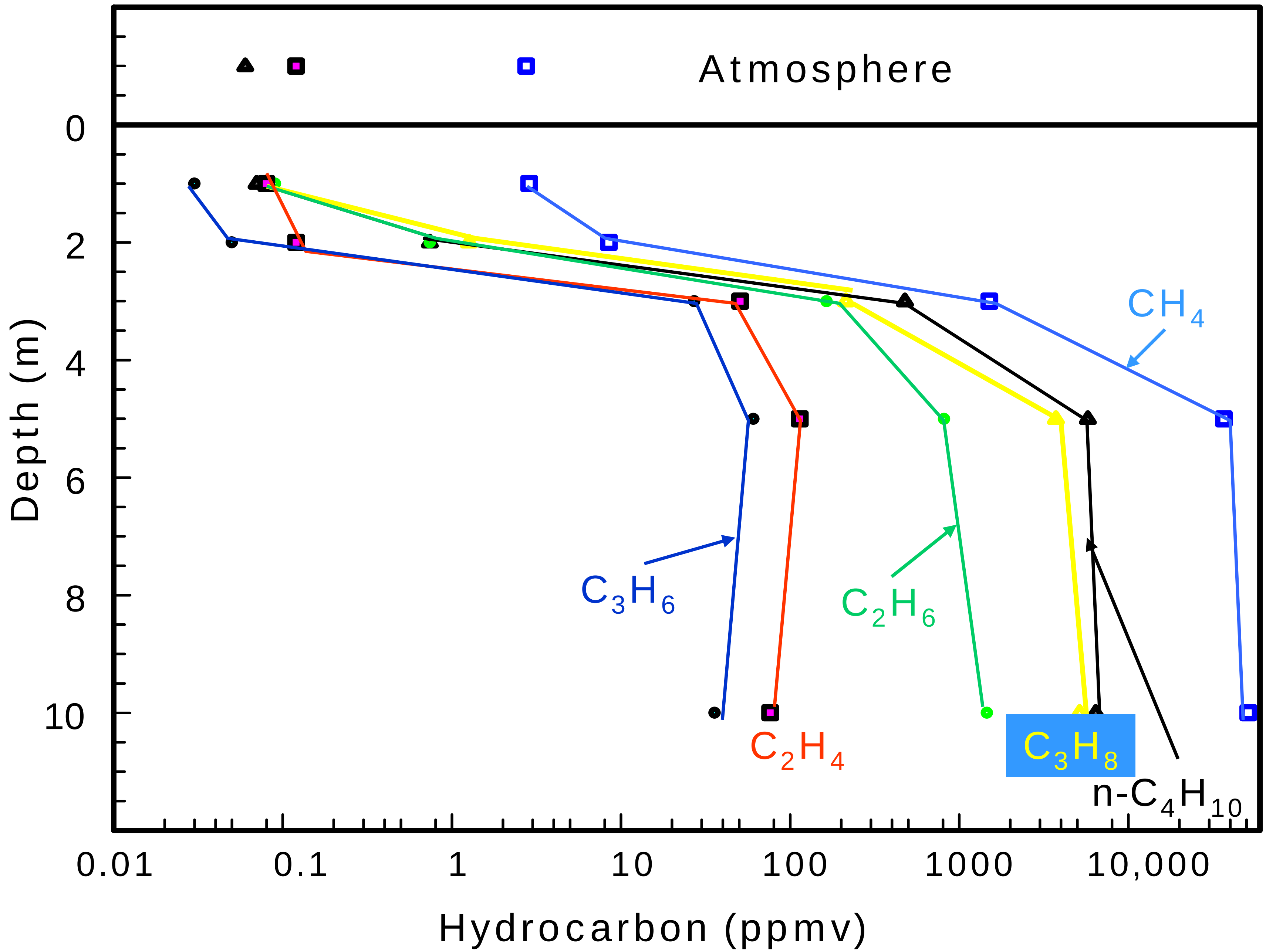
OTHER GASEOUS SPECIES - LIGHT ALKANES AND ALKENES

- Pros – a) Very effective in detection of microseepage from CO_2-EOR projects, b) multiple species measured for redundancy allows increased confidence in results.

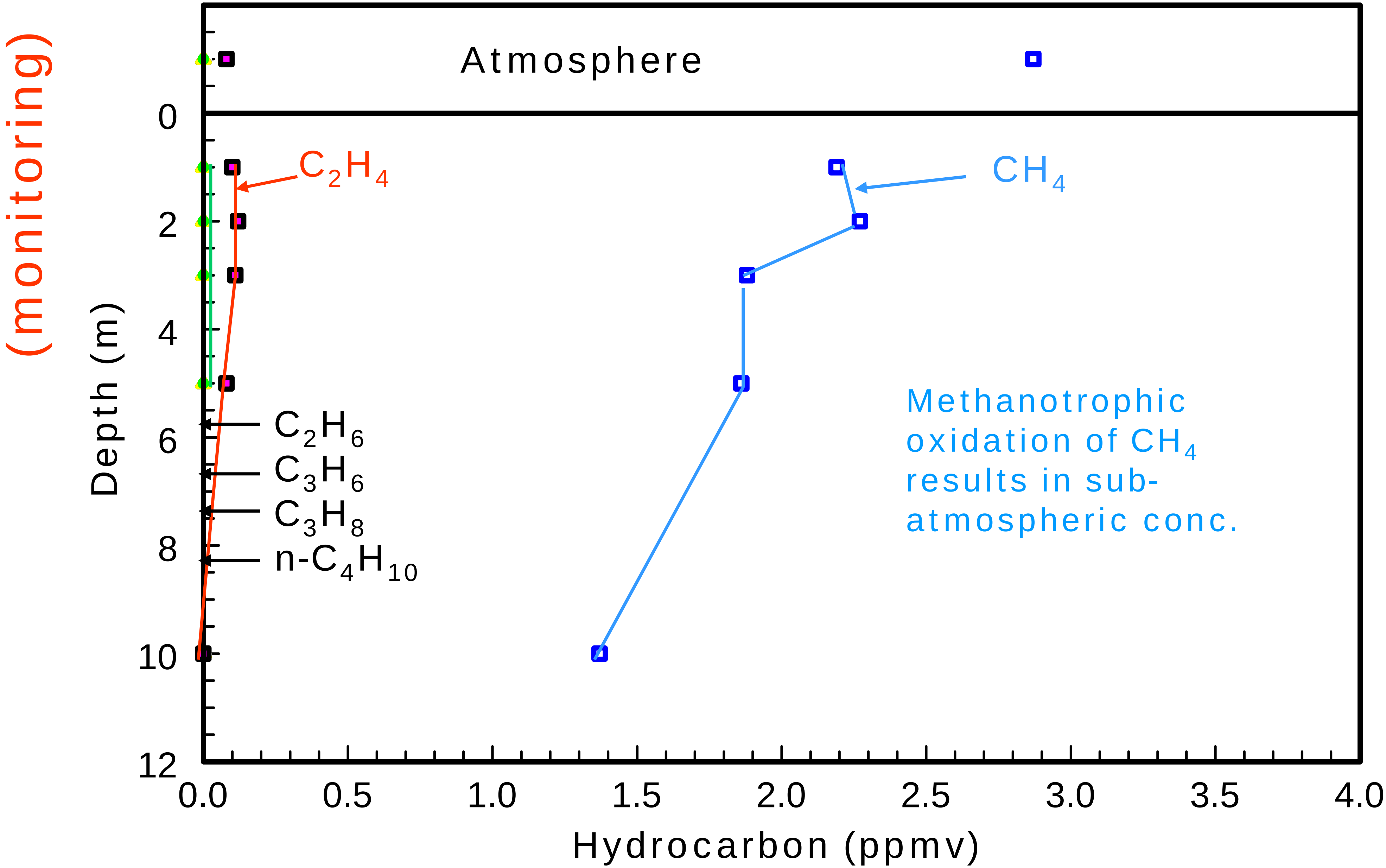
- Cons – a) Inadequate concentrations in most deep, saline aquifers to use as indigenous tracers.

TEAPOT DOME – LIGHT HYDROCARBONS IN ANOMALOUS 10-m HOLE 17; JANUARY, 2005

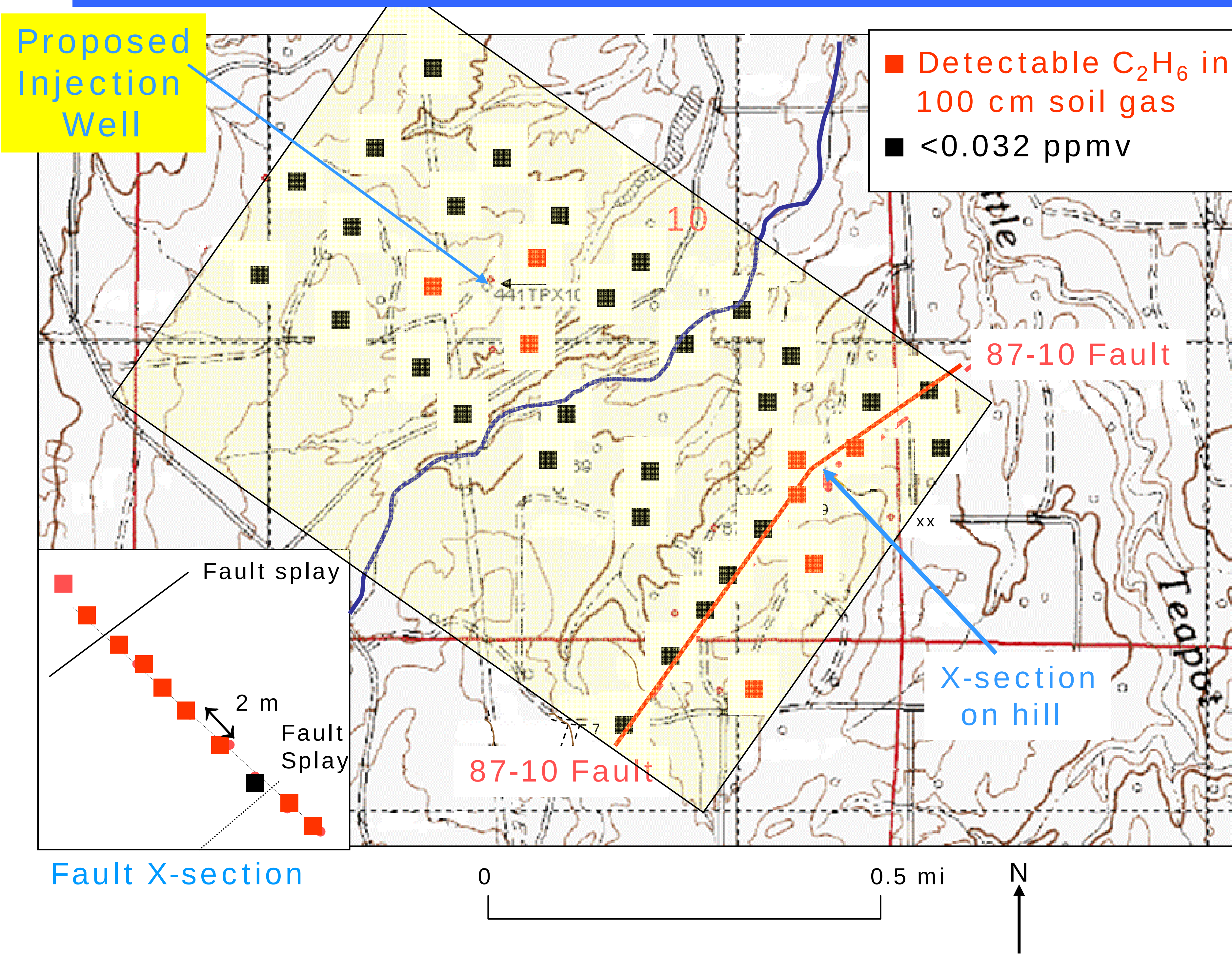
(monitoring)



TEAPOT DOME – LIGHT HYDROCARBONS IN NON-ANOM.10-m HOLE 02; JANUARY, 2005



TEAPOT DOME – SECTION 10 SOIL GAS, MARCH, 2007



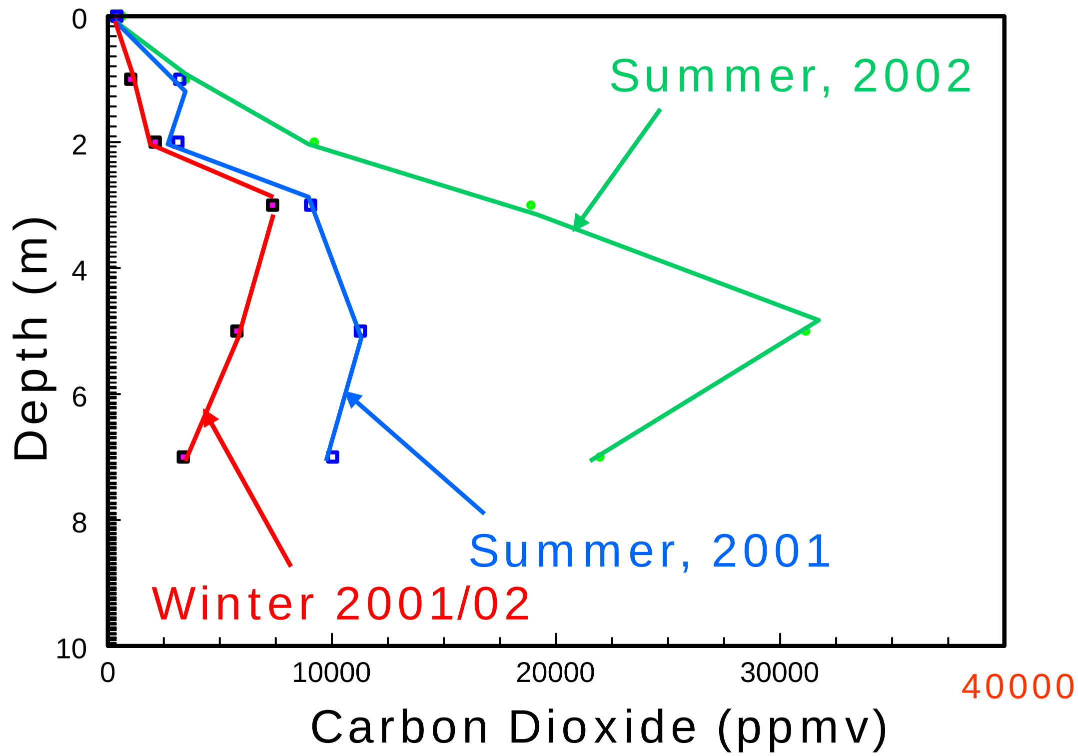
OTHER GASEOUS SPECIES - STABLE ISOTOPIC COMPOSITION OF CO_2 AND CH_4

- Pros – a) Genesis and reactions of carbon-containing gas can potentially be derived, b) isotopes readily determined for CO_2, less so for CH_4.

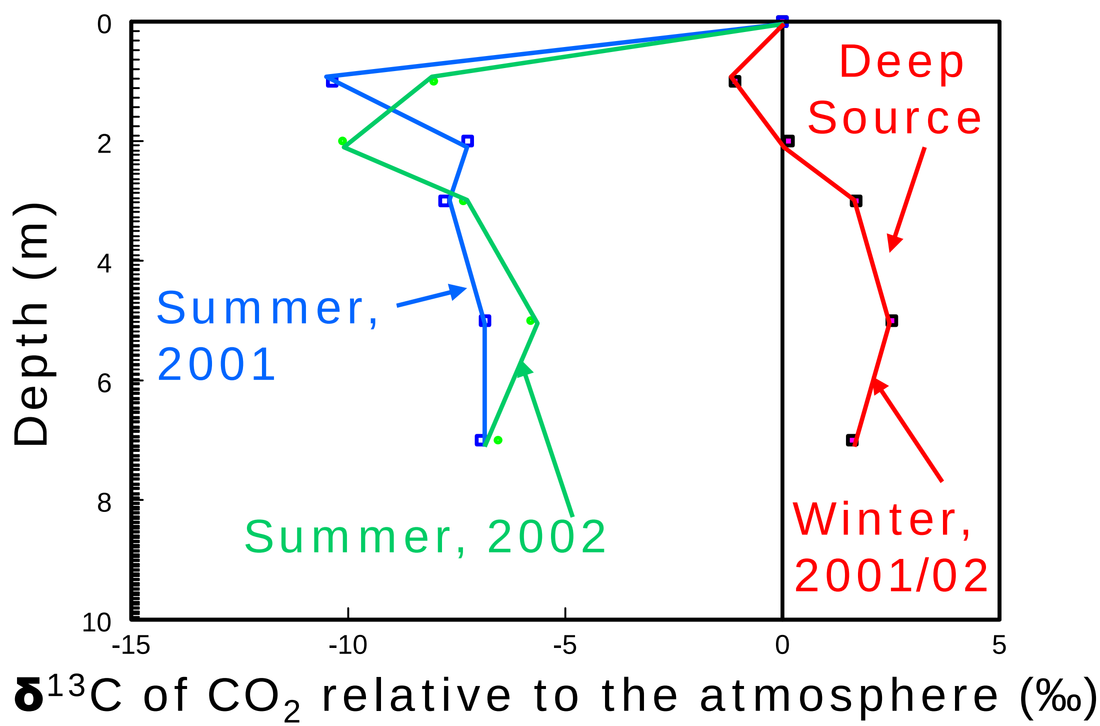
- Cons – a) Complex physical, chemical, and biological processes can make interpretation difficult, b) some seasonal variations in biological processes, c) 3-5 sources of CO_2, d) field measurements of carbon isotopic ratios on CO_2 not practical yet.

RANGELY – Anomalous Hole 01 (monitoring)

Carbon Dioxide

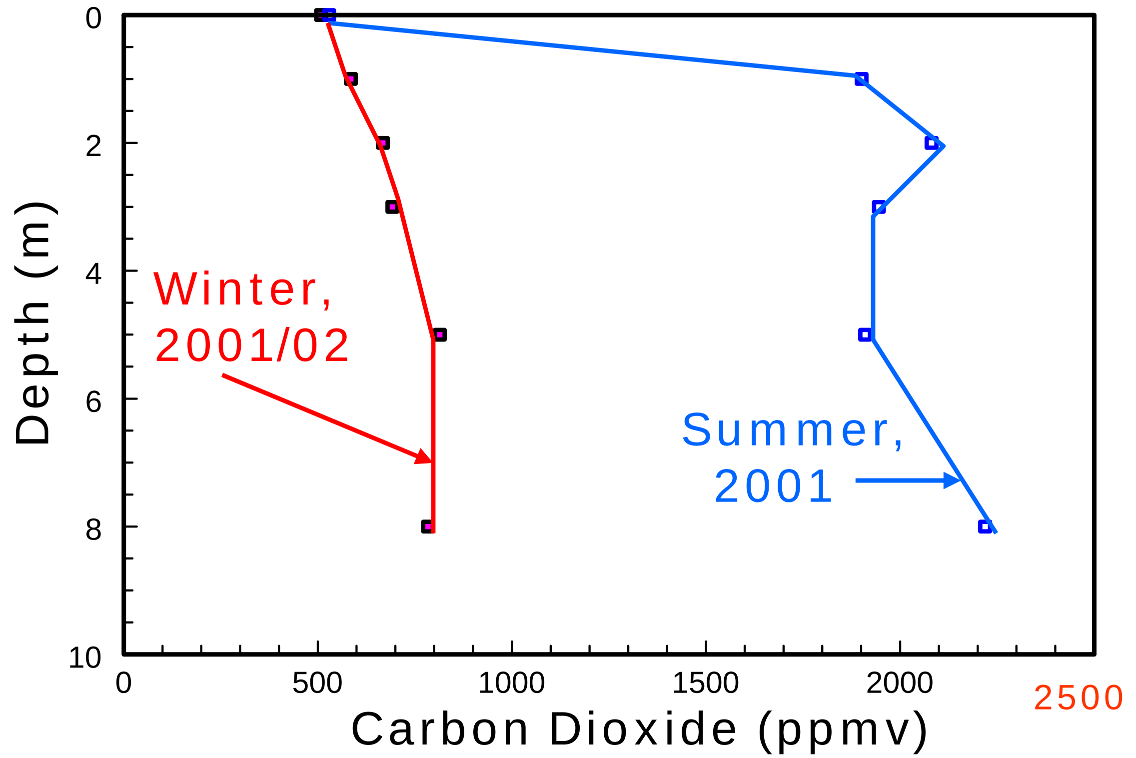


$\delta^{13}C$ of CO_2 relative to the atmosphere

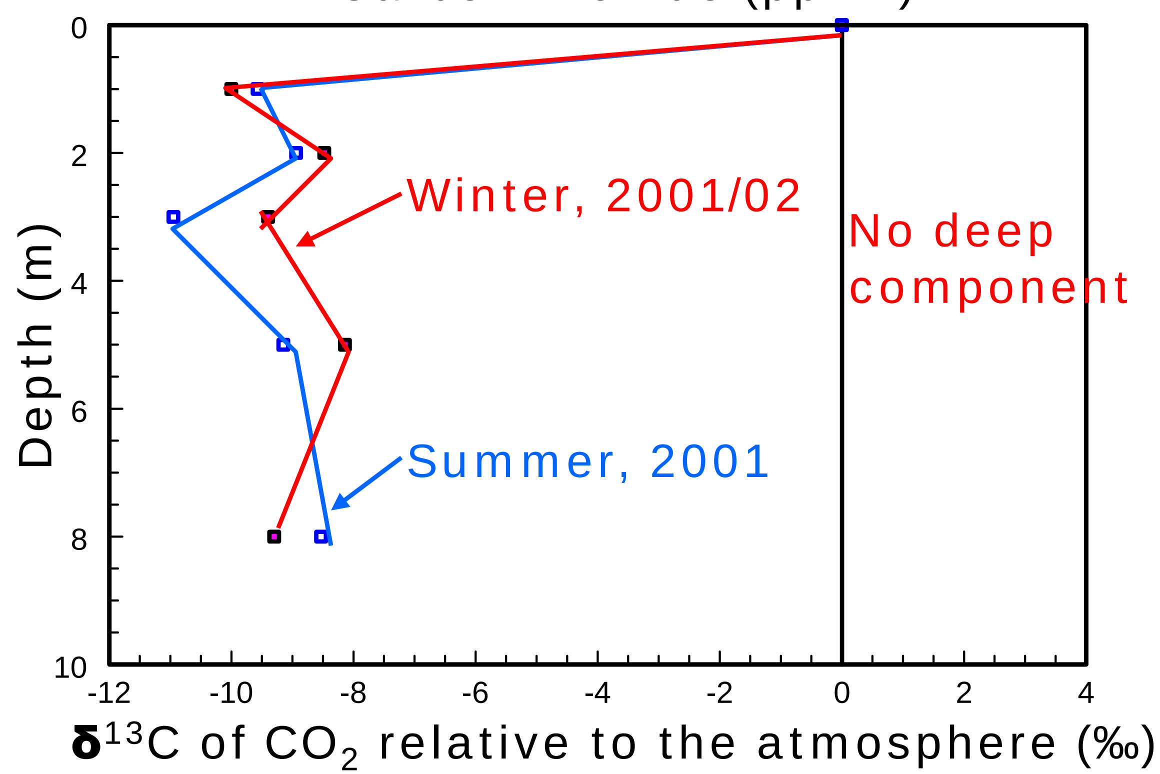


RANGELY – Non- anomalous Hole 28 (monitoring)

Carbon Dioxide



$\delta^{13}C$ of CO_2 relative to the atmosphere



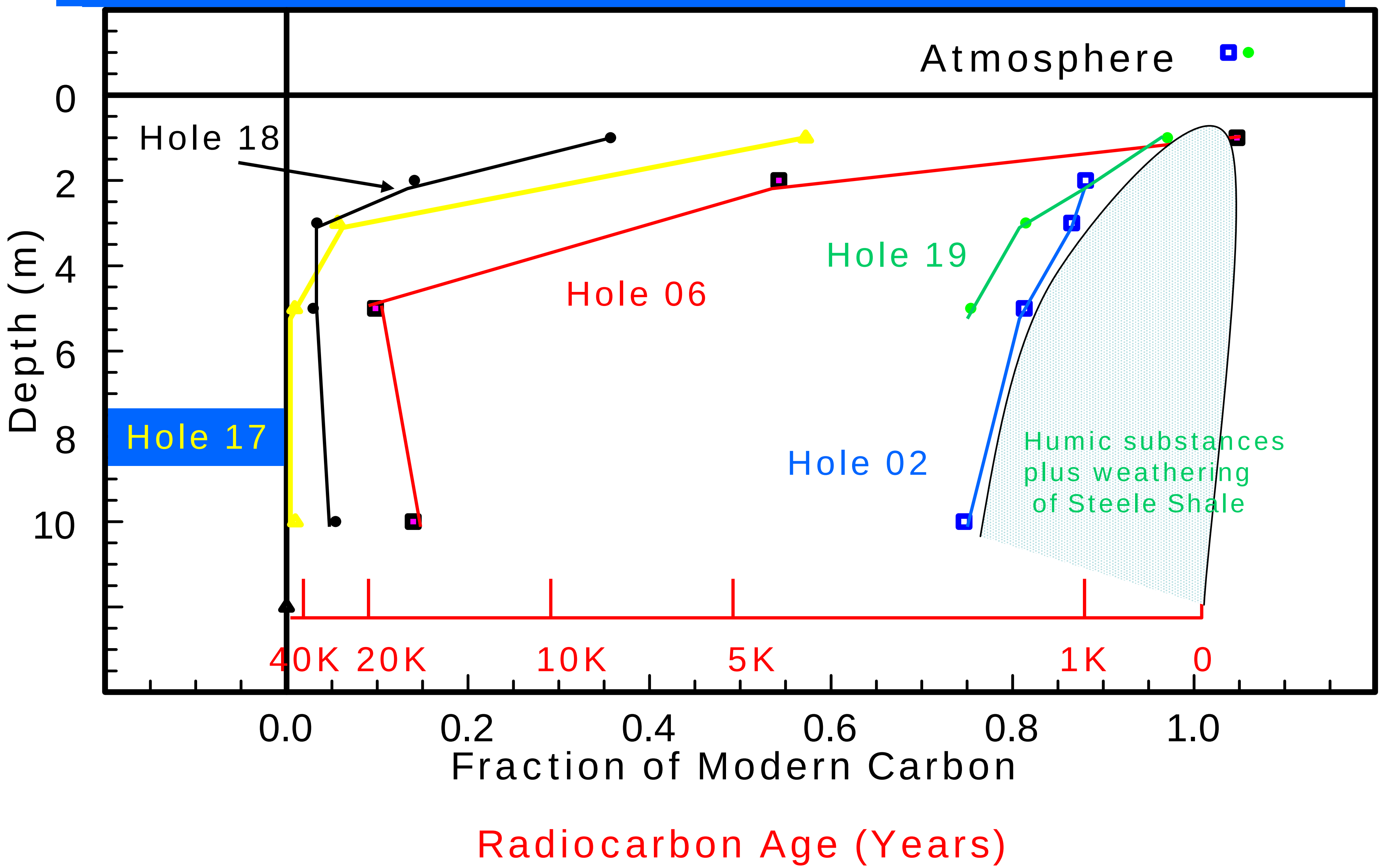
OTHER GASEOUS SPECIES-CARBON-14 CONTENT OF CARBON CONTAINING GASES

- Pros – a) Definitive measurement of proportion of deep-sourced ancient gases and modern biologically-derived carbon, b) No biological influence , c) relatively low variation with season at 3-m depth or below.

- Cons – a) Strictly a laboratory measurement with fairly complicated sampling and analytical protocol, b) food-based waste CO_2 is “modern,” c) laboratory turn-around currently slow.

TEAPOT DOME – CARBON-14 IN CO_2 FROM 10-m HOLES; JANUARY, 2005

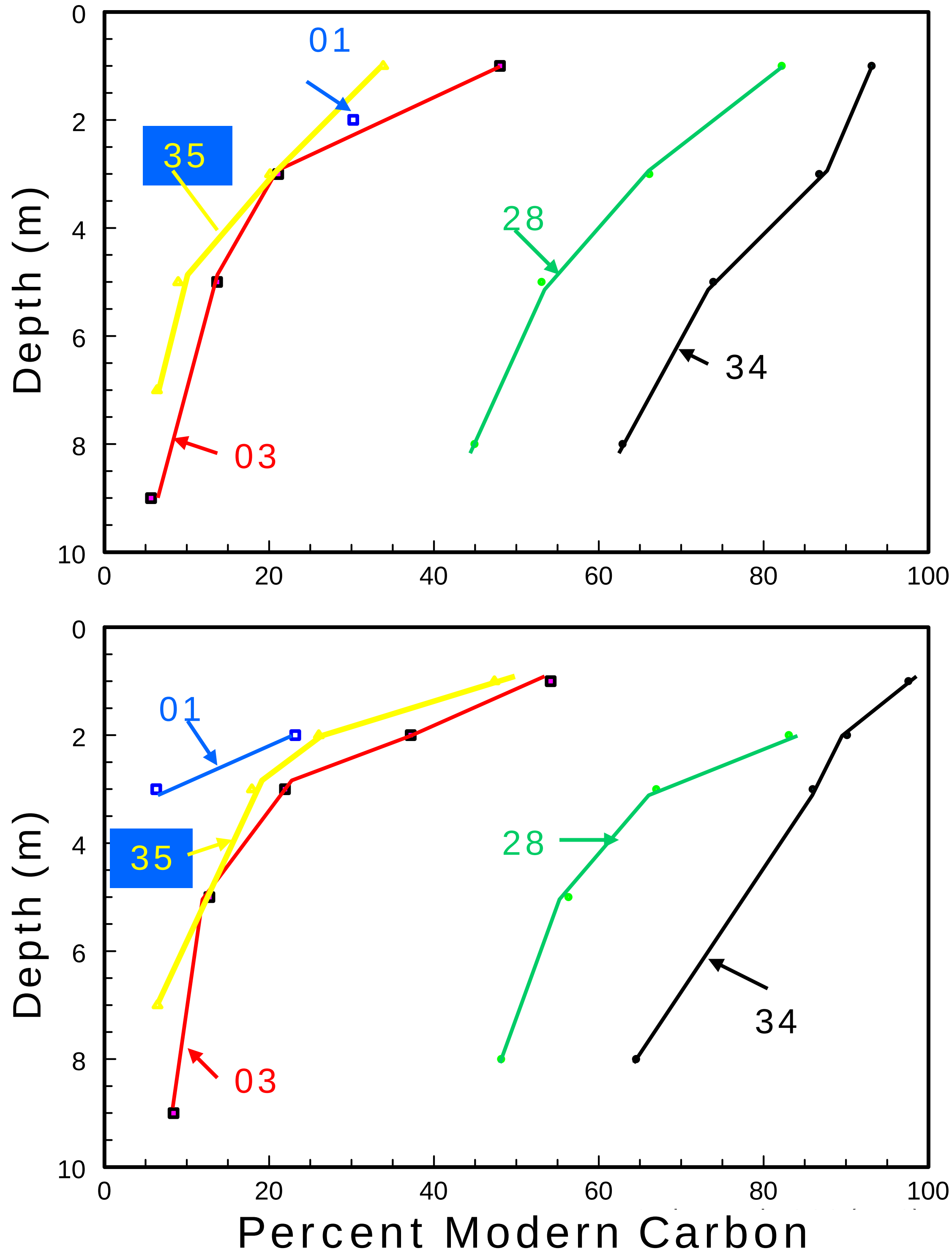
(verification)



RANGELY – C-14 IN CO_2 FROM 10-M HOLES (verification)

Winter 2001/2002

Summer, 2002

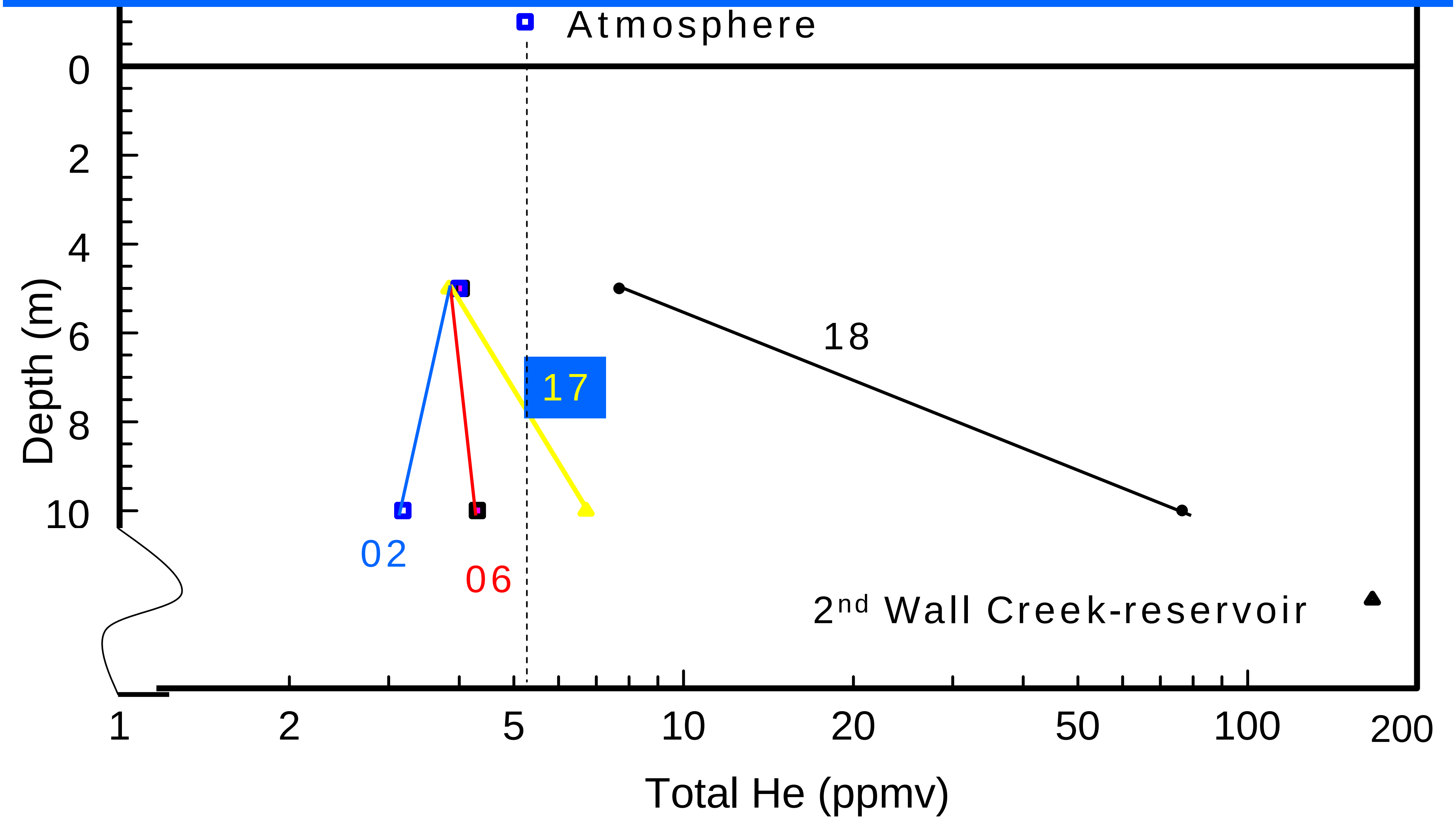


HELIUM, NEON, ARGON TOTAL CONCENTRATIONS AND ISOTOPIC RATIOS

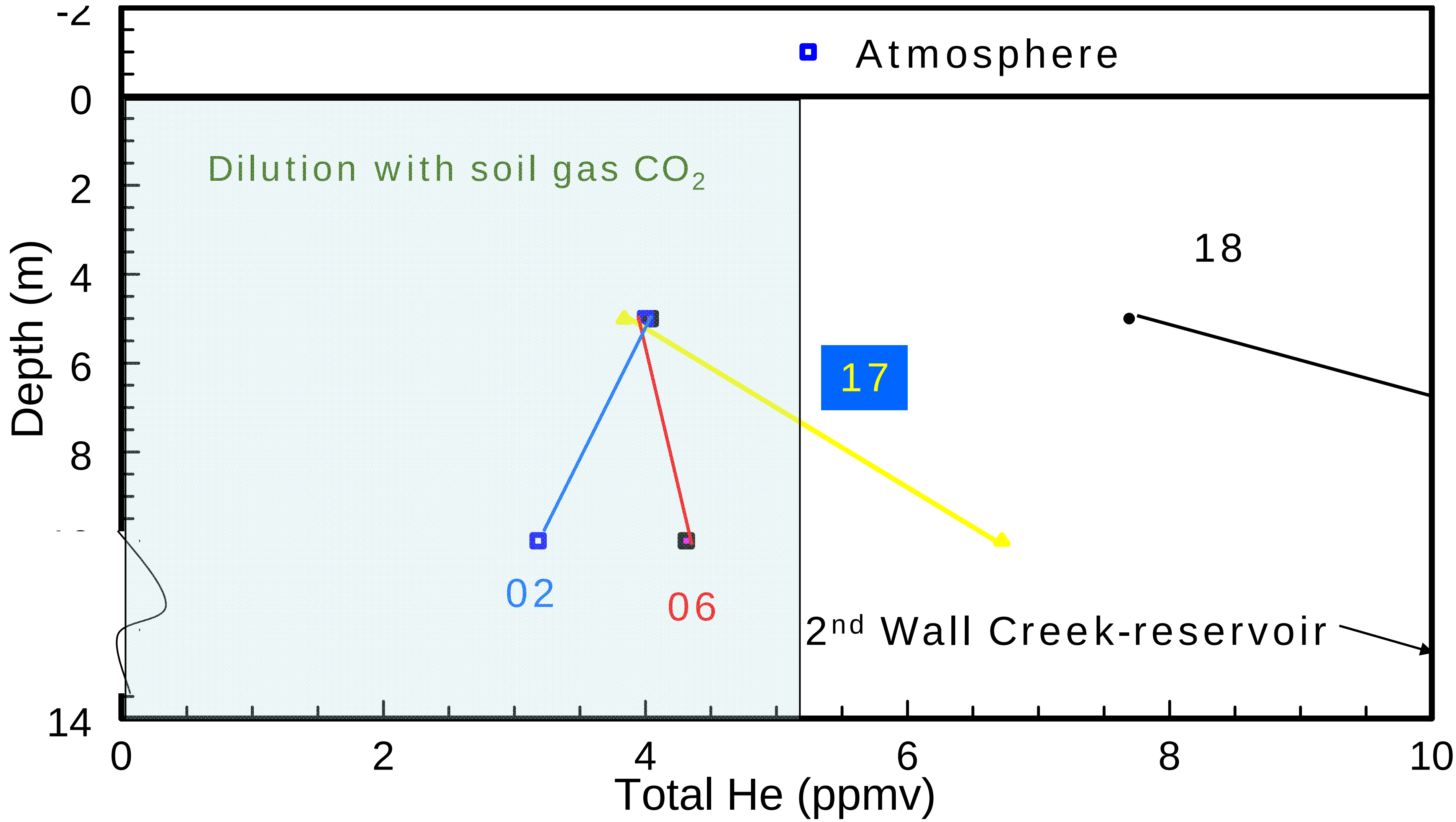
- Pros – a) Definitive measurement of proportion of deep-sourced ancient gases and atmospheric-derived gases, b) No biological influence , c) probably low seasonal variance, d) newer micro-thermal conductivity detector eliminates need for expensive isotope ratio mass spectrometric measurement, e) possible use of field laboratory or portable MS on 10-m holes.

- Cons – a) Strictly a laboratory measurement if isotope ratios are necessary, b) samples from a depth of 10-m or deeper are probably required because of diffusivity of He in the unsaturated zone and atmospheric exchange, c) usefulness of argon yet to be demonstrated, d) xenon and krypton concentrations could be effective, but are too low for GC determination, but MS probably OK.

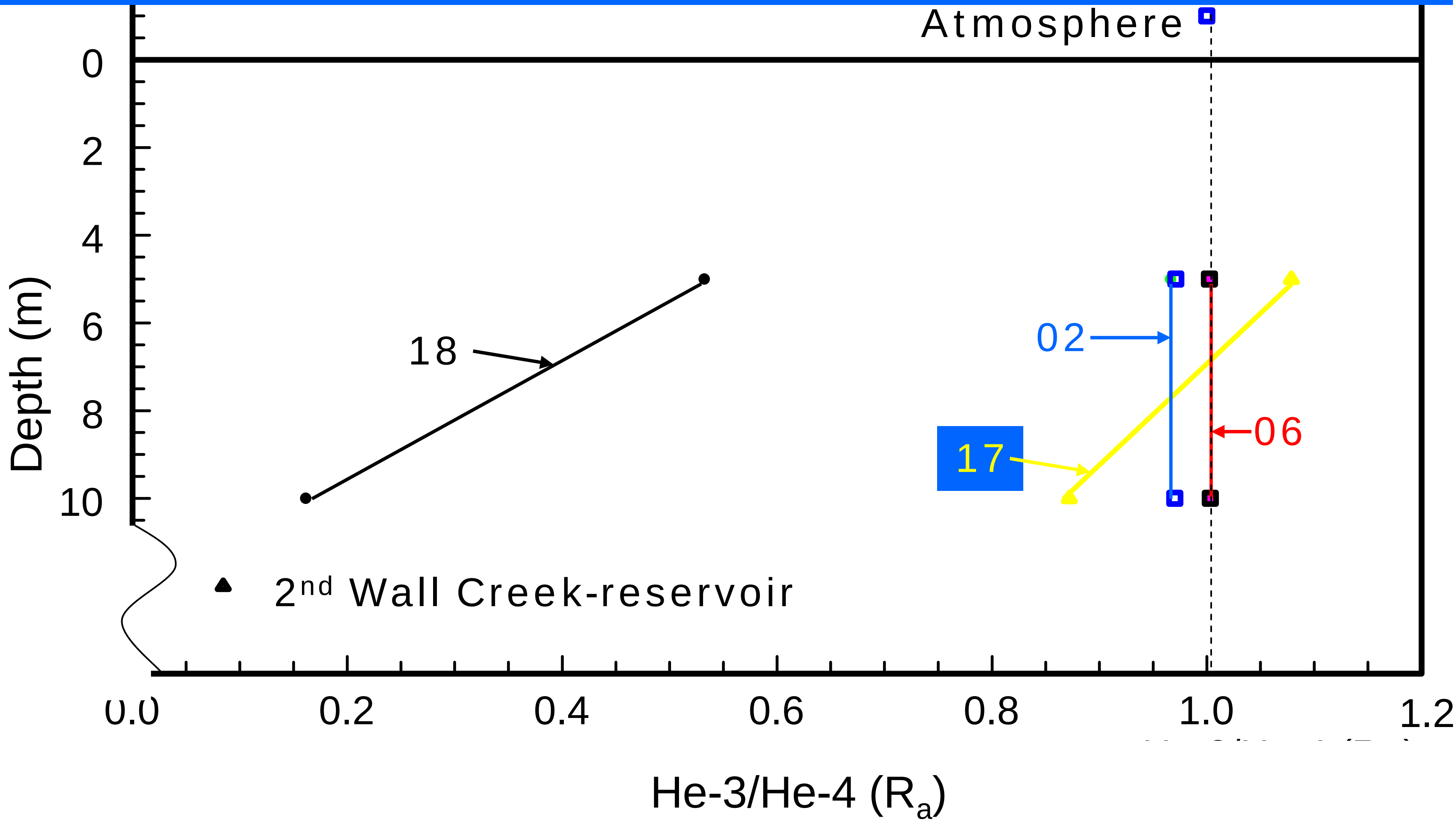
TEAPOT DOME – 10-m HOLES; MAY, 2005
TOTAL He (Mackintosh and Ballentine)
(verification)



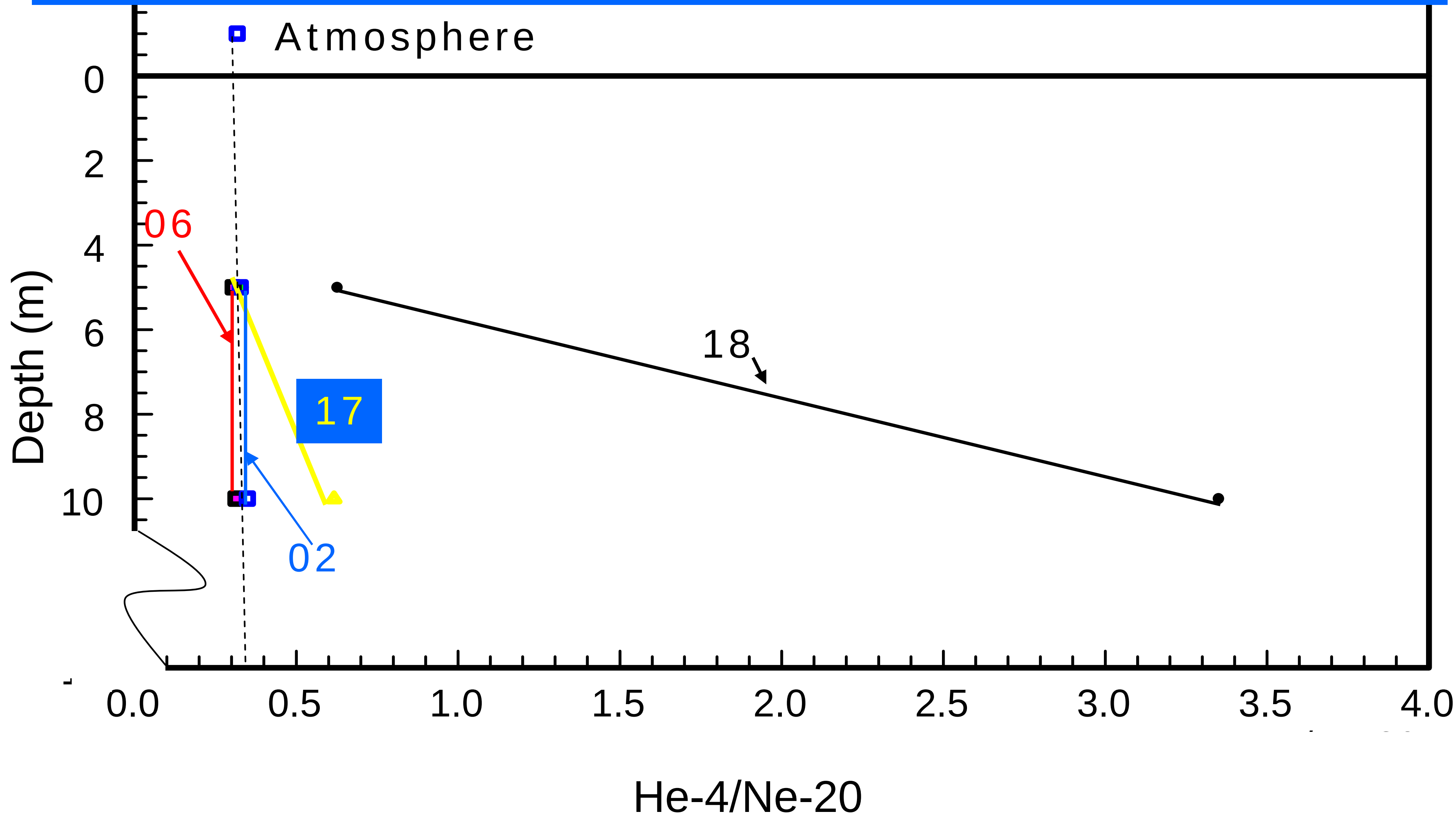
TEAPOT DOME – 10-m HOLES, MAY, 2005
TOTAL He (Mackintosh and Ballentine)
(verification)



TEAPOT DOME – 10-m HOLES; MAY, 2005
He ISOTOPES (Mackintosh and Ballentine)
(verification)



TEAPOT DOME = 10-m HOLES, MAY, 2005
He/Ne ISOTOPES (Mackintosh and Ballentine)
(verification)



OTHER GASEOUS SPECIES-ADDED TRACERS SUCH AS SULFUR HEXAFLUORIDE OR PERCHLORO-, OR PERFLUOROCARBONS

- Pros – a) May move rapidly through the stratigraphic column toward the surface(?), b) atmospheric concentrations are very low, c) GC-ECD analytical techniques are precise and accurate at low concentrations, d) high signal: noise ratio.

- Cons – a) Integrative collection required over a period of time, b) sulfur hexafluoride may not be completely conservative, c) perchloro- and perfluorohydrocarbons are “greenhouse” gases and effective degraders of stratospheric ozone, c) strict protocol necessary to prevent contamination of collectors, d) cost of tracer is high.

PERFLUOROCARBON TRACER SEEPAGE AT WEST PEARL QUEEN (WELLS ET AL. 2007)

perfluoro-1,2-dimethylcyclohexane

PDCH + PTCH (1 +2)

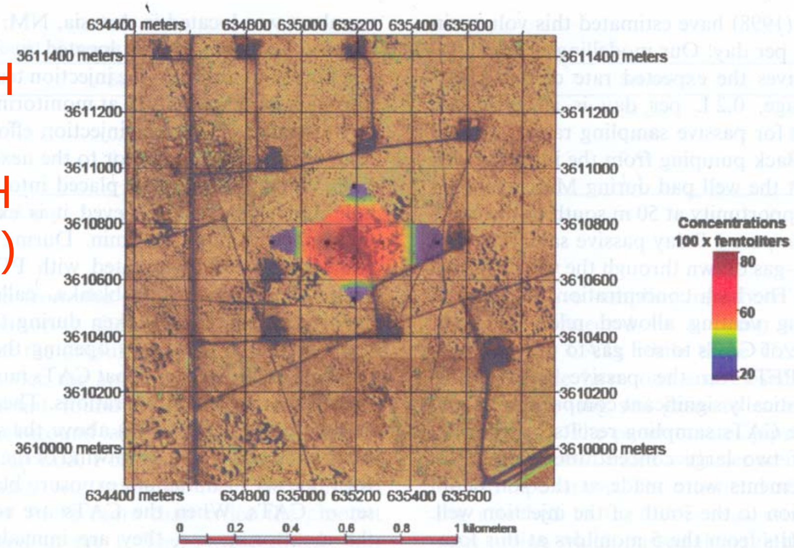
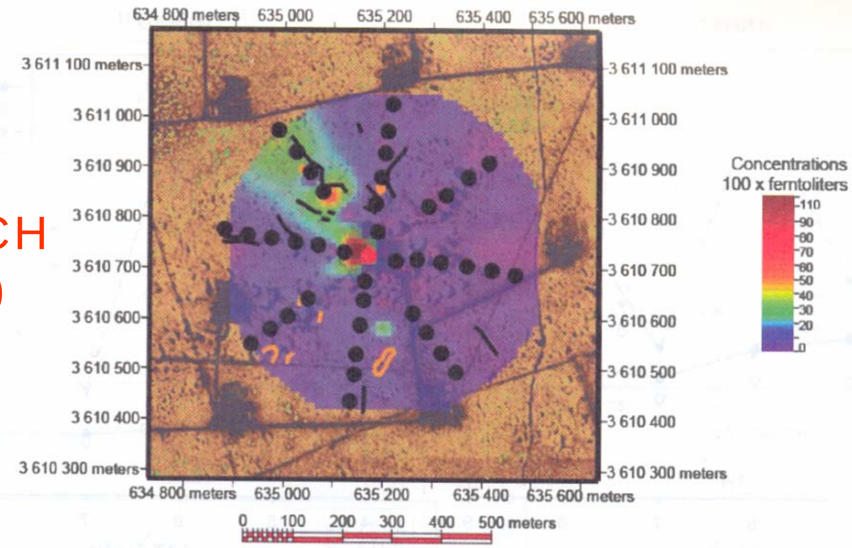


Fig. 6. Spatial distribution of average tracer concentration observed at the active sites. PDCH and PTCH concentrations observed in the first and second sets of CATs were averaged to obtain the above map. Concentration data are superimposed on an orthophoto of the ground surface. The darker colored linear features on the orthophoto are roads. Well pads appear as darker rectangular patches in the image.

perfluorotrimethylcyclohexane

PTCH (3)

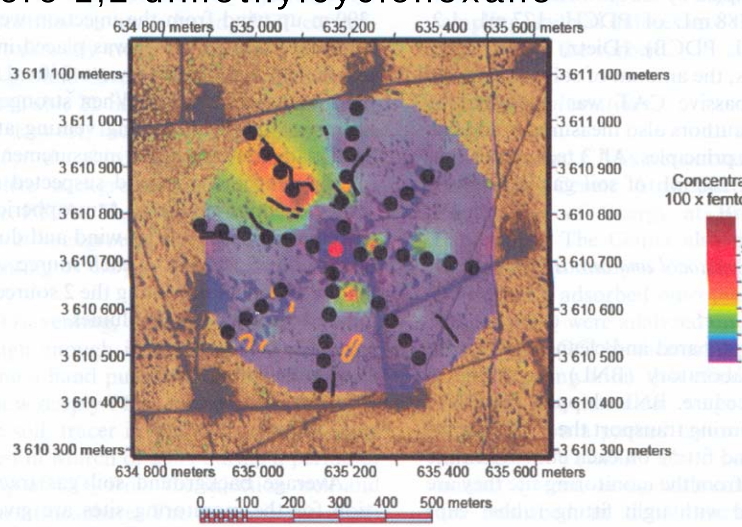


CH concentrations (3rd set) measured during the 54 day exposure period are superimposed on an orthophoto v

n #4 injection well (red dot) is surrounded by the radial distribution of CAT samplers (black dots).

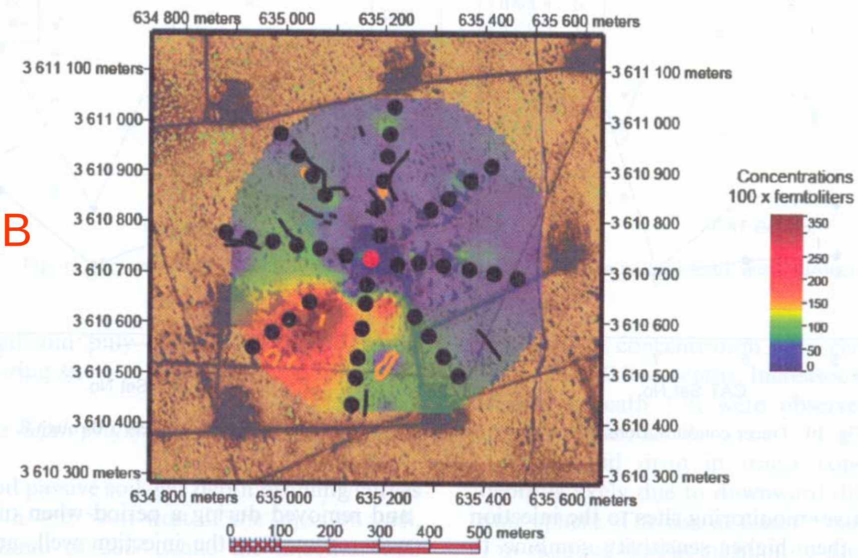
perfluoro-1,2-dimethylcyclohexane

PDCH (3)



perfluorodimethylcyclobutane

PDCB (3)

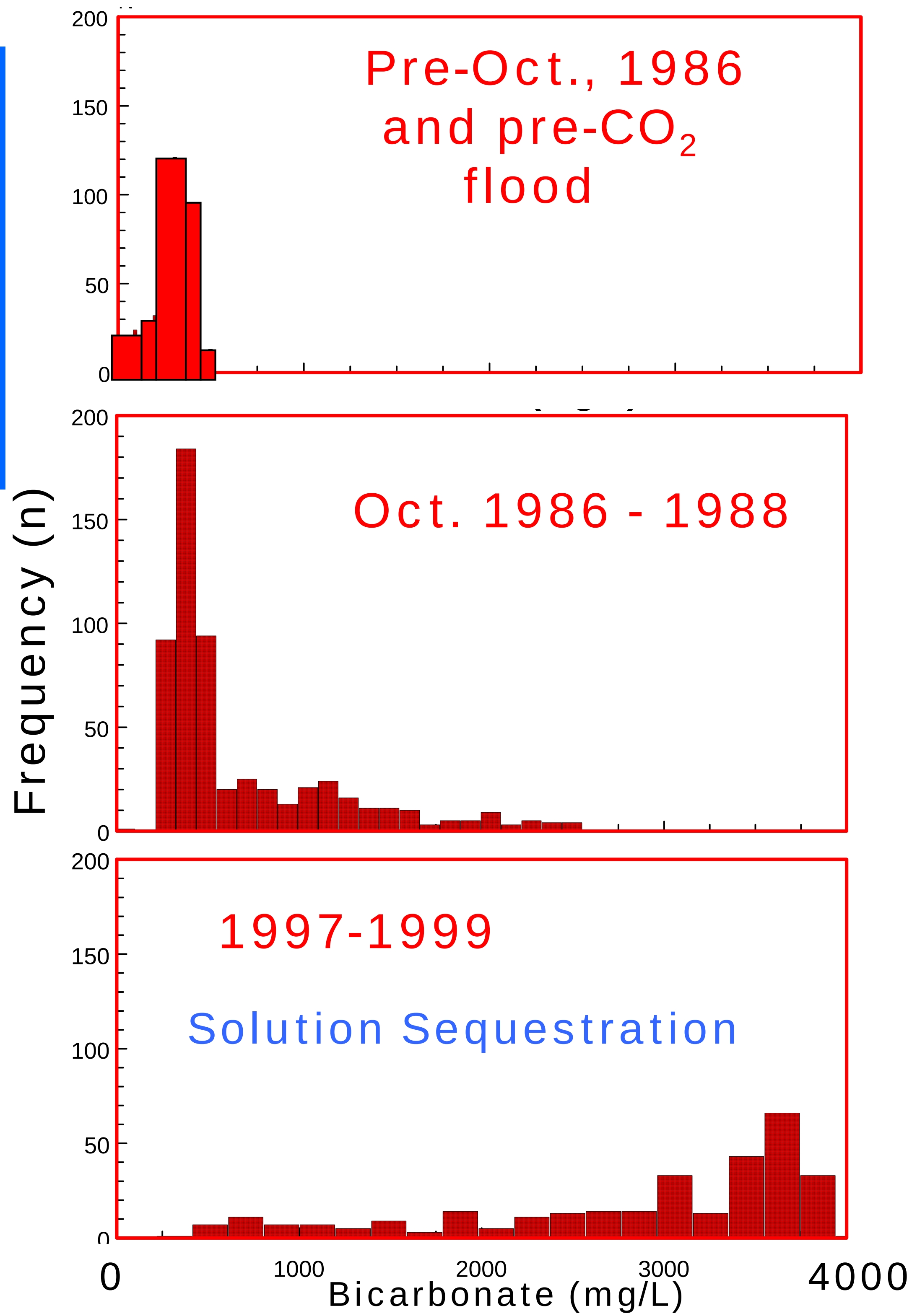


DISSOLVED BICARBONATE CONTENT OF SHALLOW GROUNDWATER

- Pros – a) Easy-to-measure shallow groundwater parameter that changes rapidly if CO_2 is migrating upward, b) will likely be effective in any climate, c) low-cost, low-tech method if appropriate wells are already in place, d) geochemical modeling can provide data on the potential for dissolution and precipitation of solid phases.

- Cons – a) Must measure 4 major cations, 3 major anions, and pH in order to model the evolution of the water composition, b) sample depressurization and temperature change will alter aqueous composition, c) if CO_2 is reaching shallow groundwater to form bicarbonate, seepage process is already rather advanced.

RANGELY
Bicarbonate in Weber Formation (reservoir) waters (monitoring)



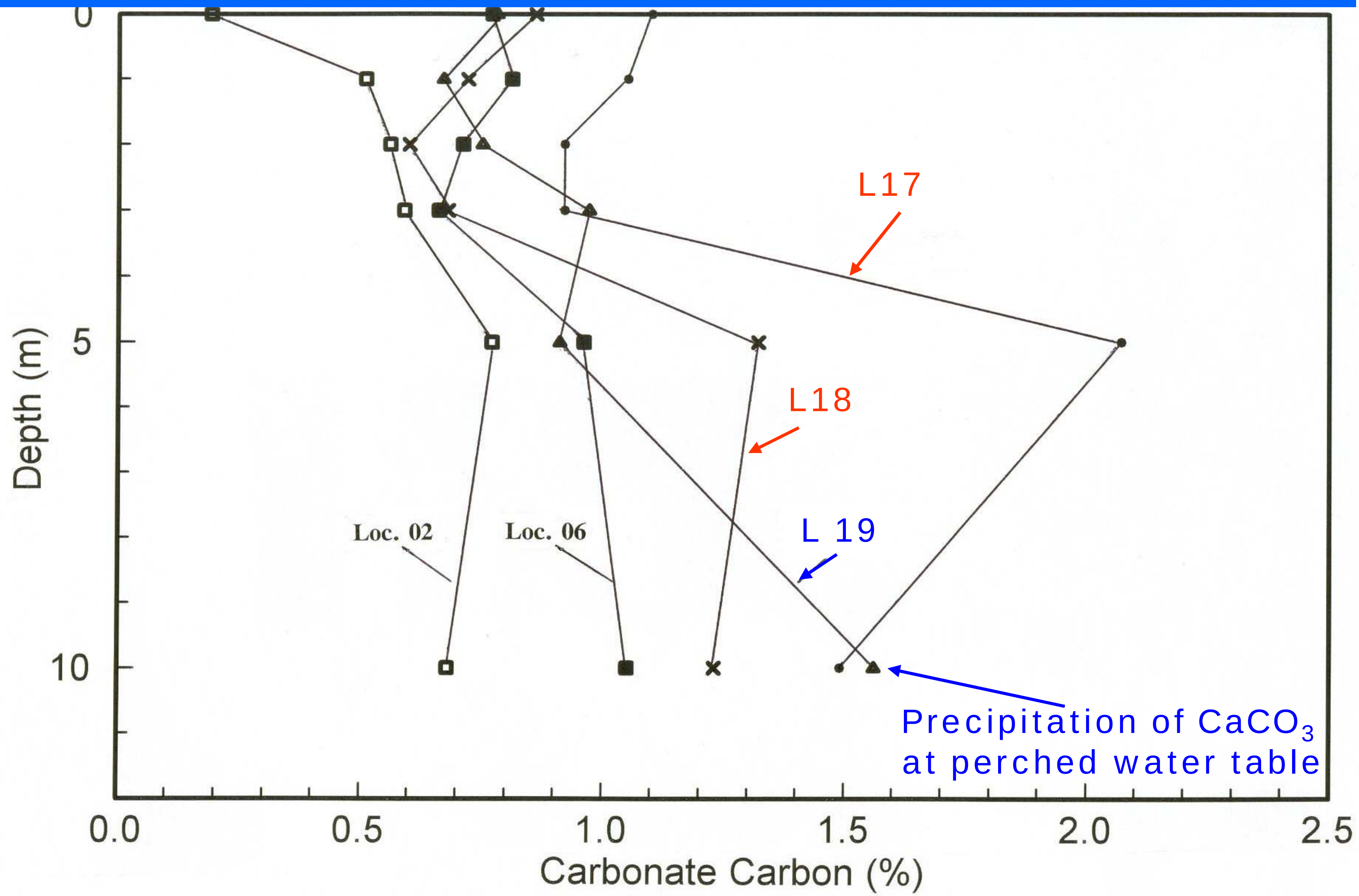
STABLE CARBON AND OXYGEN ISOTOPES IN SECONDARY CARBONATES OF VEINS AND SOILS

- Pros – a) Provides evidence for presence or absence of past (fossil) microseepage during baseline determination, and prior to initiation of an injection project, b) identification of potential microseepage pathways, if pressurized, c) simple sample collection and preparation for measurement, d) sample splits can be retained for future use.

- Cons – a) Strictly a laboratory measurement, b) not a monitoring method that can be used to follow potential microseepage from injection.

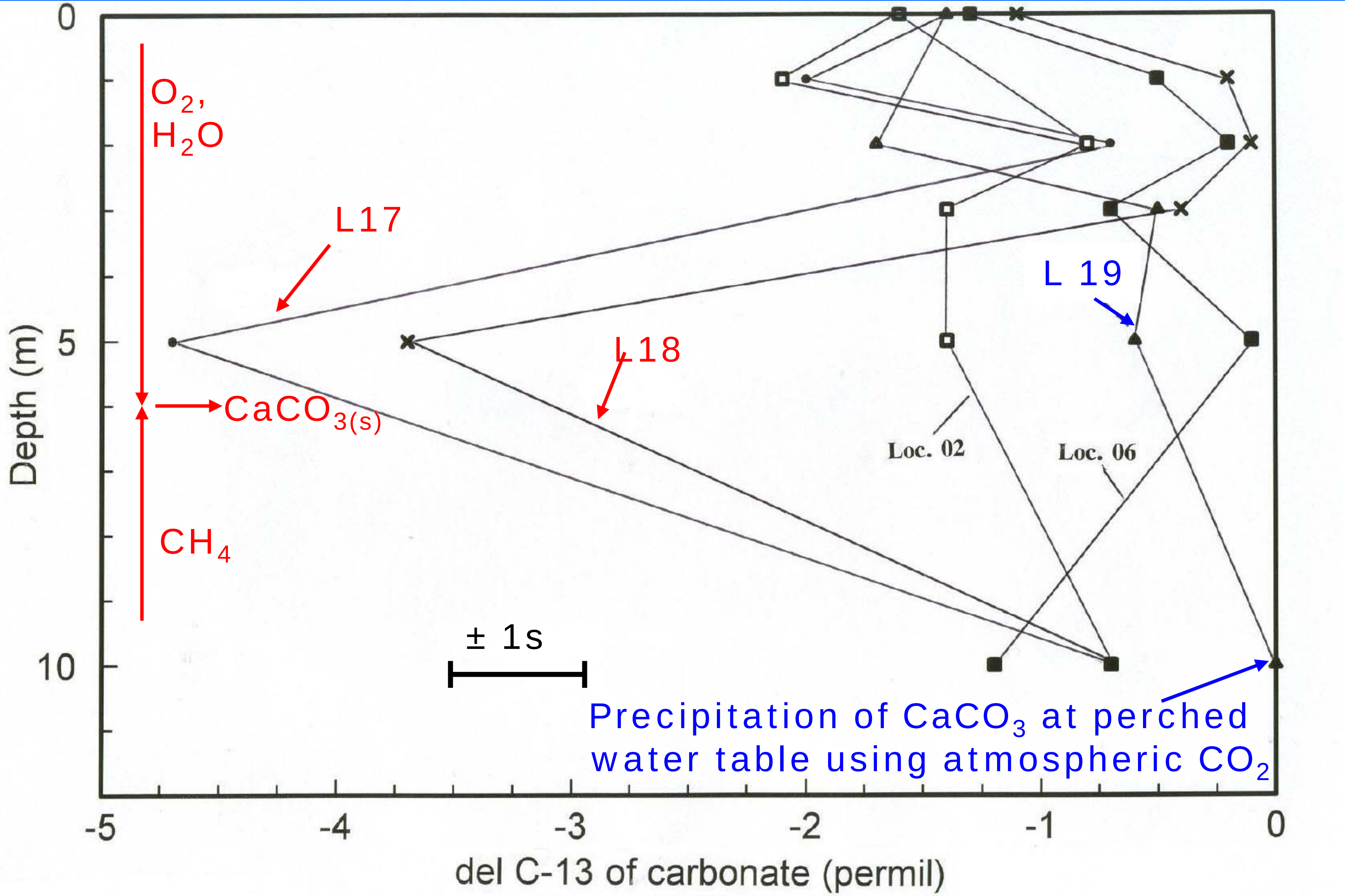
TEAPOT DOME – 10-m HOLE CUTTINGS CARBONATE (INORGANIC) CARBON CONTENT

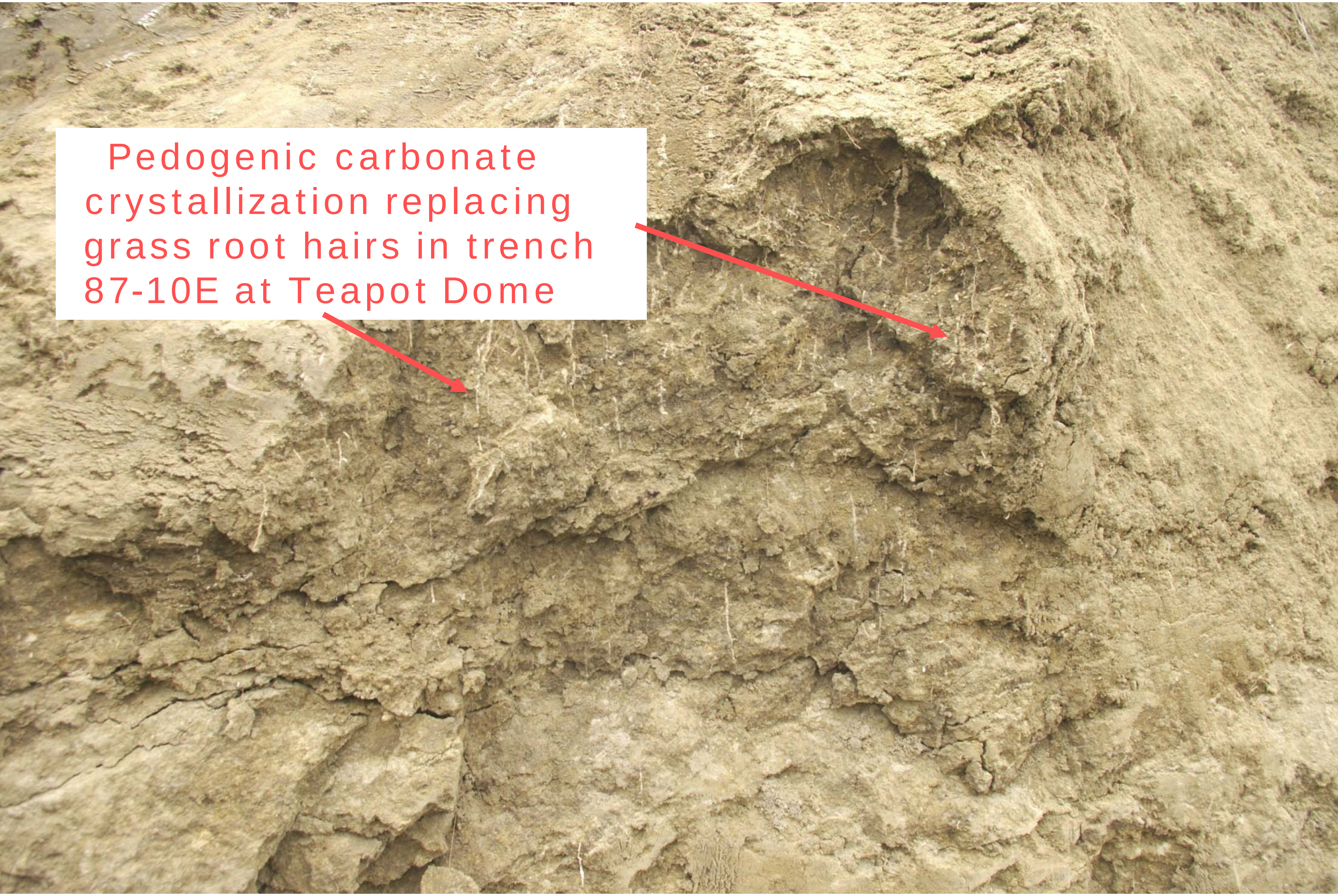
(baseline condition)



TEAPOT DOME – 10 m CUTTINGS
$\delta^{13}C$ OF CARBONATE (INORGANIC CARBON

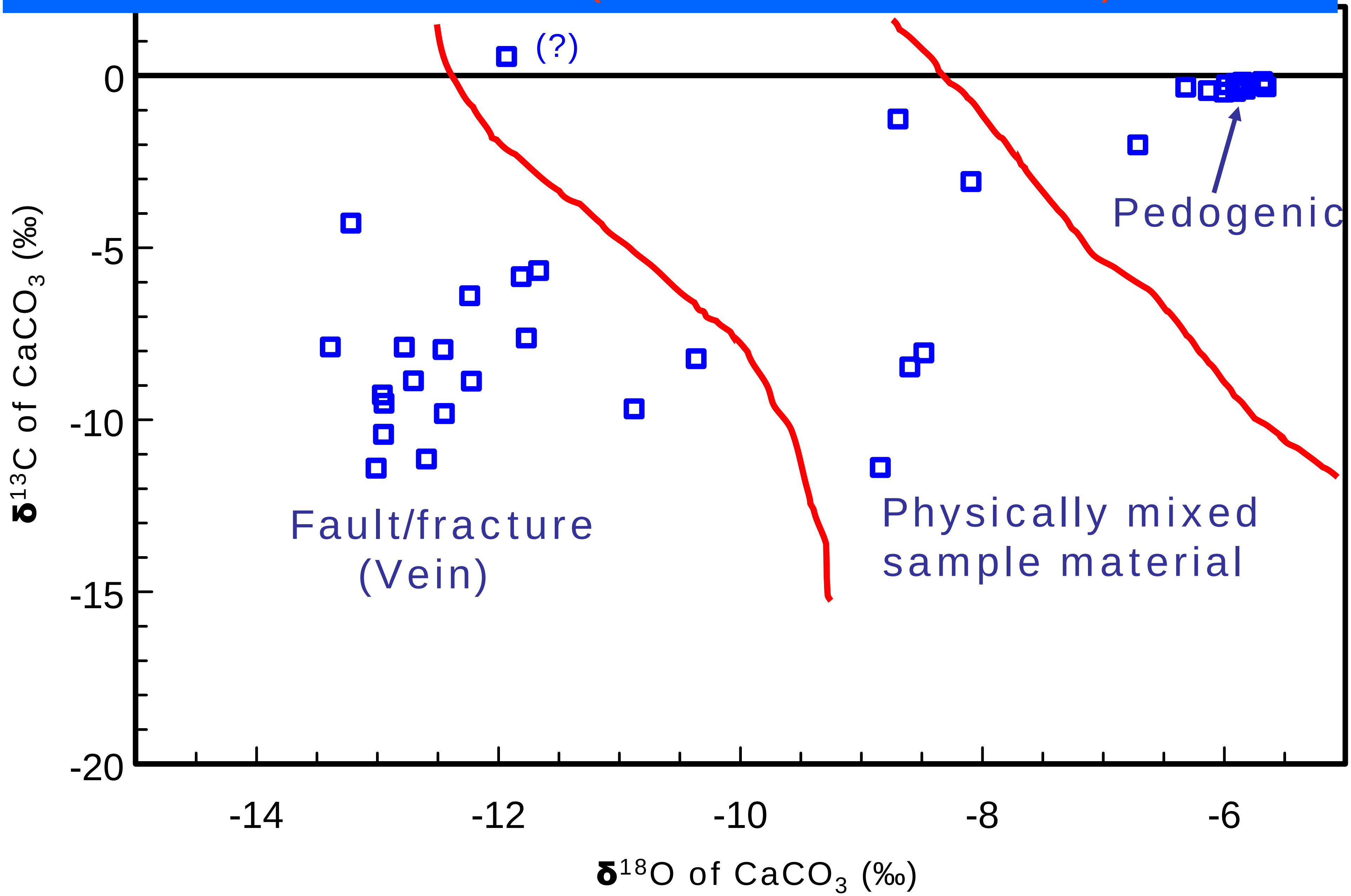
(baseline condition)



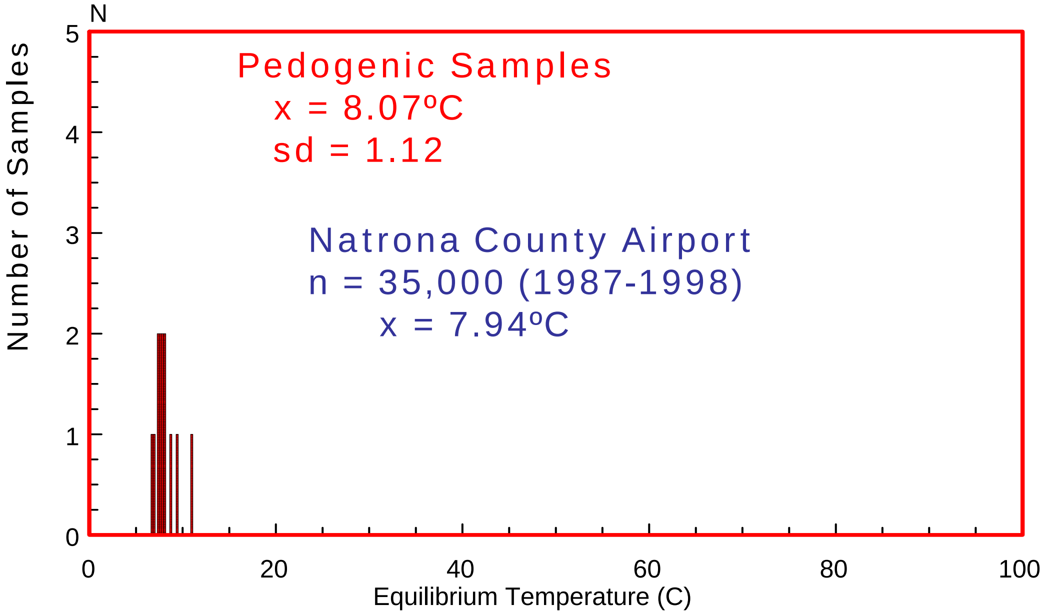

Pedogenic carbonate crystallization replacing grass root hairs in trench 87-10E at Teapot Dome

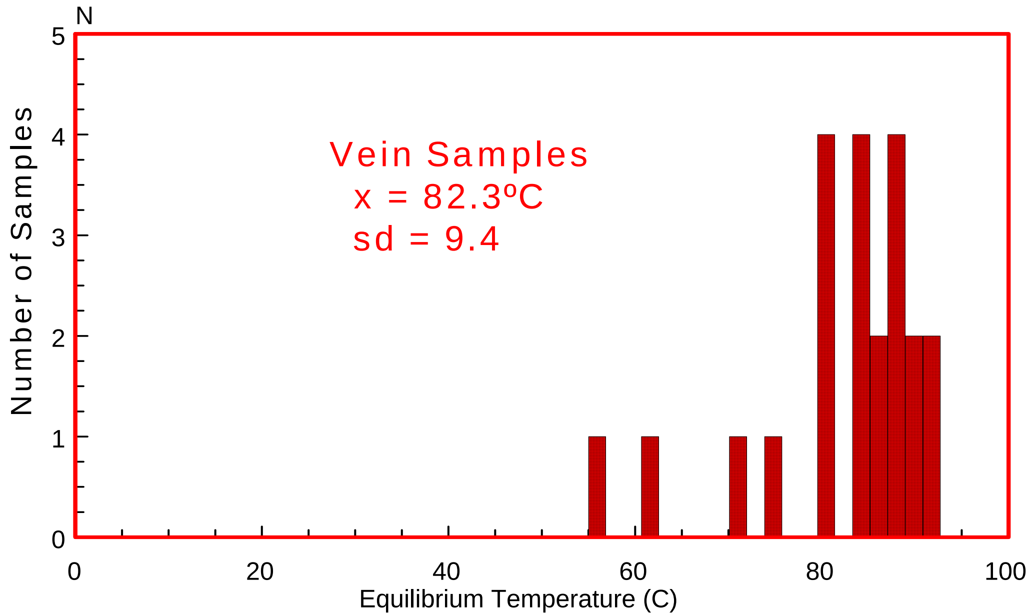

Coarse-grained calcite in trench 87-10E across fault at Teapot Dome

TEAPOT DOME -SECTION 10 – TRENCHES 87-10W AND 87-10E (baseline condition)



TEAPOT DOME- SECTION 10 TRENCH
EQUILIBRIUM TEMPERATURE (ºC) BASED ON $\delta^{18}O$
(baseline condition)





DEEP WELLS TO MONITOR PRESSURE, TEMPERATURE, AND COMPOSITION IN OVERLYING FORMATIONS

- Pros – a) Early detection of migration and its general position.

- Cons – a) Very expensive to install, b) once plume passes a monitoring well, future usefulness may be limited, c) deterioration of wells provide a future pathway to the surface.

CONCLUSIONS

- Monitoring protocols will need to be developed for each project that reflects climate, geology, and accommodates cultural interferences,
- A tracer that has low atmospheric concentration and low variability offers the best chance for early detection of gas microseepage,
- No single method is likely to be completely satisfactory for most sites,
- Measurement of carbon-containing gases will require liberal use of isotopes,
- The promotion of tower methods only measuring CO_2 as the answer to monitoring has been excessive; indeed, probability of early seepage detection may be limited.

ESTIMATION OF CO_2 MICROSEEPAGE INTO THE ATMOSPHERE AT RANGELY – (a start on accounting)

- Using total winter-time CO_2 flux gives an estimate of 8600 metric tonnes year^{-1} for the 78 km^2 area ,
- Using the $\boldsymbol{\delta}^{13}C$ offset for CO_2 from atmospheric value reduces estimate to <3800 metric tonnes year^{-1},
- Using the C-14 data on 4 anomalous locations gives **≈** 90% of the CO_2 in these 4 locations is ancient and deep-sourced,
- The average winter CO_2 flux over the field is 0.302 g m^{-2} day^{-1}, 4/41 locations on the field are "anomalous," yielding 170 metric tonnes year^{-1} as the estimate,
- The anomalous CO_2 is primarily derived from methanotrophic oxidation of CH_4, so <170 tonnes is the final estimate of CO_2 flux rate,
- (15 yr x 170 tonnes/yr)/23x10^6 tonnes = 0.00011 (**≈** 0.01%/year).

ESTIMATION OF CO_2 MICROSEEPAGE INTO THE ATMOSPHERE AT RANGELY – (a start on accounting)

- BUT, the computer modeling of the methanotrophic oxidation of CH_4 indicates very high rates in the anomalous 10 m holes,
- It is probable that most of the radiocarbon "dead" CO_2 is produced from oxidation of microseeping radiocarbon "dead" CH_4, being the previously described 4th specific source of CO_2 ,
- The seepage of injected CO_2 (5th source) into the atmosphere must be <170 metric tonnes year^{-1} and is probably near "zero".

ESTIMATION OF CH_4 MICROSEEPAGE INTO THE ATMOSPHERE AT RANGELY – (a start on accounting)

- The gross CH_4 microseepage into the atmosphere over 78 km^2 is 700±1200 tonnes $year^{-1}$ using the winter rate'
- The net CH_4 microseepage into the atmosphere is 400 metric tonnes $year^{-1}$ ±?, subtracting the control area.

' non- parametric estimated rate is positive with **α** =0.015.

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