Monitoring, Verification and Accounting (MVA) Applied to CO_2-EOR Projects*

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Abstract

Previous geochemical measurements at three operational or proposed CO_2-EOR projects; Rangely, CO, Teapot Dome, WY, Weyburn, SK are presented as indicators of effectiveness of selected MVA methods. Seasonal fluxes and soil gas concentrations of carbon-containing gases have been determined by the author at Rangely and Teapot Dome. Similar measurements were made at Weyburn by a group led by the British Geological Survey. Methane and light hydrocarbon measurements will be more effective than CO_2 for monitoring of EOR projects, whereas CO_2 measurements have dominated proposals at pure sequestration projects. Measurement of inert gases as indigenous tracers in soil gas and shallow ground waters for monitoring will be effective in both pure sequestration and CO_2-EOR projects. Isotopic measurements provide stronger data necessary for verification. In climates with strong seasonal variations, carbon-containing gas fluxes can vary by a factor of ten and shallow soil gas concentrations by a factor three, primarily due to seasonality of shallow biological processes. Winter or dry season measurements allow improved recognition of a deep source component. Modeling of CH_4 and light alkane vertical migration at Rangely indicated an estimated improvement of the signal to noise ratio by a factor of five during winter measurements. A first-order estimate of deep source gas leakage at Rangely is <170 tonnes of CO_2 and 400 tonnes of CH_4 annually. Trace CH_4 leakage at Teapot Dome was detected over faults. An IPAC-sponsored study over an alleged localized leak at Weyburn used carbon-containing gases to verify the absence of leakage at this location. The results support the particular strength of isotopic measurements on inert gases in shallow groundwater for purposes of verification.

Selected References

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Romanak, K.D., P.C. Bennett, C. Yang and S.D. Hovorka, 2012, Process-Based Approach to Soil Gas Monitoring at Geologic Carbon Storage Sites: Geophysical Research Letter, p. 39.

MONITORING, VERIFICATION AND ACCOUNTING (MVA) APPLIED TO CO_2-EOR PROJECTS

Ronald W. Klusman

Emeritus Professor

Colorado School of Mines

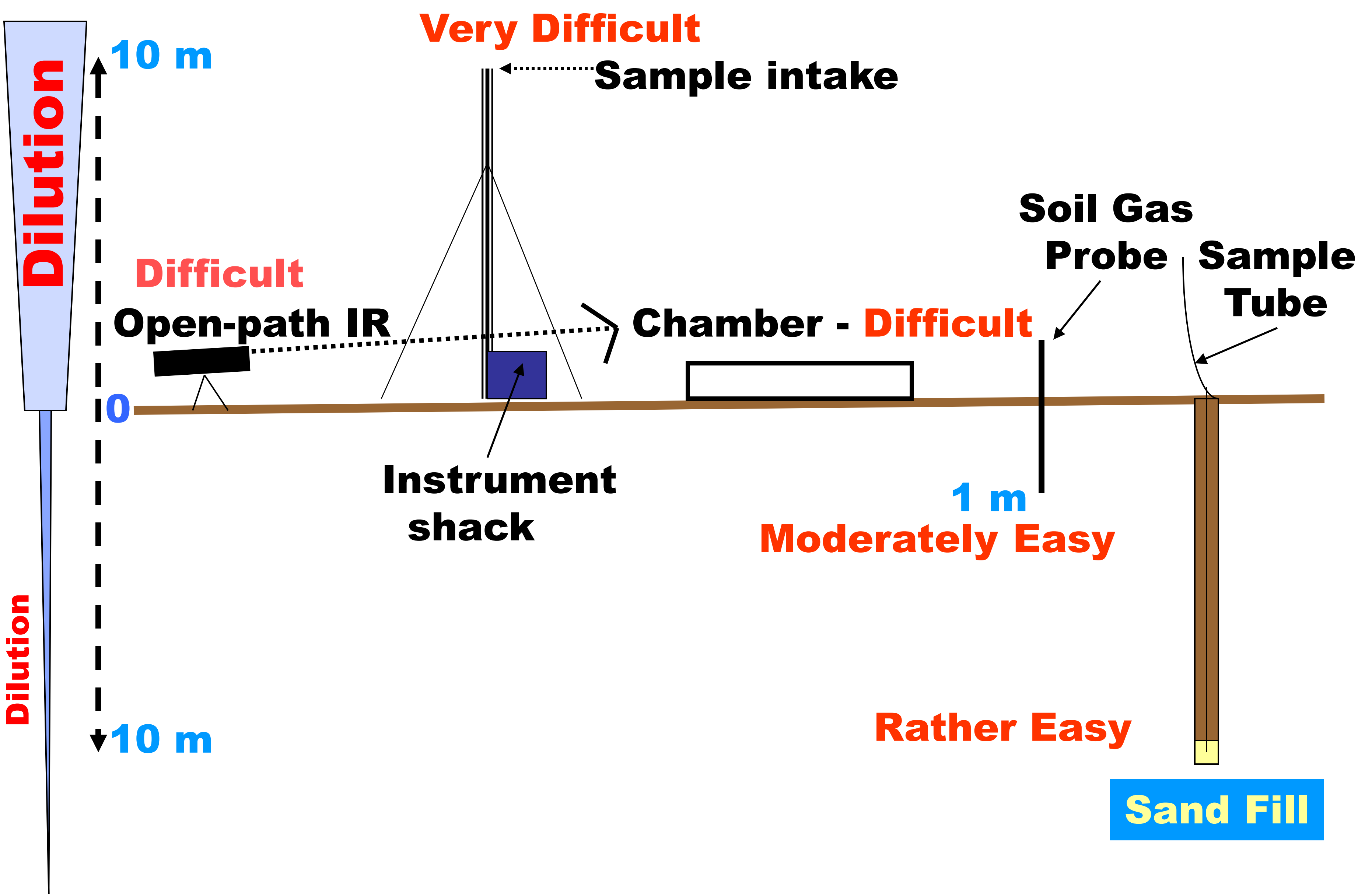
and

Geochemical Applications

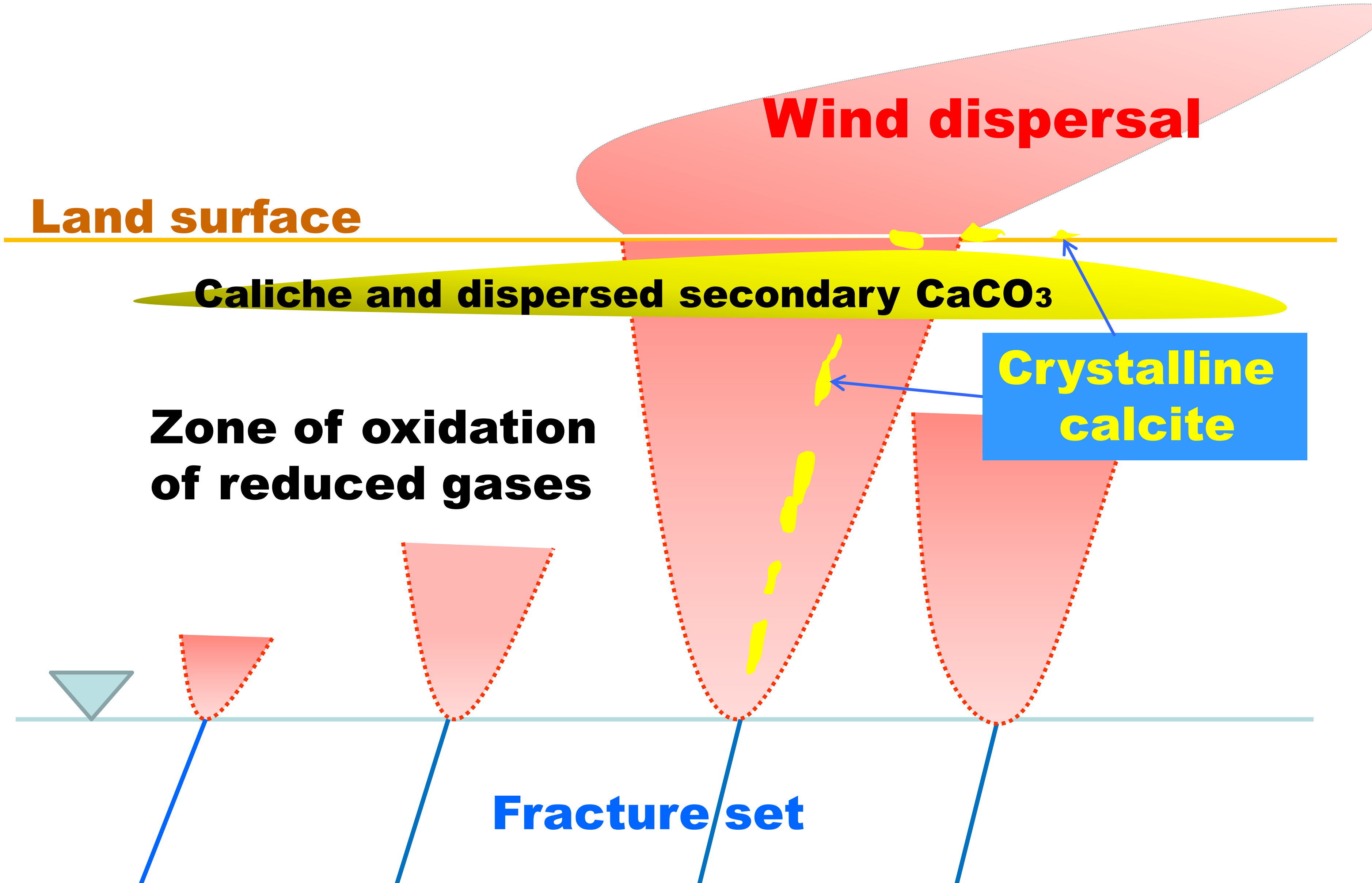
Evergreen, CO

Four areas of study

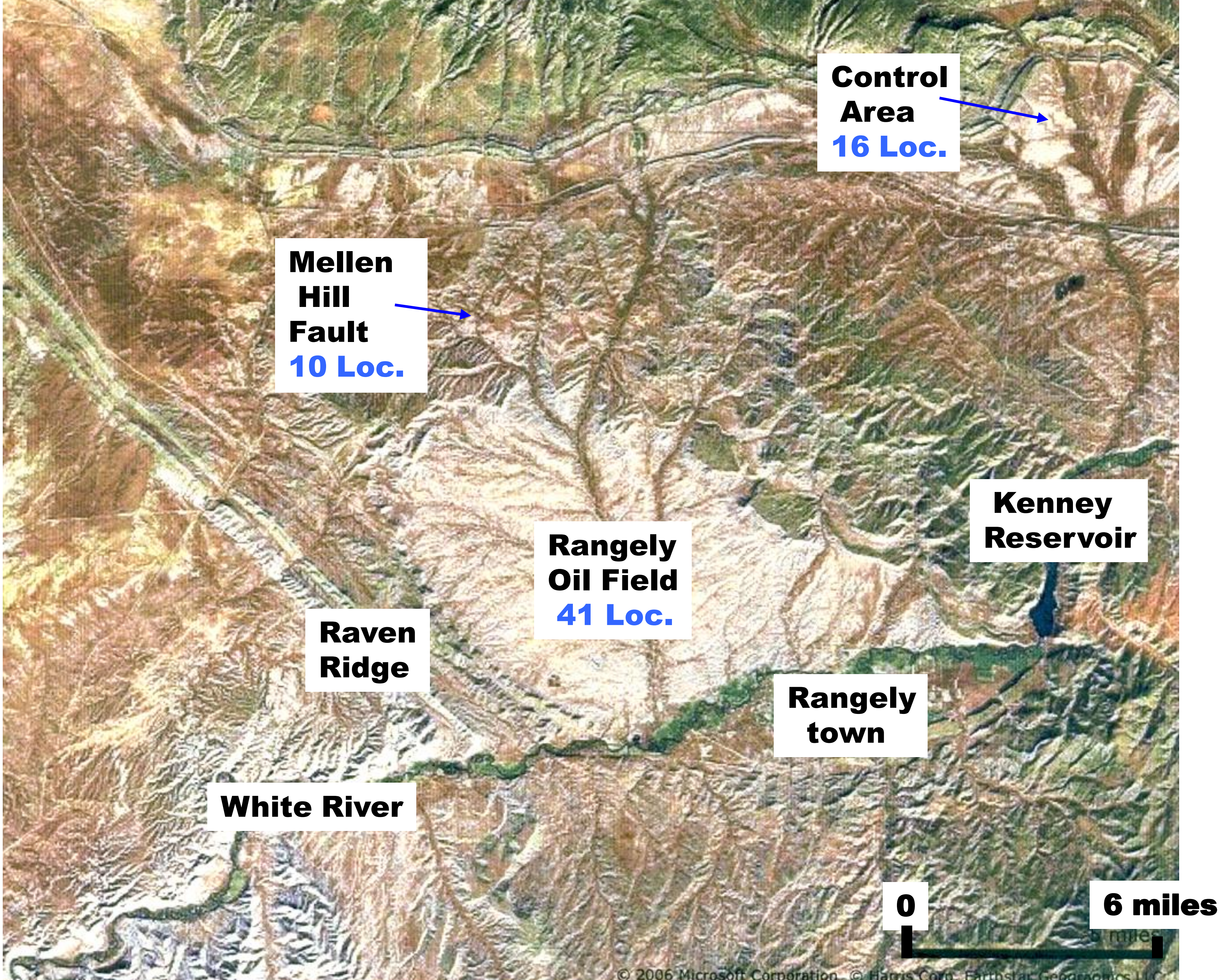
DETECTION OF GAS MICROSEEPAGE (Klusman, 2011)



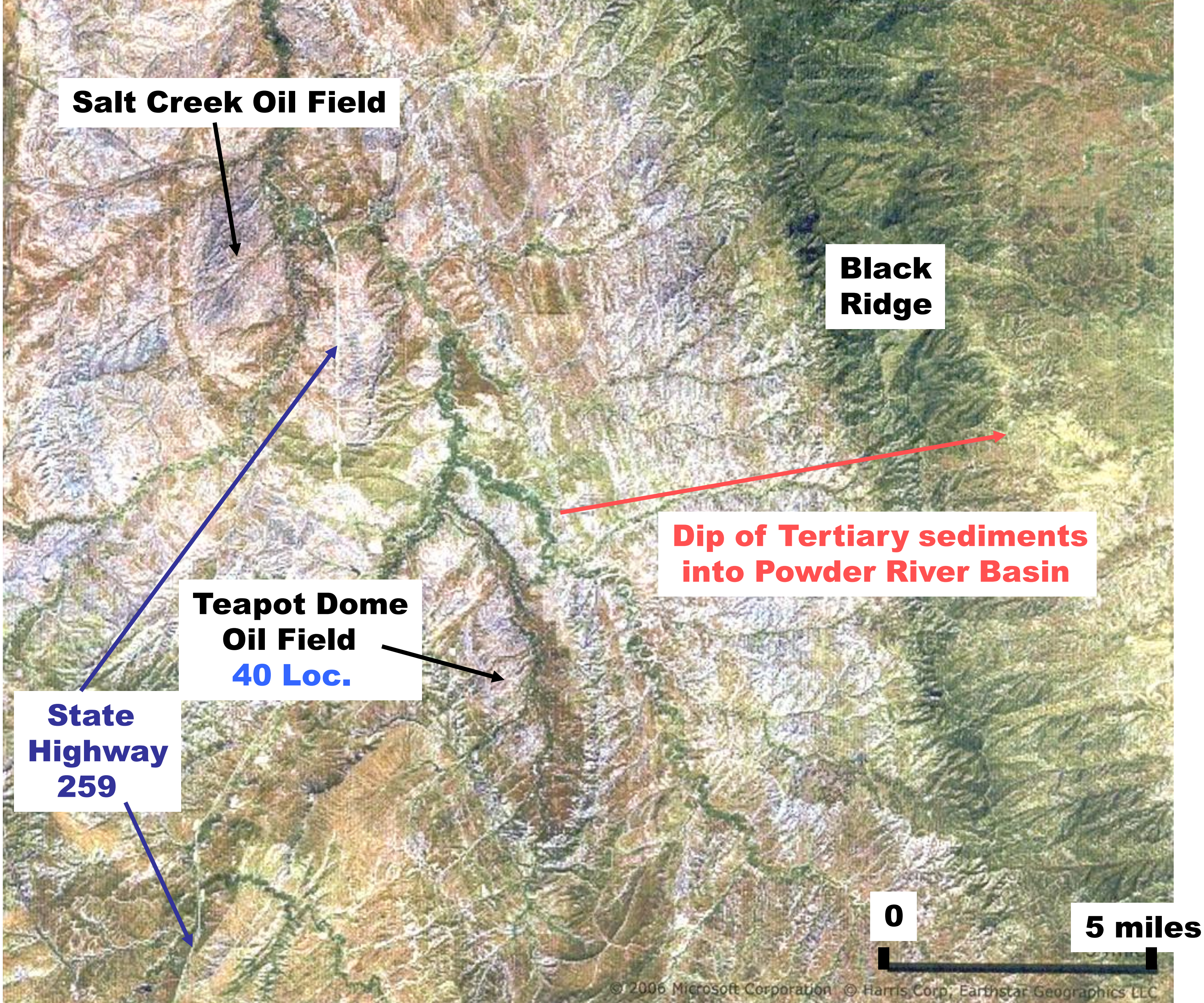
MICROSEEPAGE OF GAS



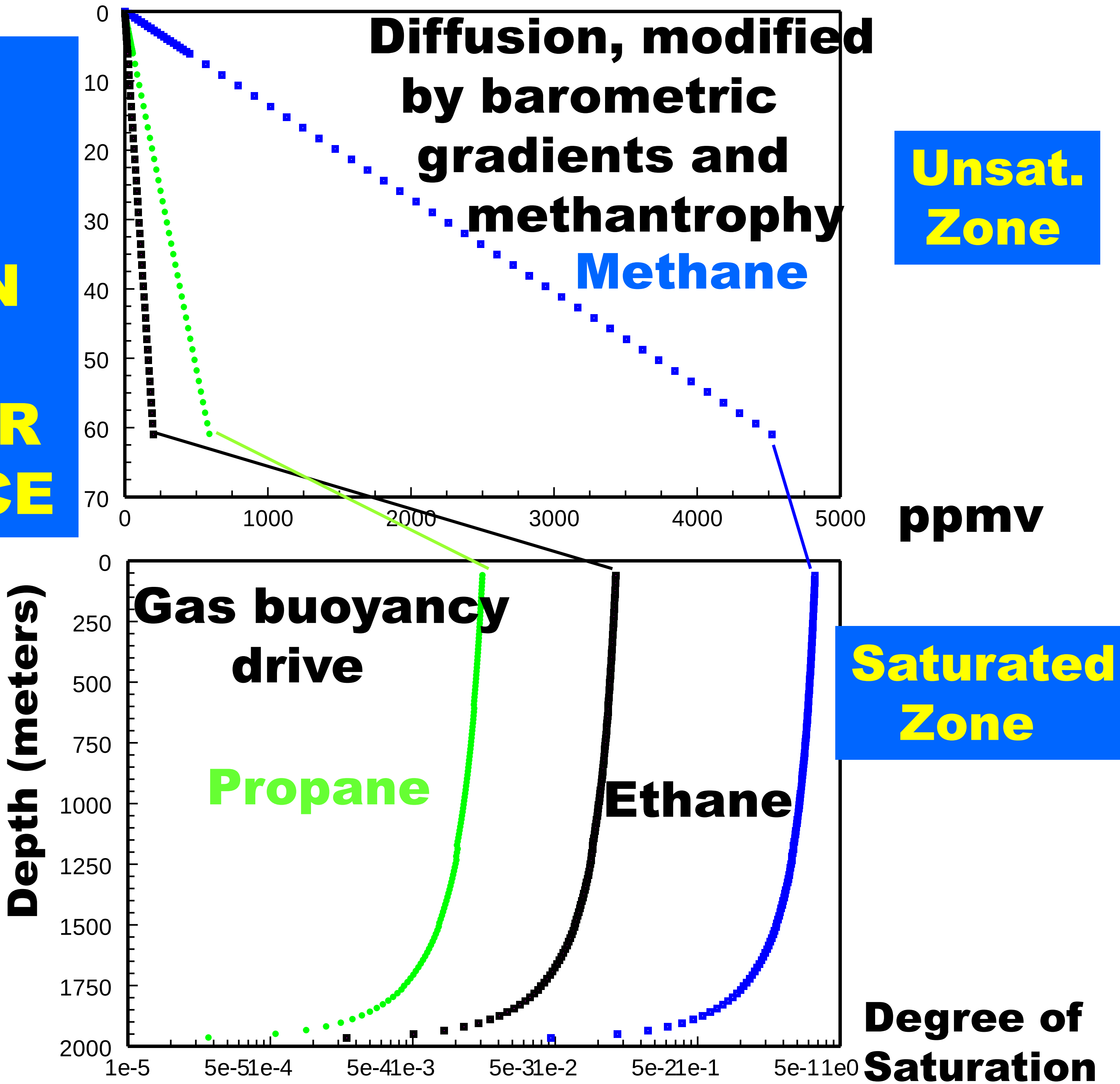
Calcite vein in fault zone at Teapot Dome



Control Area
16 Loc.
Mellen Hill Fault
10 Loc.
Kenney Reservoir
Rangely Oil Field
41 Loc.
Raven Ridge
Rangely town
White River
0
6 miles
© 2006 Microsoft Corporation


Salt Creek Oil Field
Black Ridge
Dip of Tertiary sediments into Powder River Basin
Teapot Dome Oil Field
40 Loc.
State Highway 259
0
5 miles
© 2006 Microsoft Corporation © Harris Corp, Earthstar Geographics LLC

RANGELY MODELING OF GAS MIGRATION FROM RESERVOIR TO SURFACE

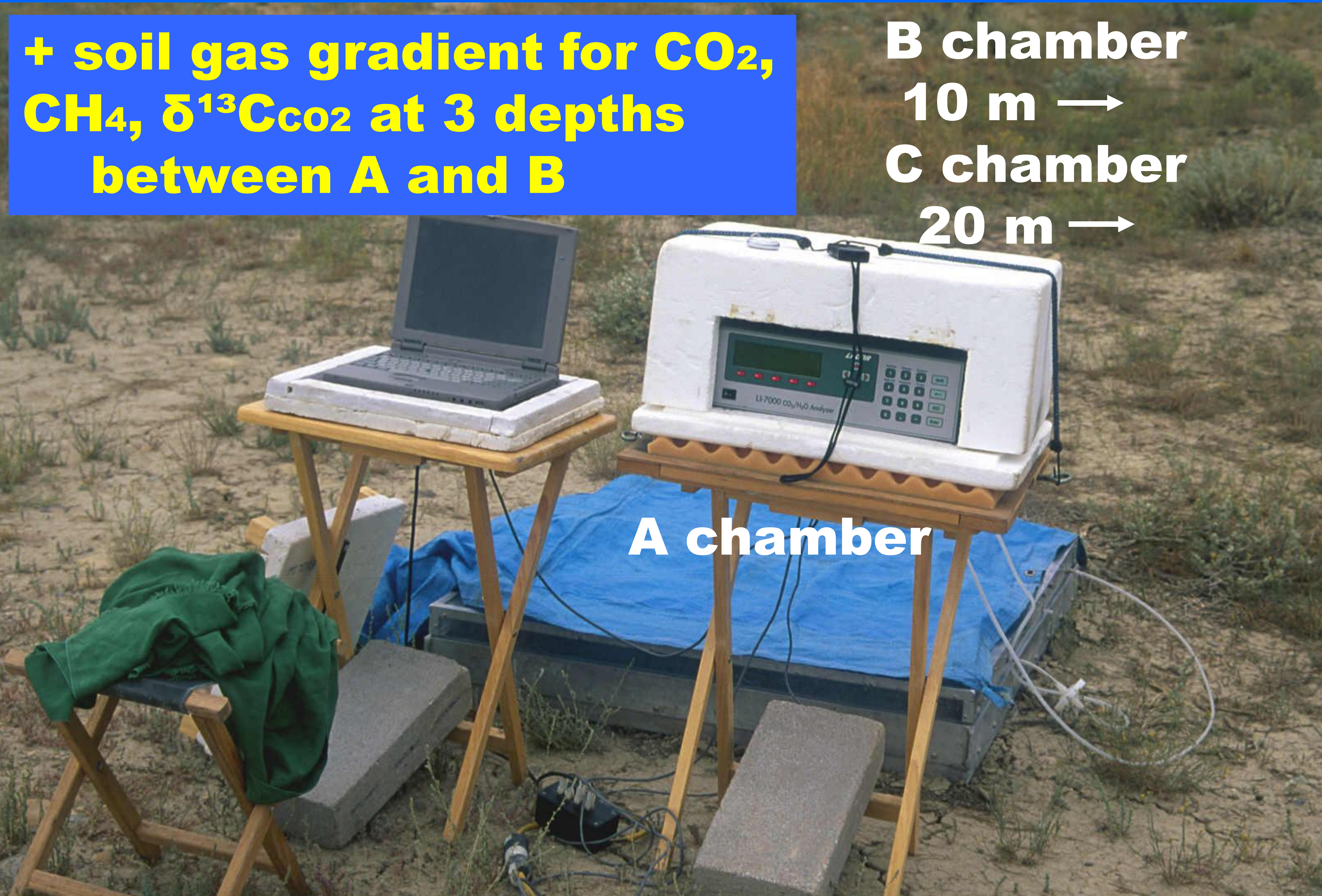


SUMMARY OF MODELED COMPOSITION AND FLUXES AT RANGELY

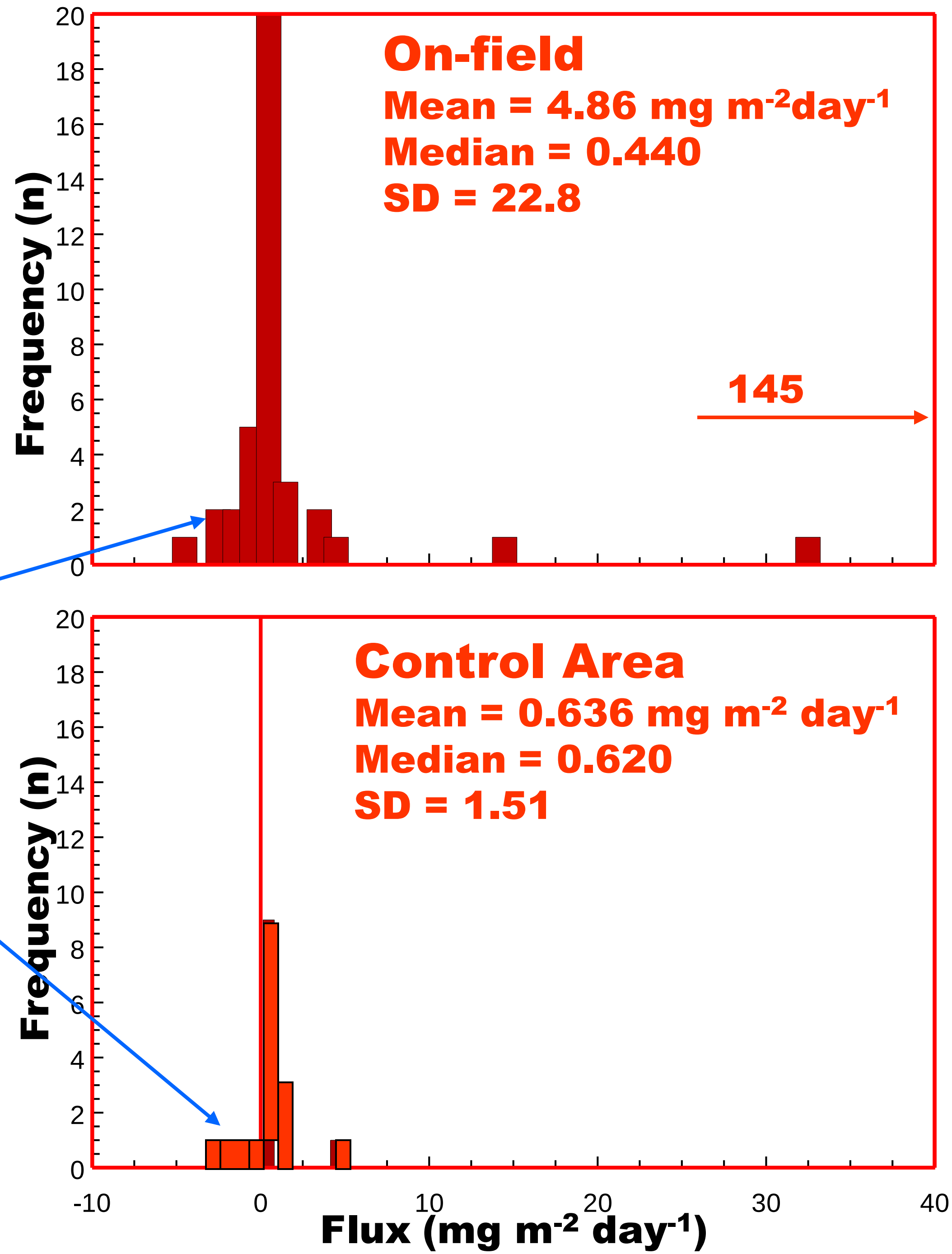
Field Condition, Parameter	Methane	Ethane	Propane
Pre-development, hydrostatic pressure 95% C_1, 4% C_2, 0.5% C_3			
Soil gas conc. at 61 m (ppmv)	4523	200	594
Flux to surface ($g\ m^{-2} day^{-1}$)	0.742	0.029	0.073
One year pressurization, 92% CO_2, 7.6% C_1, 0.34% C_2, 0.04% C_3			
Soil gas conc. at 61 m	365	211	557
Flux to surface	0.060	0.031	0.069
15 years operation at 24.82 MPa			
Soil gas conc. at 61 m	361	213	559
Flux to surface	0.059	0.031	0.069

CO_2 and CH_4 fluxes measured at 10-m intervals

+ soil gas gradient for CO_2, CH_4, $\delta^{13}C_{CO2}$ at 3 depths between A and B



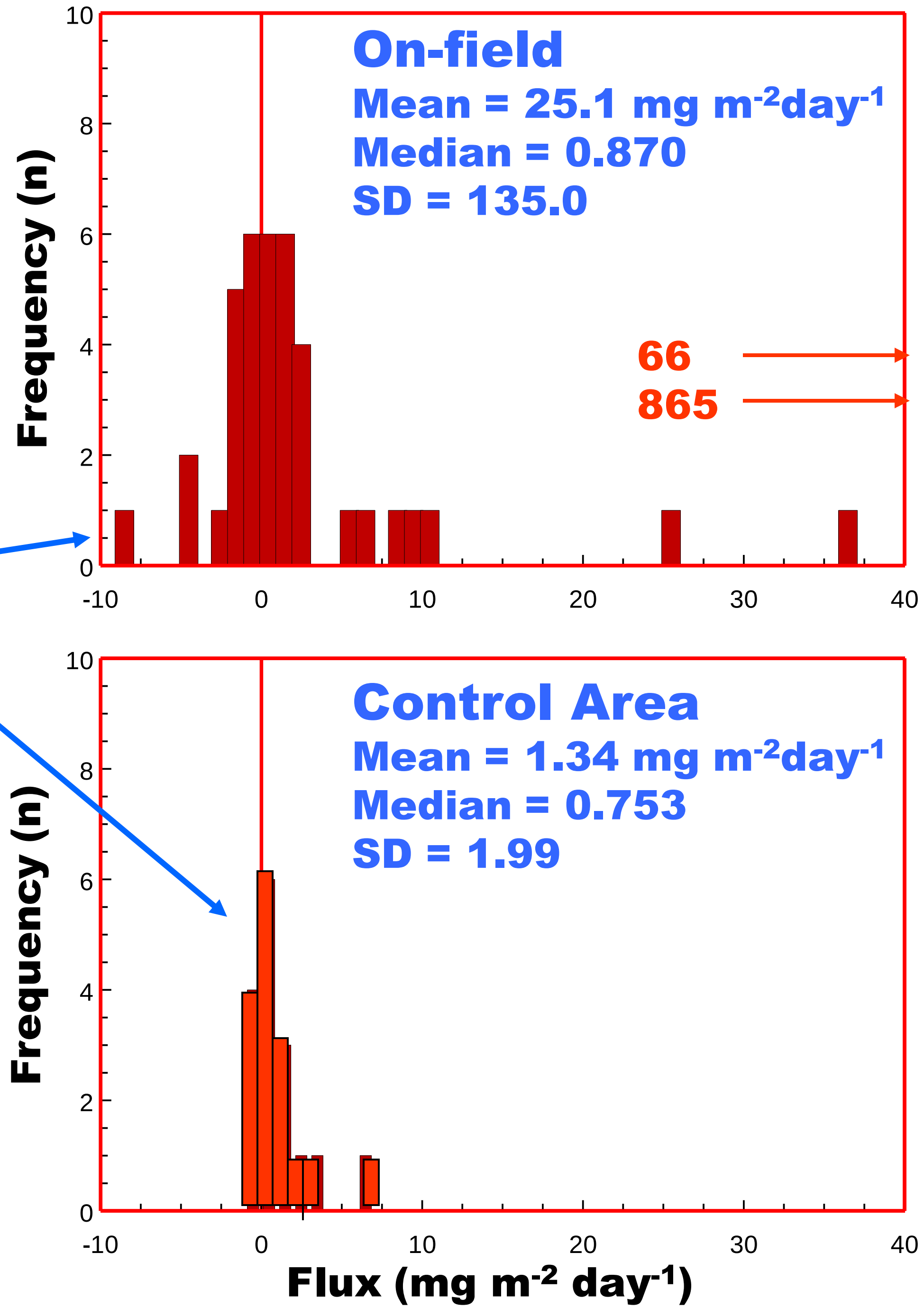
Rangely – CH_4 Flux; Summer 2001



Note negative flux due to methanotrophy

Rangely – CH_4 Flux; Winter 2001/2002

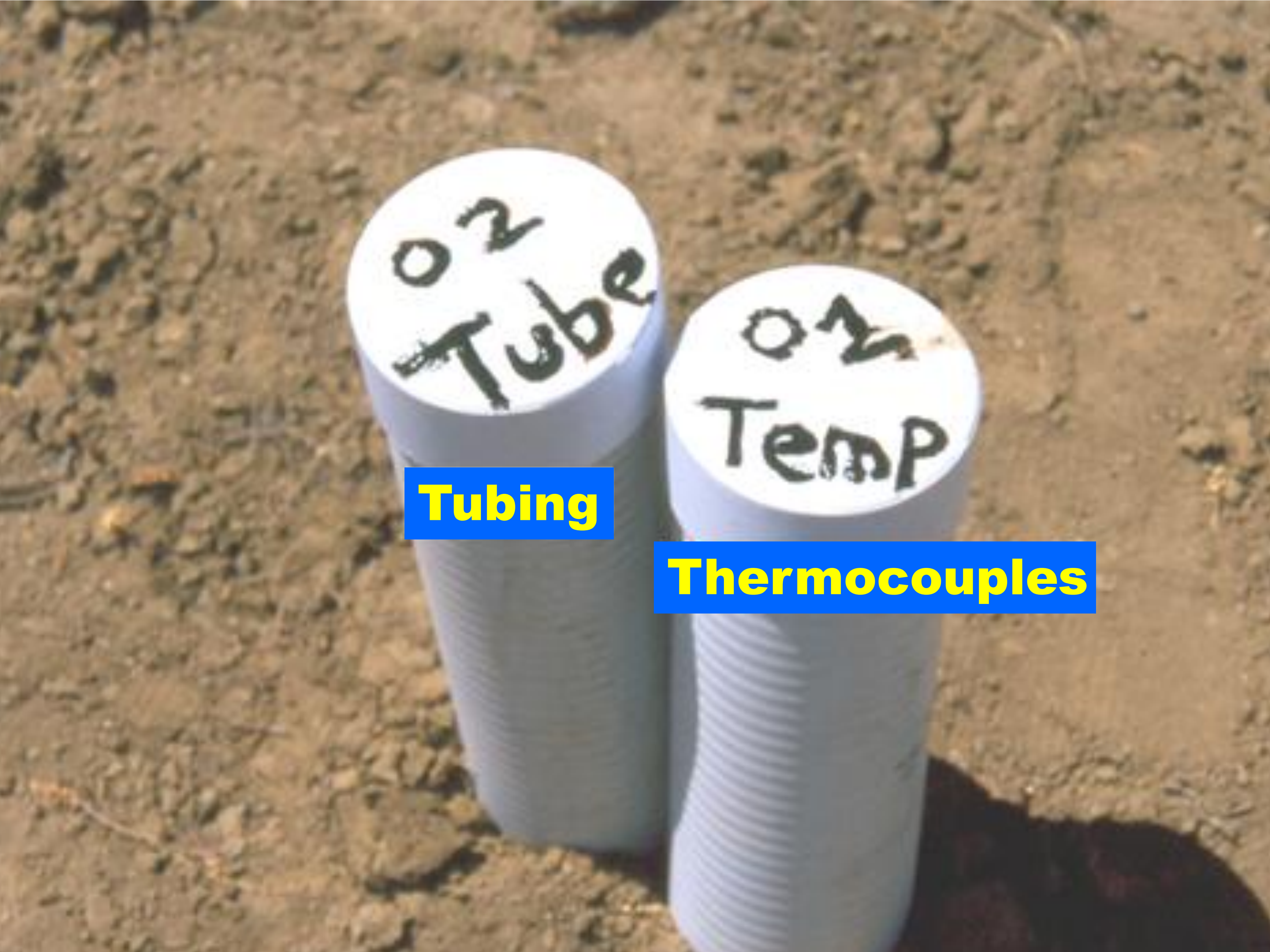
Note negative flux due to methanotrophy



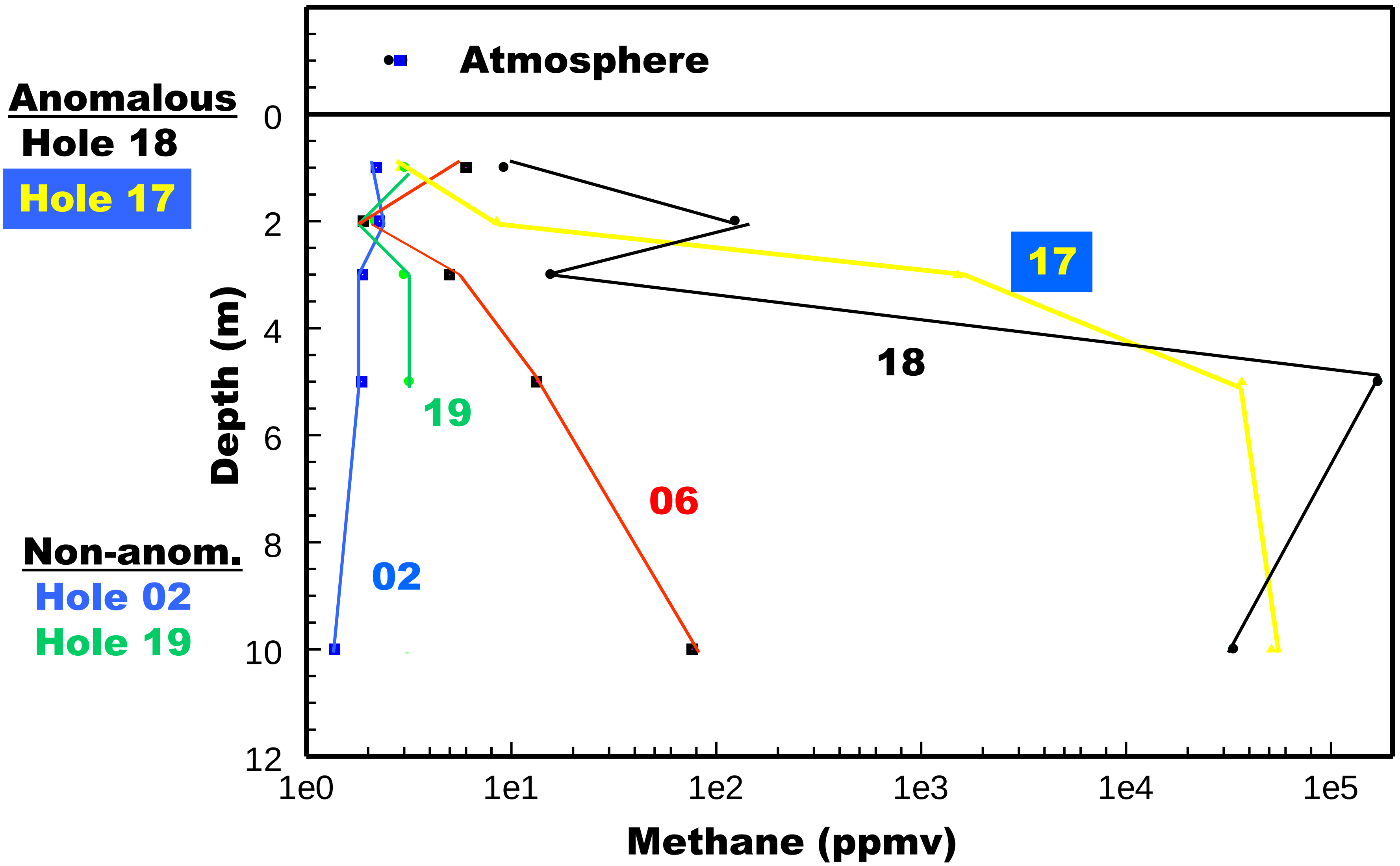
SELECTION OF "INTERESTING" LOCATIONS FOR 10-M HOLES

- **Magnitude <u>and</u> direction of <u>both</u> CO_2 and CH_4 fluxes,**
- **Magnitude <u>and</u> gradient of <u>both</u> CO_2 and CH_4 in soil gas profiles,**
- **Isotopic shift in 60-, and 100 cm soil gas CO_2 from atmospheric CO_2,**
- **Selected locations with microseepage evident, and with microseepage absent; soil gas contributes more to the selection process than fluxes.**

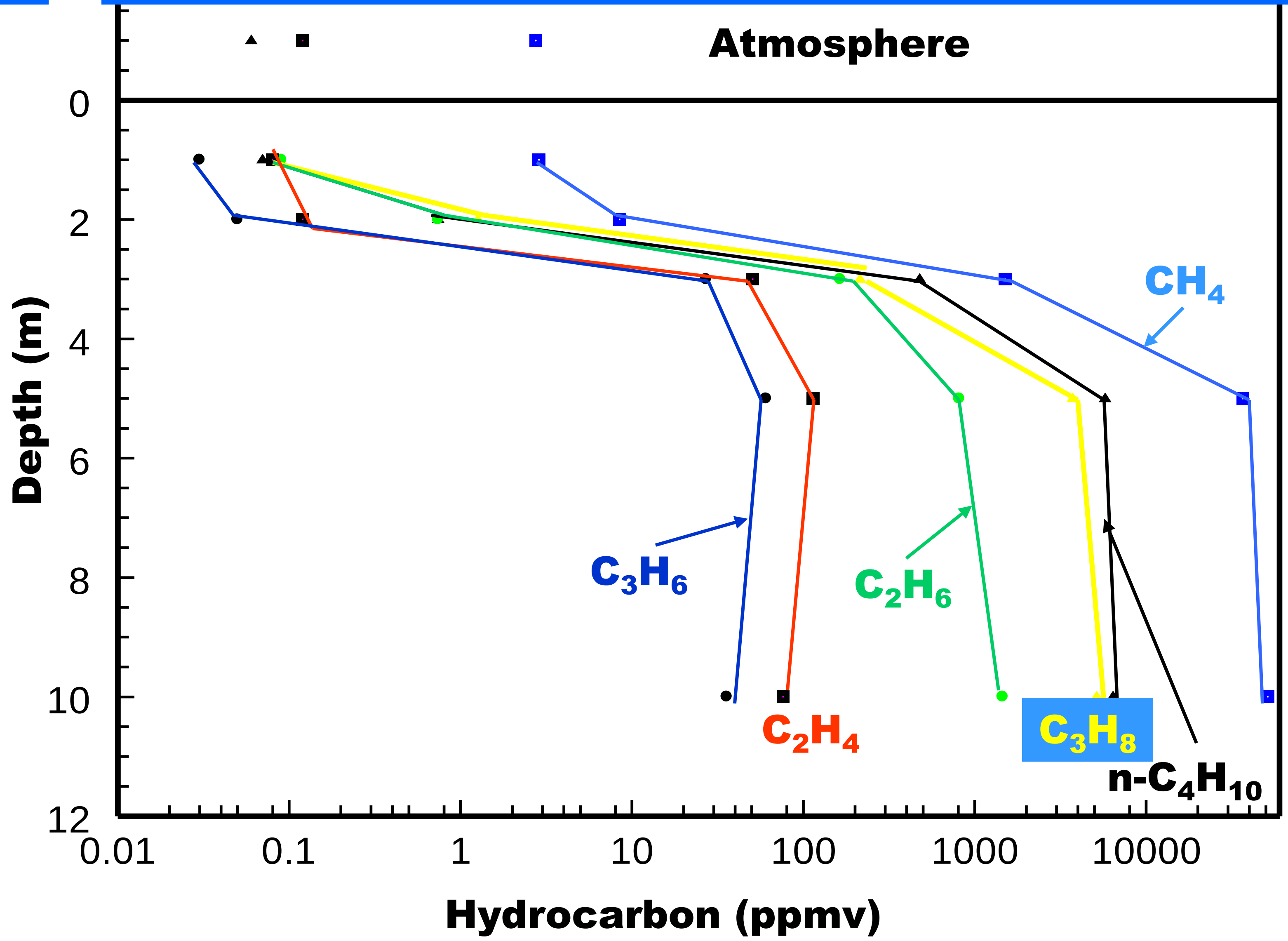
Tubing and thermocouples from 5 depth intervals in 10-meter holes


O2
Tube
Tubing
O2
Temp
Thermocouples

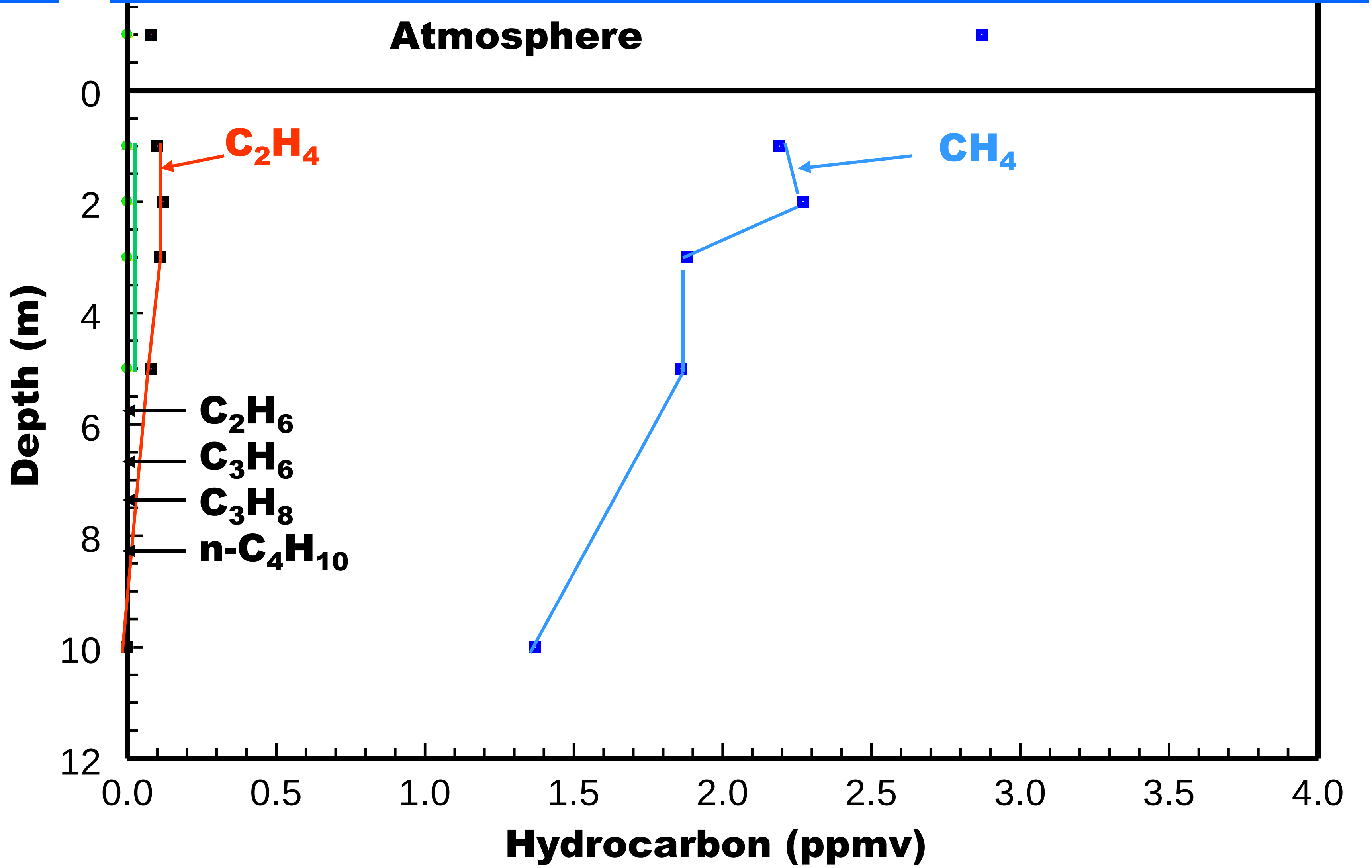
TEAPOT DOME – METHANE IN 10-m HOLES, JANUARY, 2005 (Klusman, 2006)



TEAPOT DOME – LIGHT HYDROCARBONS IN ANOMALOUS 10-m HOLE 17; JANUARY, 2005; (Klusman, 2006)

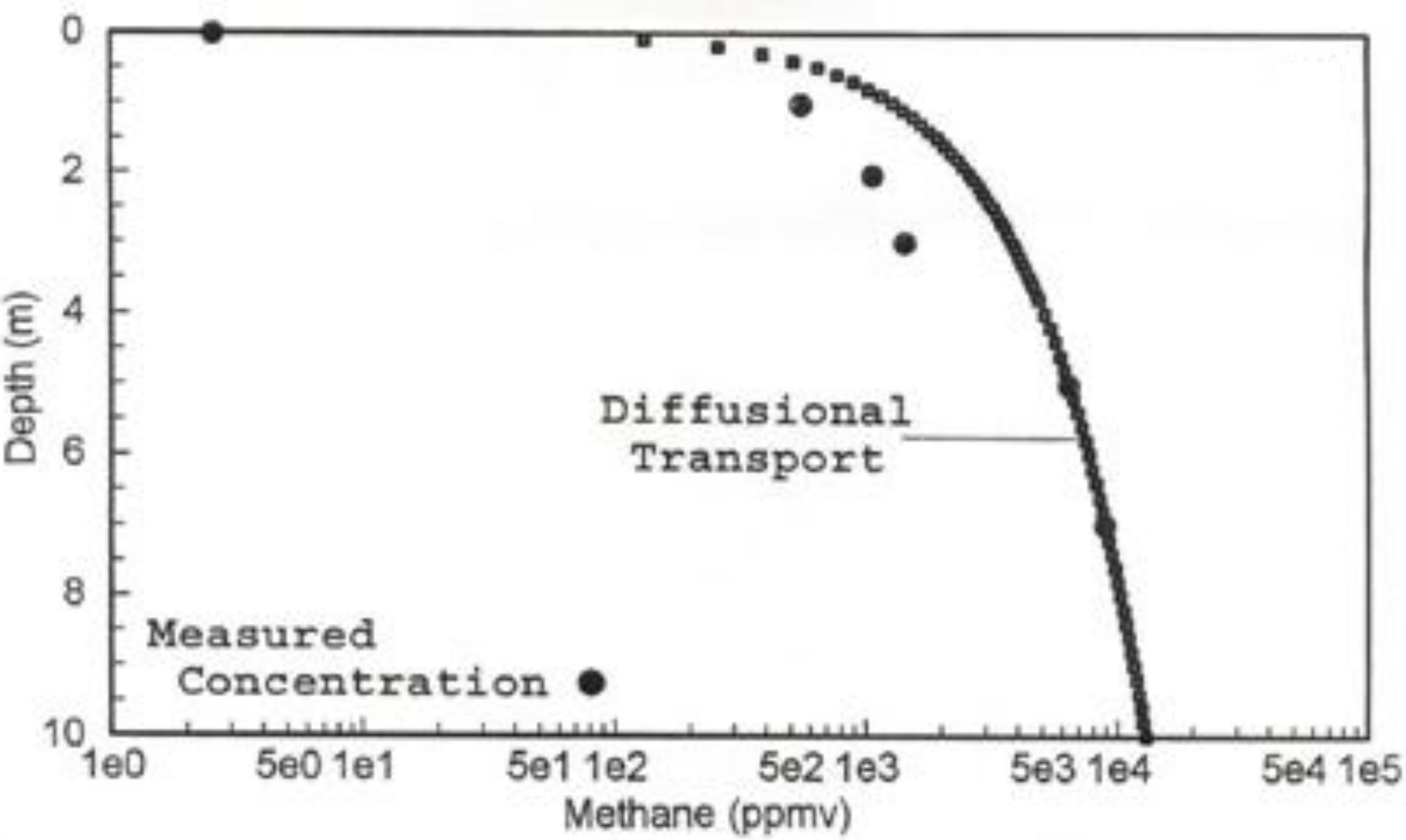


TEAPOT DOME – LIGHT HYDROCARBONS IN NON-ANOM.10-m HOLE 02; JANUARY, 2005 (Klusman, 2006)



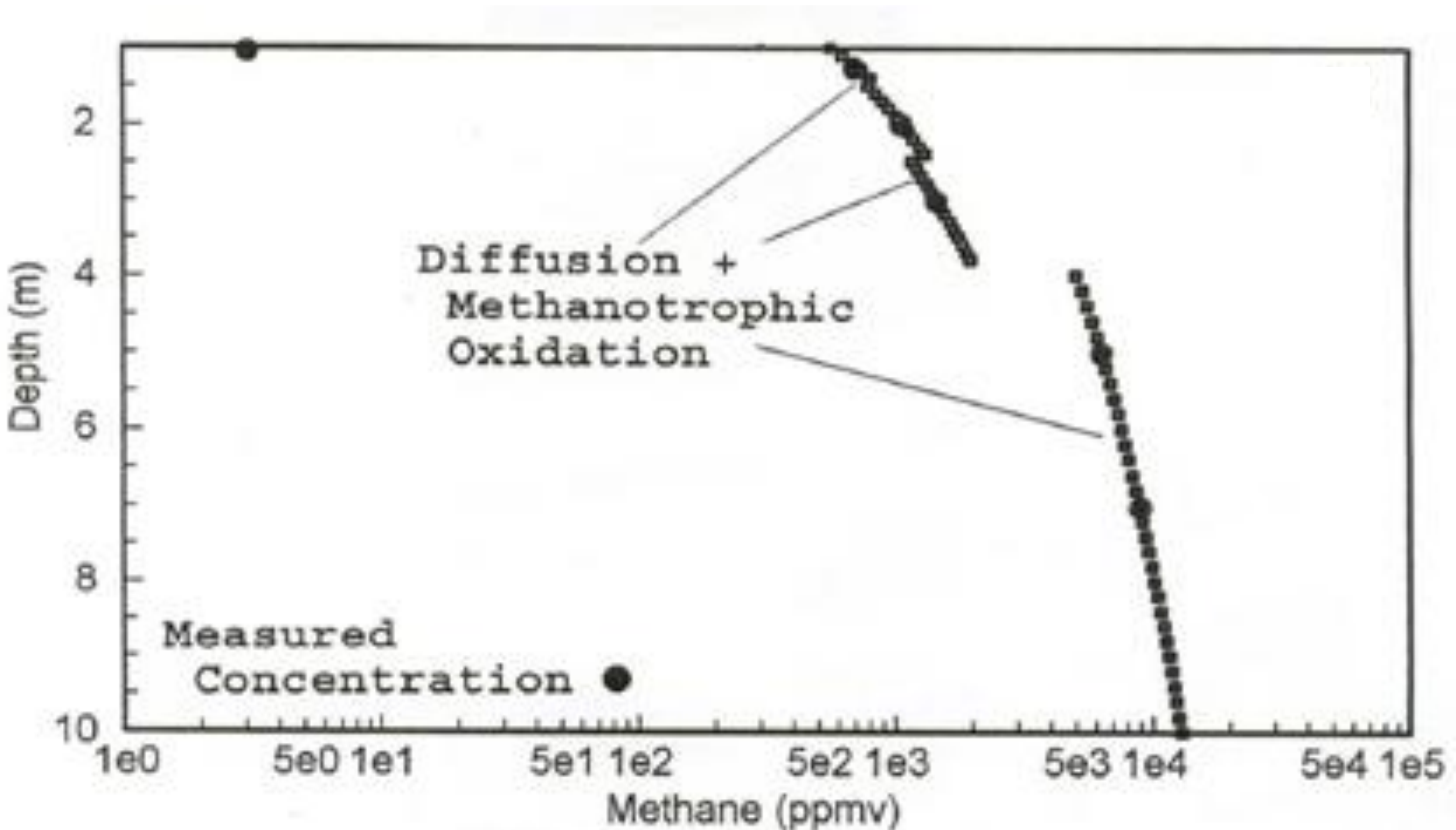
SIMPLE DIFFUSIONAL TRANSPORT OF CH_4

Rangely – Anomalous 10-m hole 01; Winter 2001/02



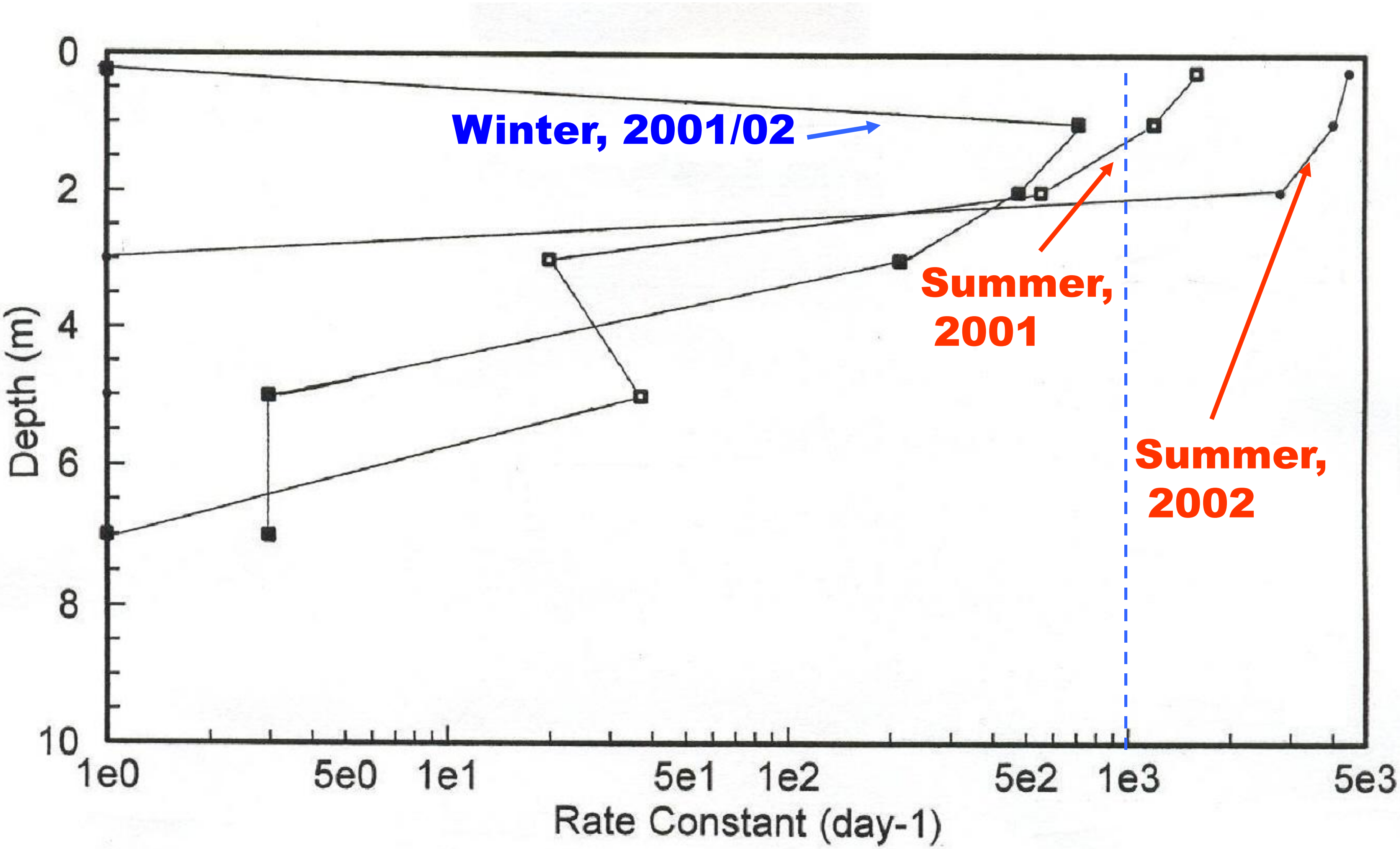
DIFFUSION + METHANOTROPIC OXIDATION

Rangely – Anomalous 10-m hole 01; Winter 2001/02



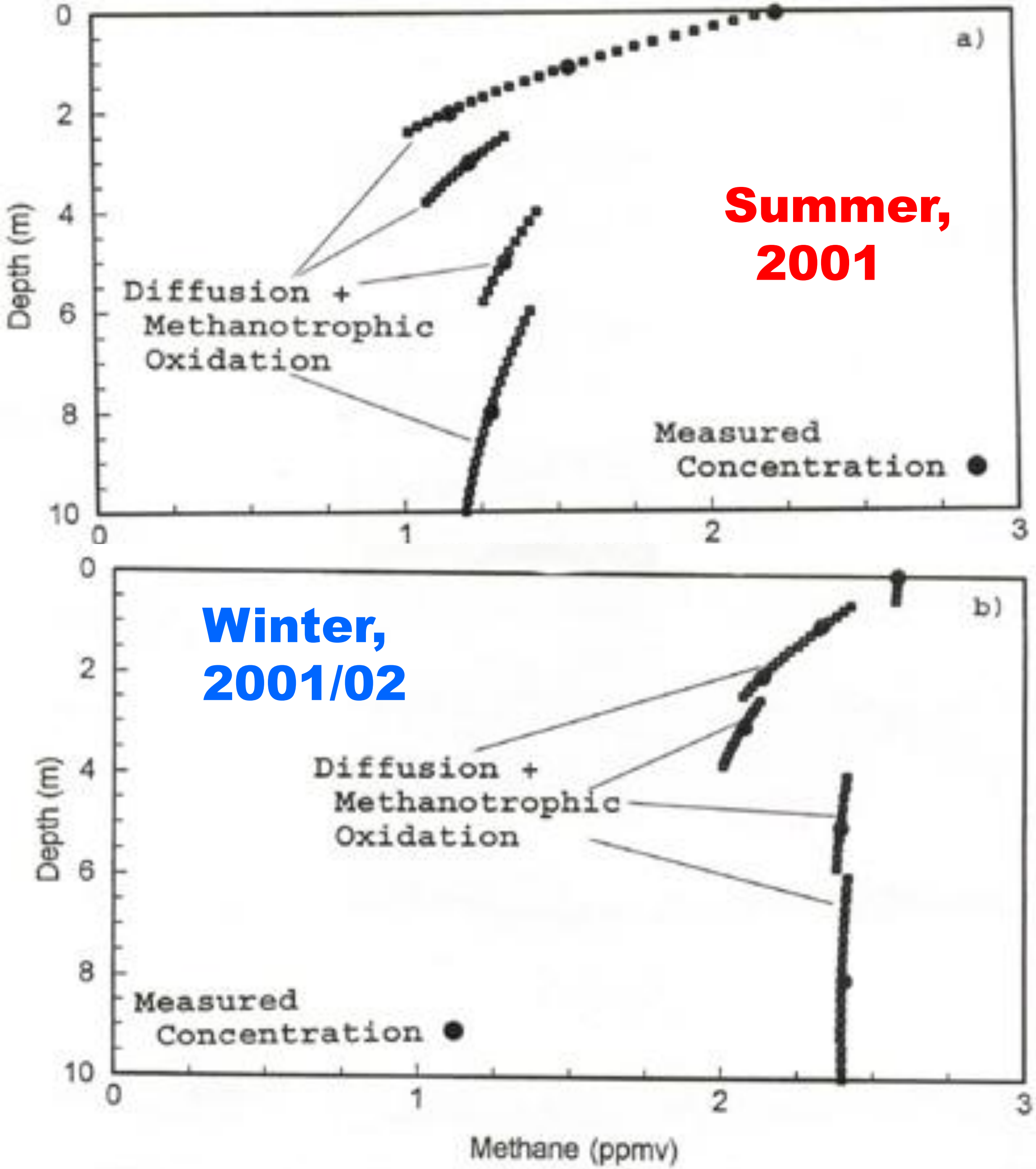
FIRST-ORDER METHANOTROPHY RATE

Rangely – Anomalous 10m Hole 01



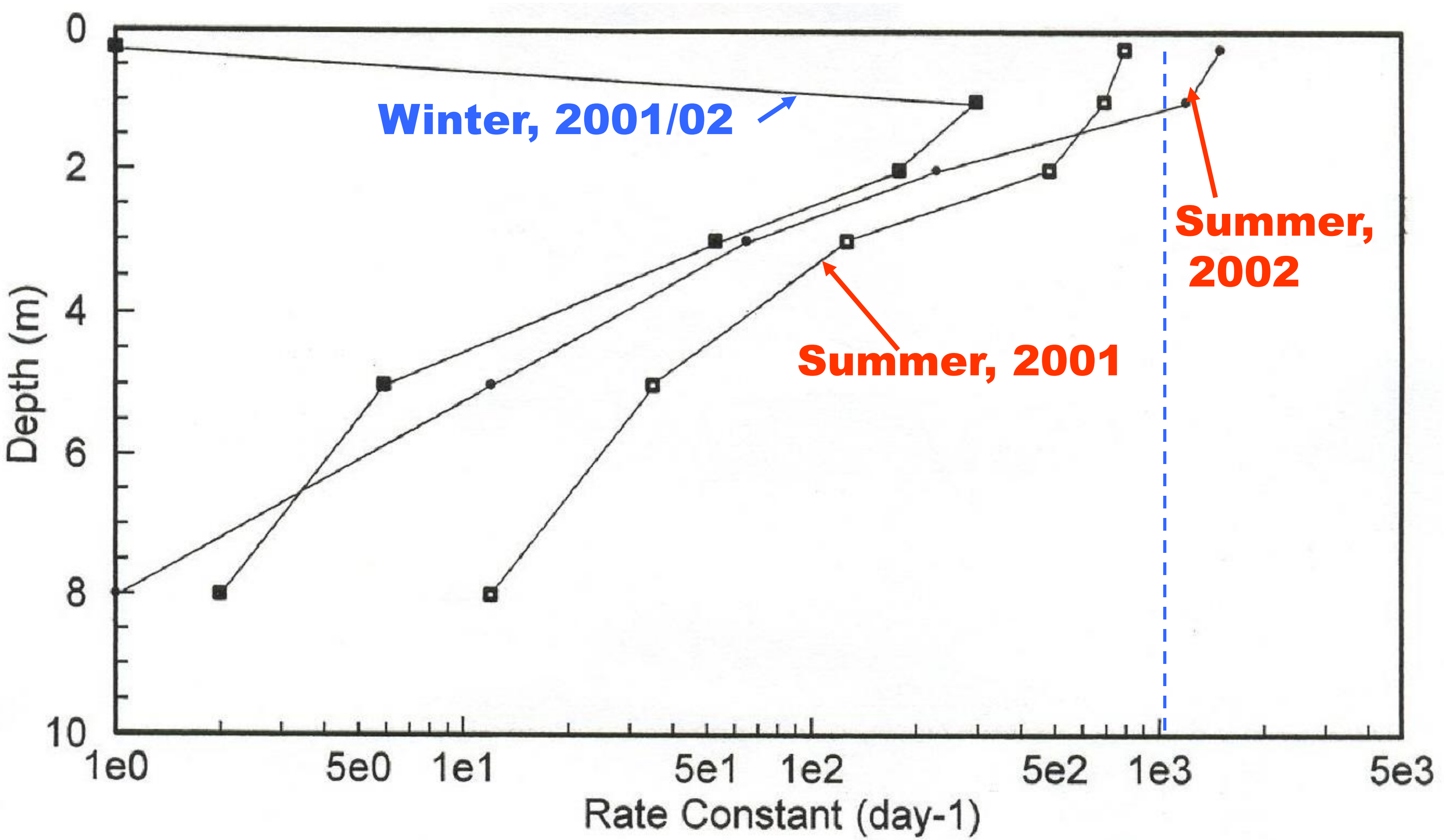
Measured and Modeled Methanotrophy

Rangely Non-anom. 10-m Hole 28

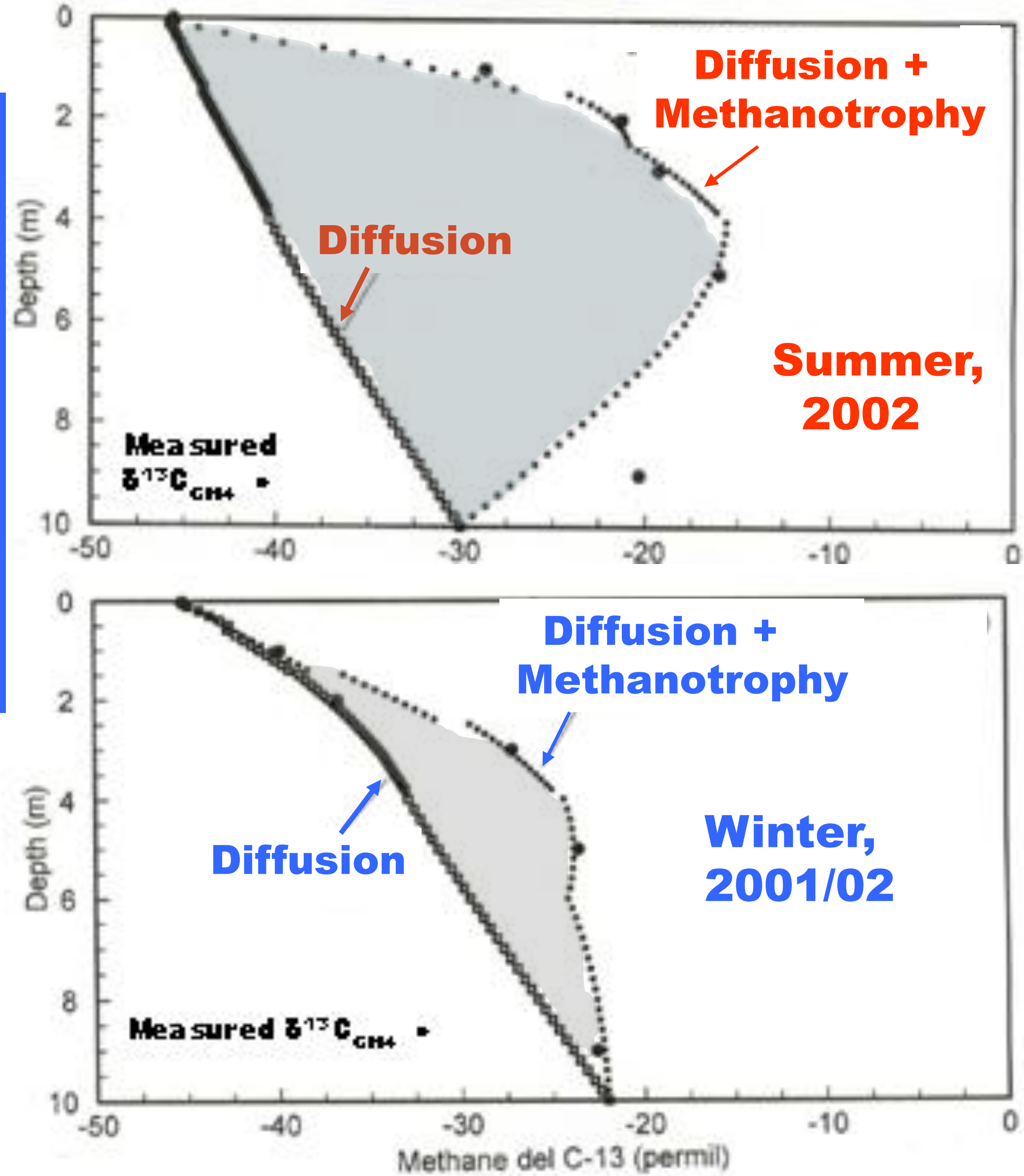


FIRST-ORDER METHANOTROPHY RATE

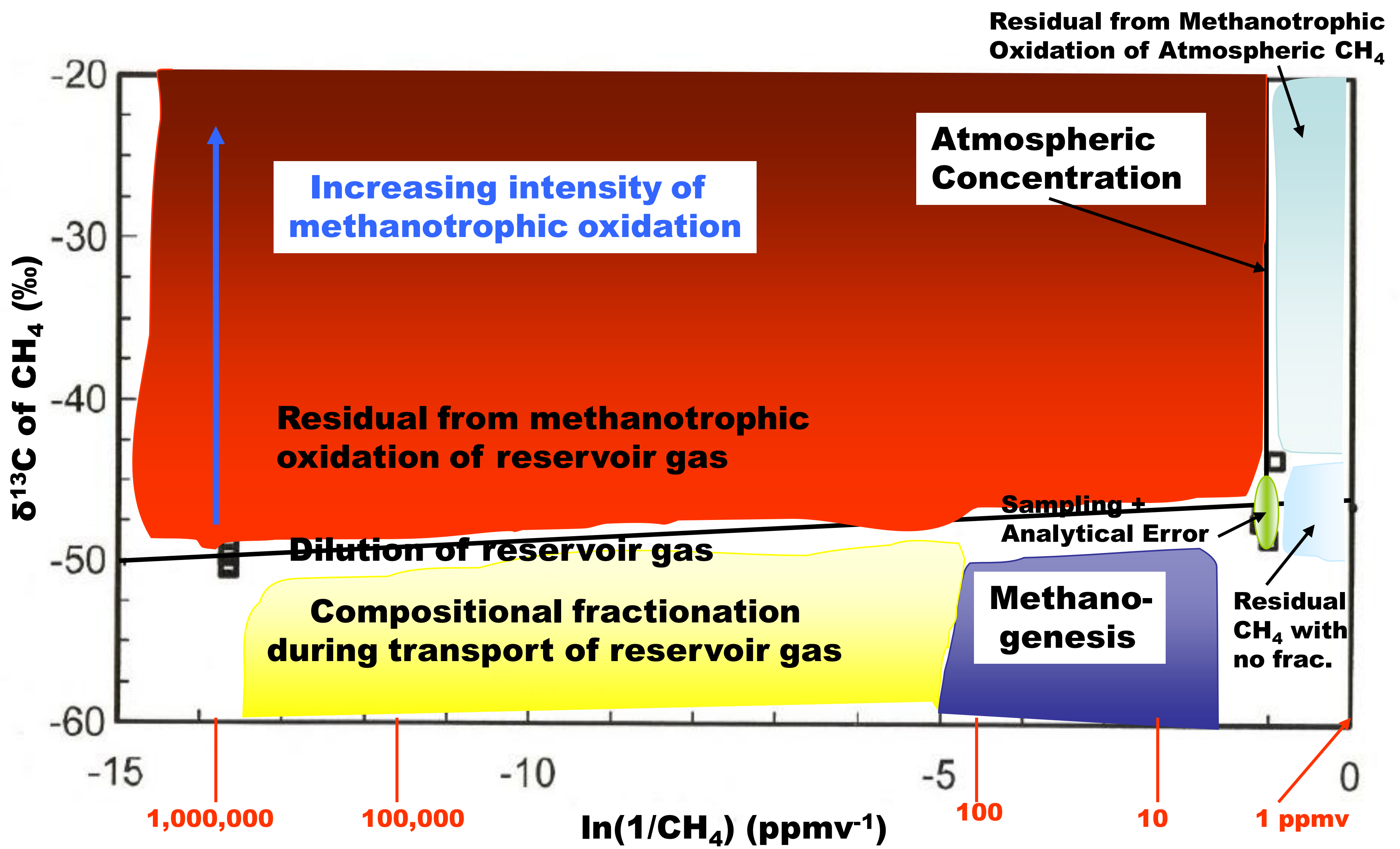
Rangely – Non-anomalous 10-m Hole 28



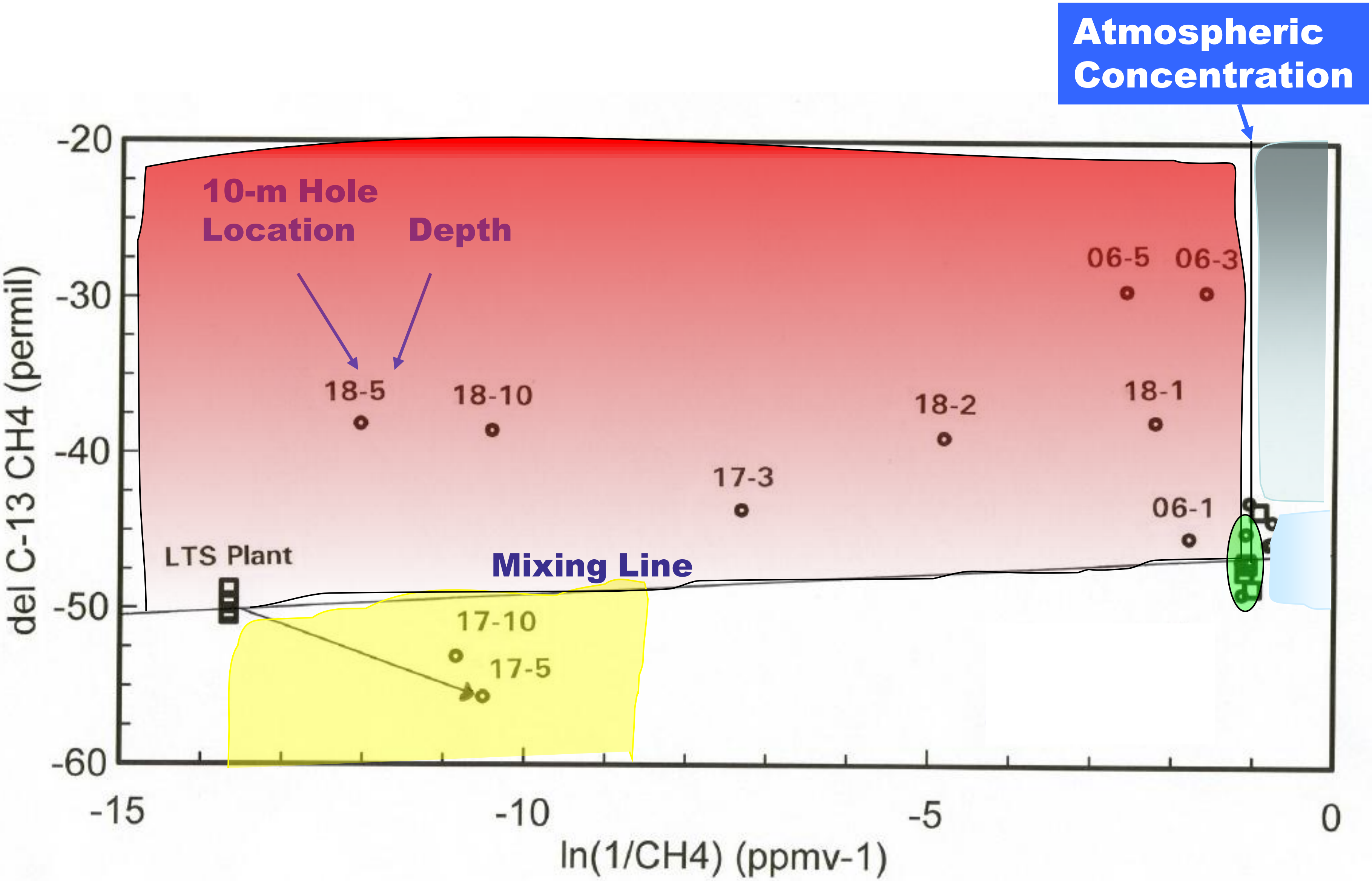
RANGELY - DIFFUSION AND METHANOTROPHY OF CH_4 IN ANOMALOUS 10-M HOLE



RELATING BIOGEOCHEMICAL PROCESSES TO METHANE CONCENTRATION AND $\delta^{13}C_{CH4}$

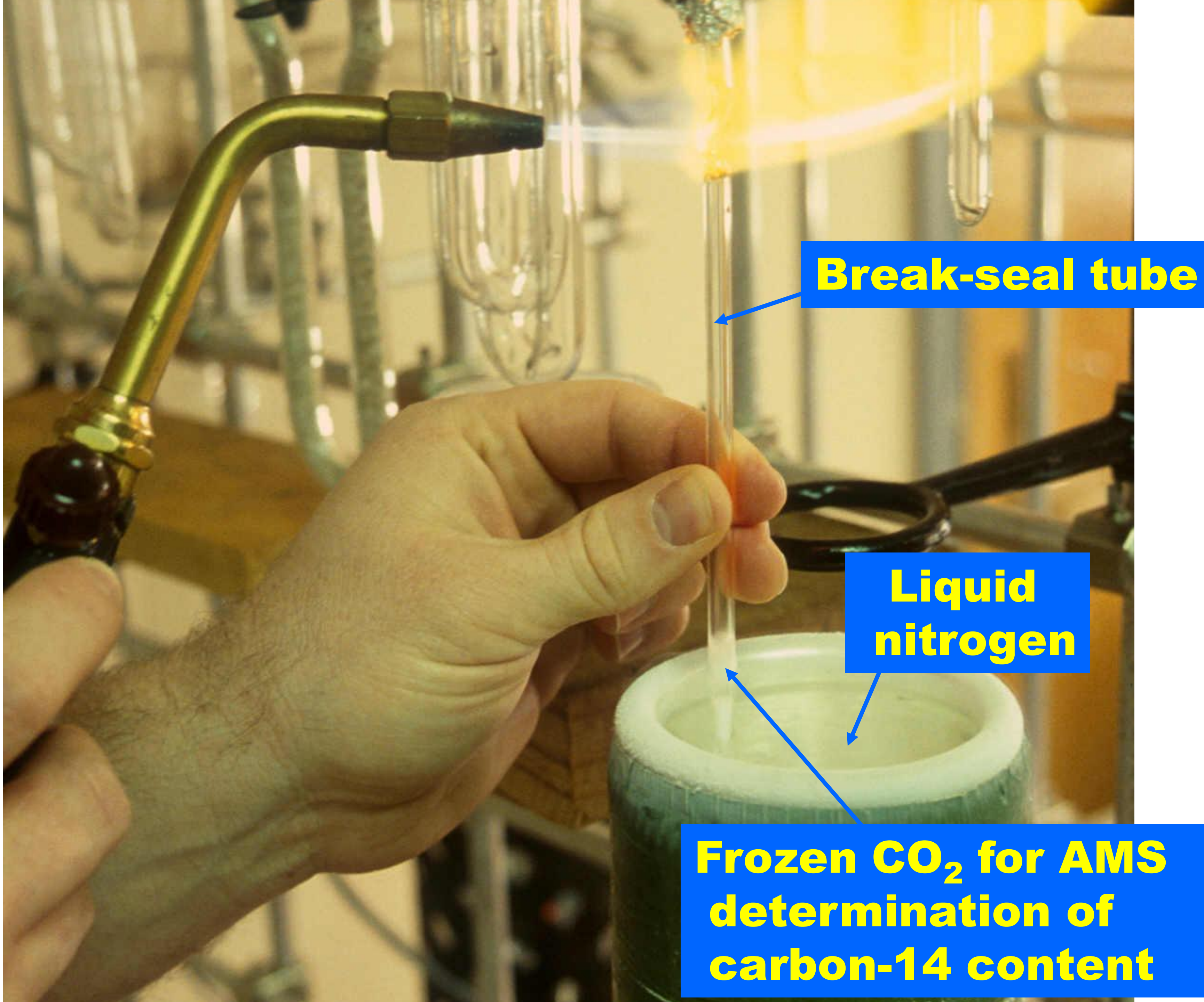


TEAPOT DOME – 10-m HOLES; Jan. 2005

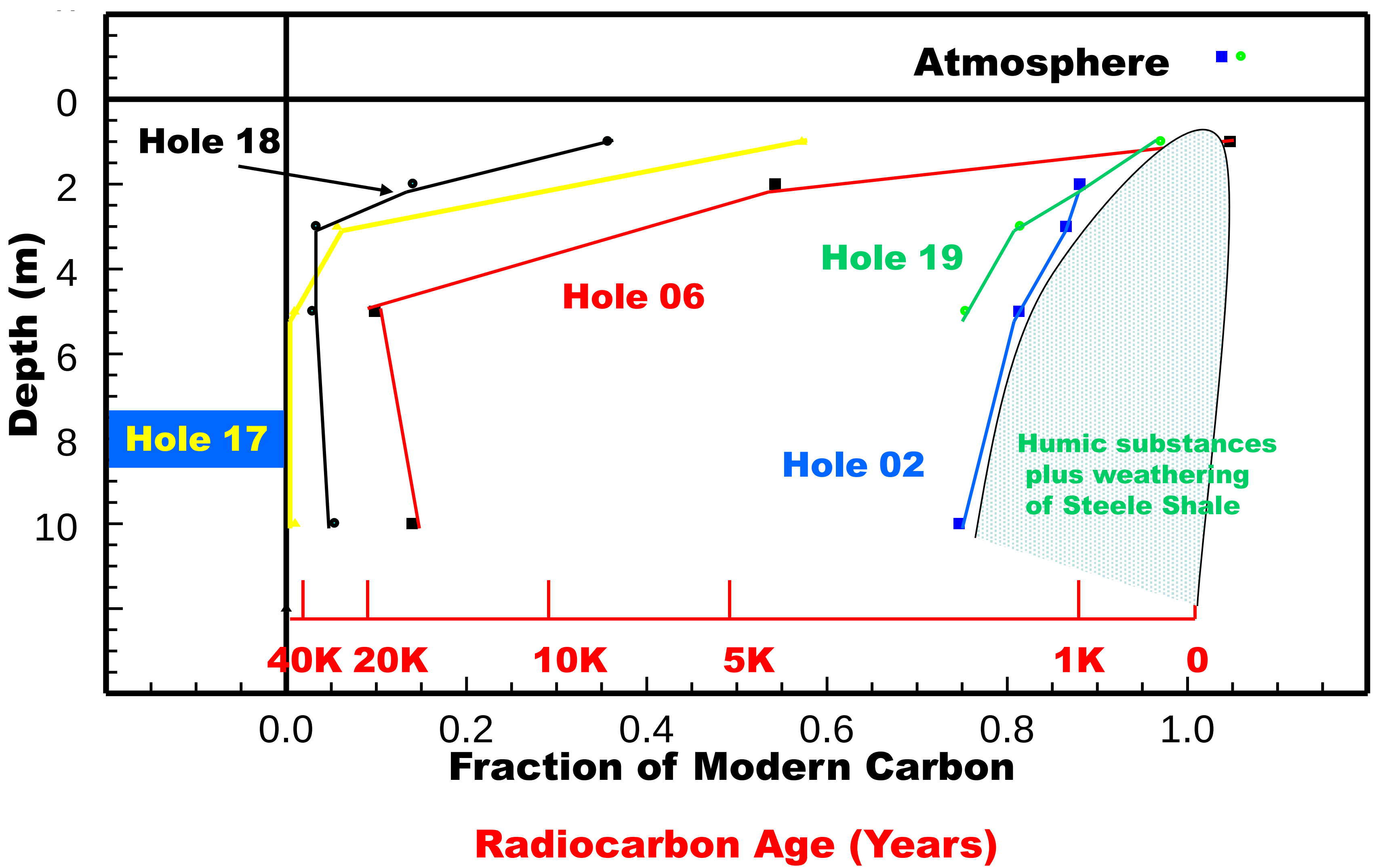


OTHER GASEOUS SPECIES – CARBON-14 CONTENT OF CARBON-CONTAINING GASES (VERIFICATION)

- **Pros** – a) <u>Definitive</u> measurement of proportions of deep-sourced ancient gases and atmospheric-derived gases, b) <u>No biological influence</u> , c) low seasonal variance at depths of 3-m or more.
- **Cons** – a) Strictly a laboratory measurement with fairly complicated sampling, laboratory purification, and analytical protocol, b) food based CO_2 is enriched in carbon-14 to approximately atmospheric concentration, c) laboratory turn-around can be slow.


Break-seal tube
Liquid nitrogen
Frozen CO_2 for AMS determination of carbon-14 content

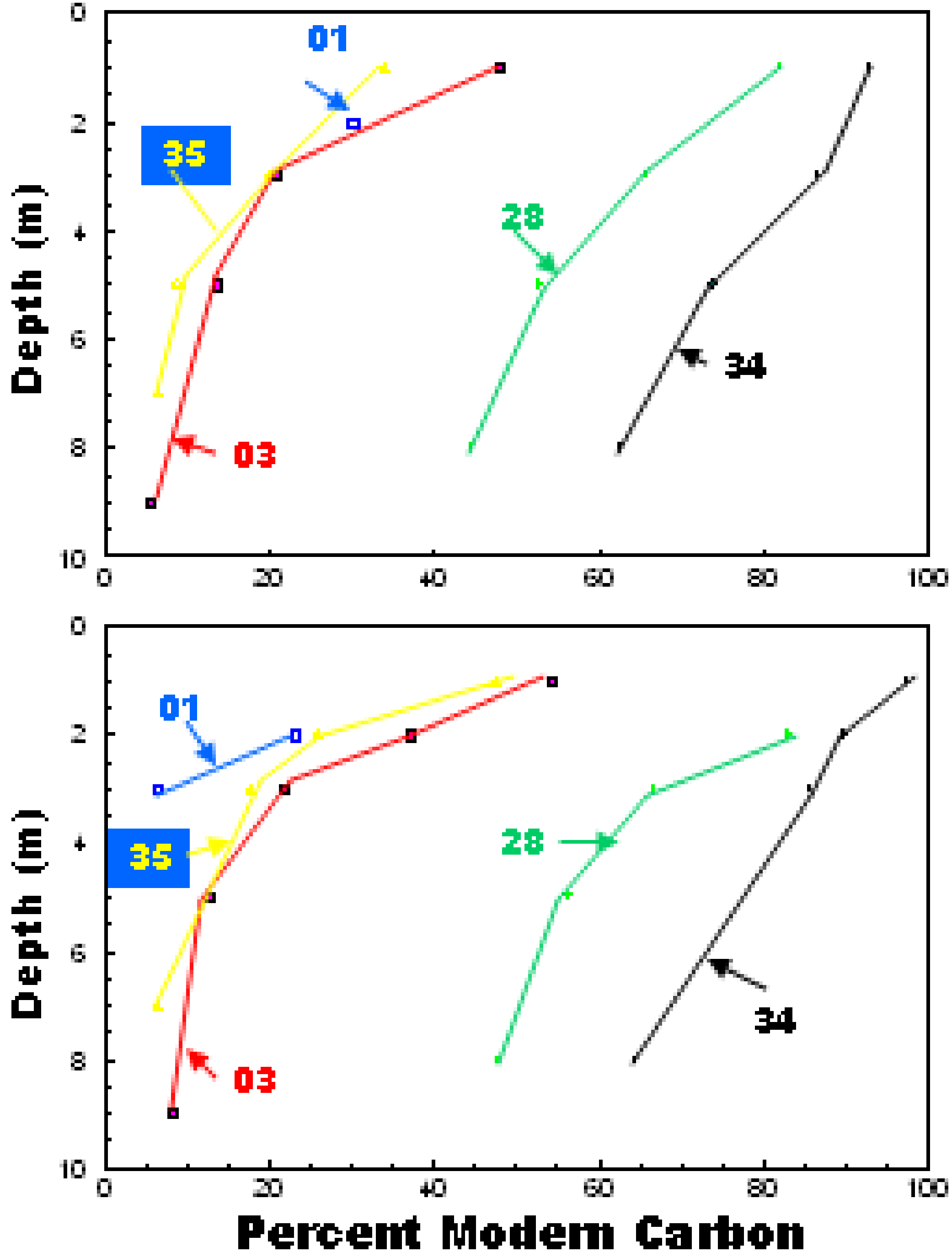
TEAPOT DOME – CARBON-14 IN CO_2 FROM 10-m HOLES; JANUARY, 2005 (VERIFICATION)



RANGELY – C-14 IN CO_2 FROM 10-m HOLES (VERIFICATION)

Winter 2001/2002

Summer, 2002



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 from the on-field data.**
- ***non-parametric estimated rate is positive with α = 0.015.**

COMPARISON OF MODELED AND MEASURED METHANE FLUX

The modeled CH_4 flux from the Rangely reservoir presented earlier was 59 mg m^{-2} day^{-1}.

Summer: 3.59/59 = 0.06, suggesting that ≈ 94% was oxidized in the unsaturated zone; Rangely field only; 4.86/59 = 0.08 or ≈ 92% was oxidized.

Winter: 17.8/59 =0.30, suggesting that ≈ 70% was oxidized in the unsaturated zone; Rangely field only; 25.1/59 = 0.43 or ≈ 57% was oxidized.

Dividing 0.43/0.08 = 5.4; The signal:noise ratio improved by a factor of 5 in the winter.

SUMMARY OF SURFACE GEOCHEMICAL MEASUREMENTS AT WEYBURN

British Geological	07/2001	CO_2 flux, soil gas
Survey +Italian,		CO_2, CH_4, light HC, Rn
French	09/2001	ditto
investigators	09/2002	ditto
	10/2003	ditto + He
	10/2004	ditto + He
	10/2005	ditto + He
KERR Farm		
Lefleur	08/2010	soil gas CO_2, CH_4, LHC
	02/2011	ditto
Gilfillan+Haszeldine	06/2011	GW inert gas + isotopes
Romanak	8-09/2011	soil gas CO_2, CH_4, LHC, He
BGS + It., Fr.	10/2011	ditto + He
Wolaver et al.	2011	Geohydrology

QUALITATIVE INDICATOR OF POSSIBLE ABSENCE OF GAS LEAKAGE AT KERR FARM WELL

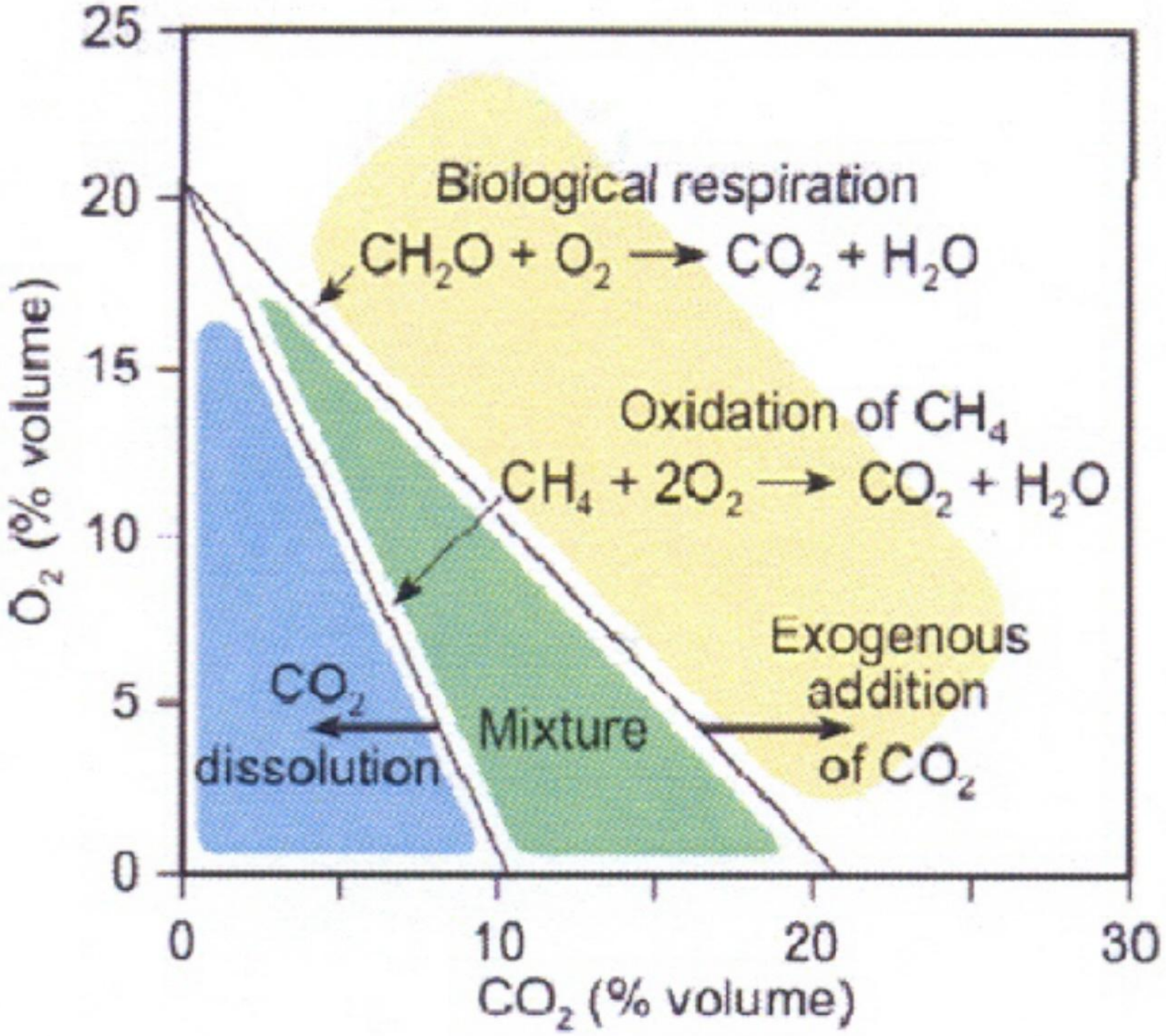
Date	pH	HCO_3^- (mg/L)
10/2002	7.8	308
05/2003	8.0	211
08/2003	7.6	272
11/2003	7.8	259
06/2005	8.0	262
07/2008	8.26	251
06/2011	7.8	351
06/2011	-	376, 410

SUMMARY OF LEFLEUR FINDINGS AT KERR FARM

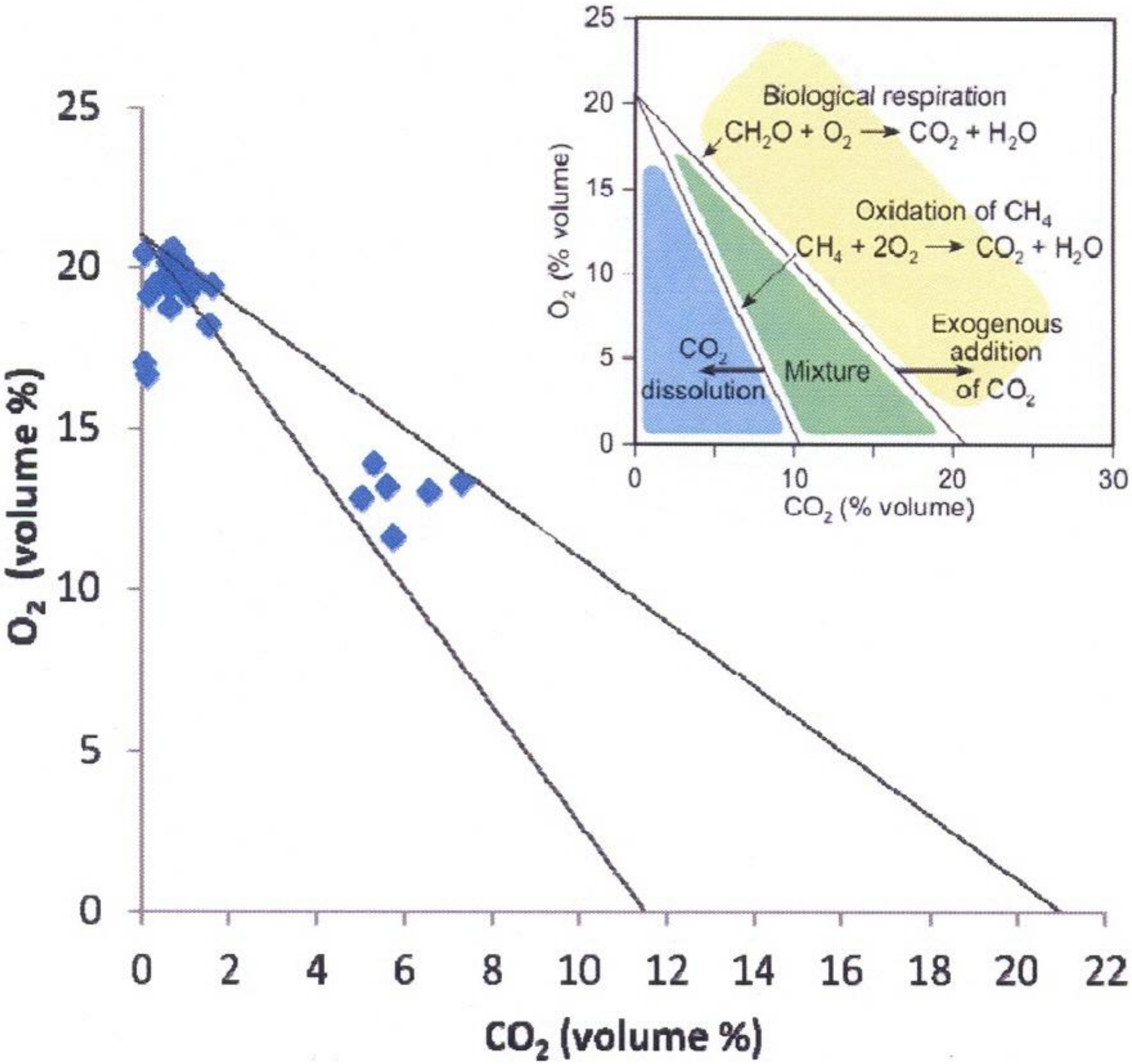
- Both CO_2 and CH_4 had lower concentrations in winter measurements relative to summer,
- Minor C_2+ light hydrocarbons were found at 2-3 locations out of 30 locations measured,
- An anomalous CO_2 location had a $\delta^{13}C$ of -23.5‰, similar to the injected CO_2 from Buelah, ND coal gasification plant,
- High correlation of CH_4 to C_2H_6 at a few locations.

LEFLEUR CONCLUSION: There is leakage of reservoir gases to the surface on the Kerr farm.

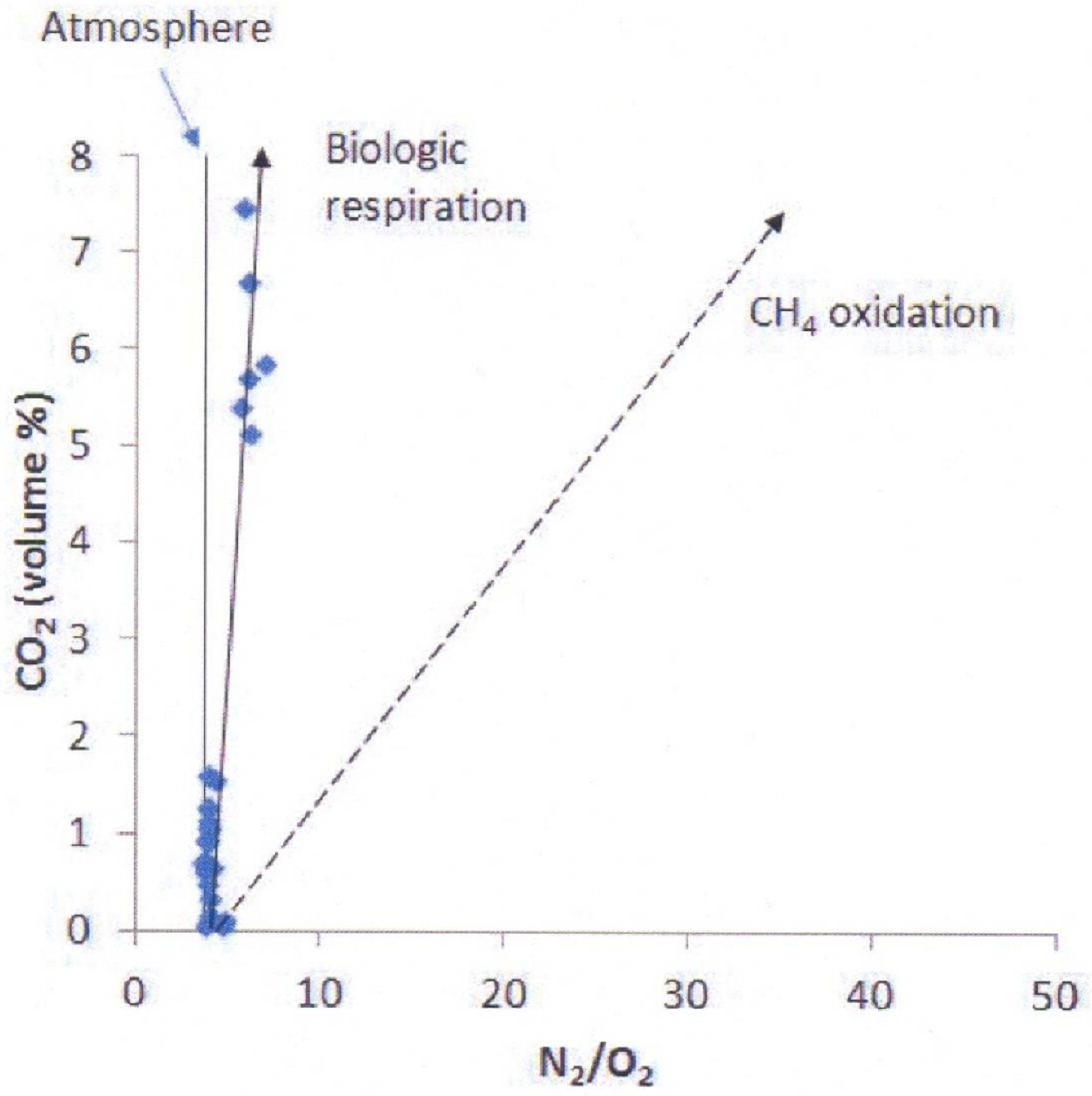
PROCESS CONTROLLED O_2-CO_2 (from Romanak, 2011)



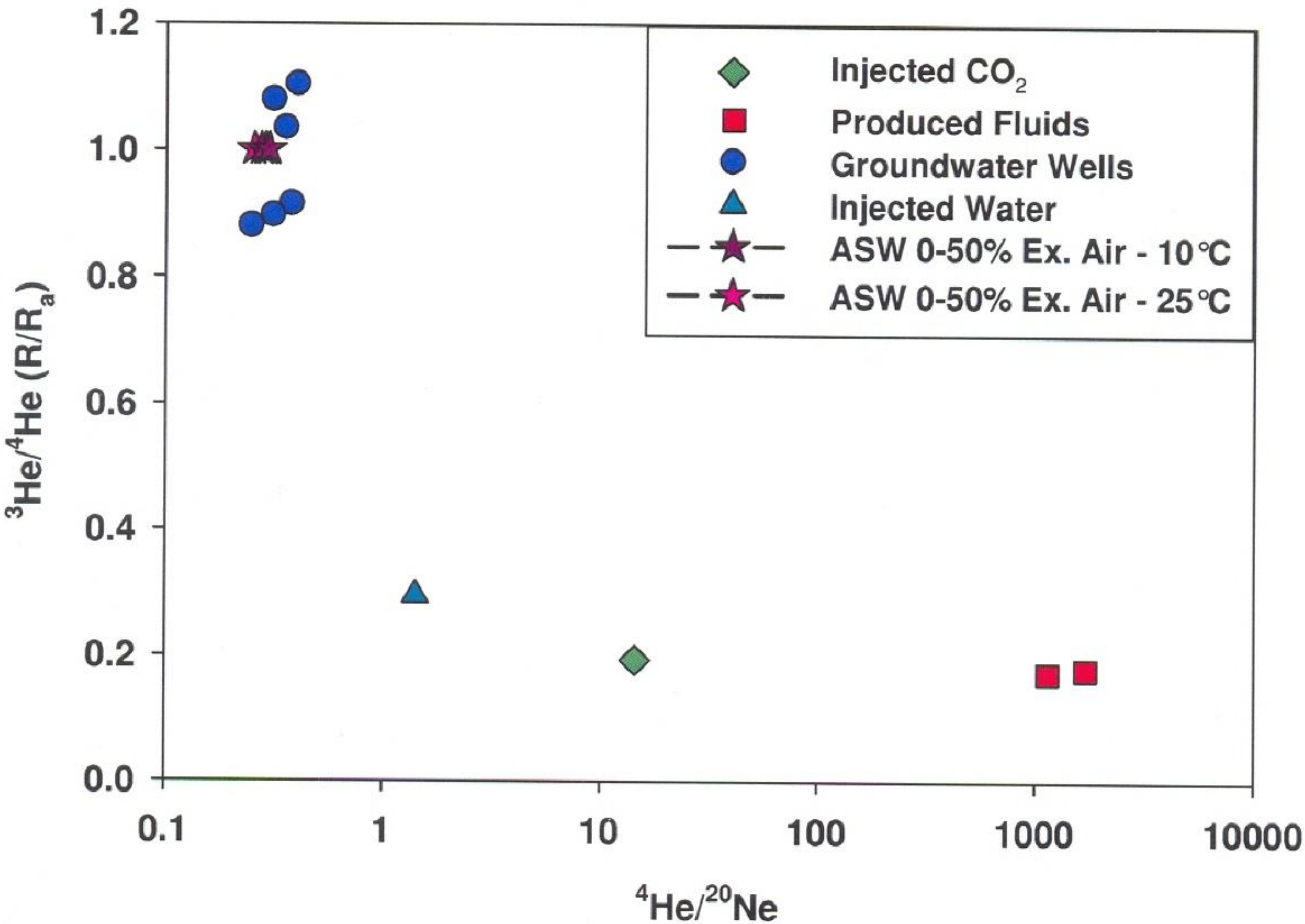
O_2-CO_2 at Kerr farm (from Romanak, 2011)



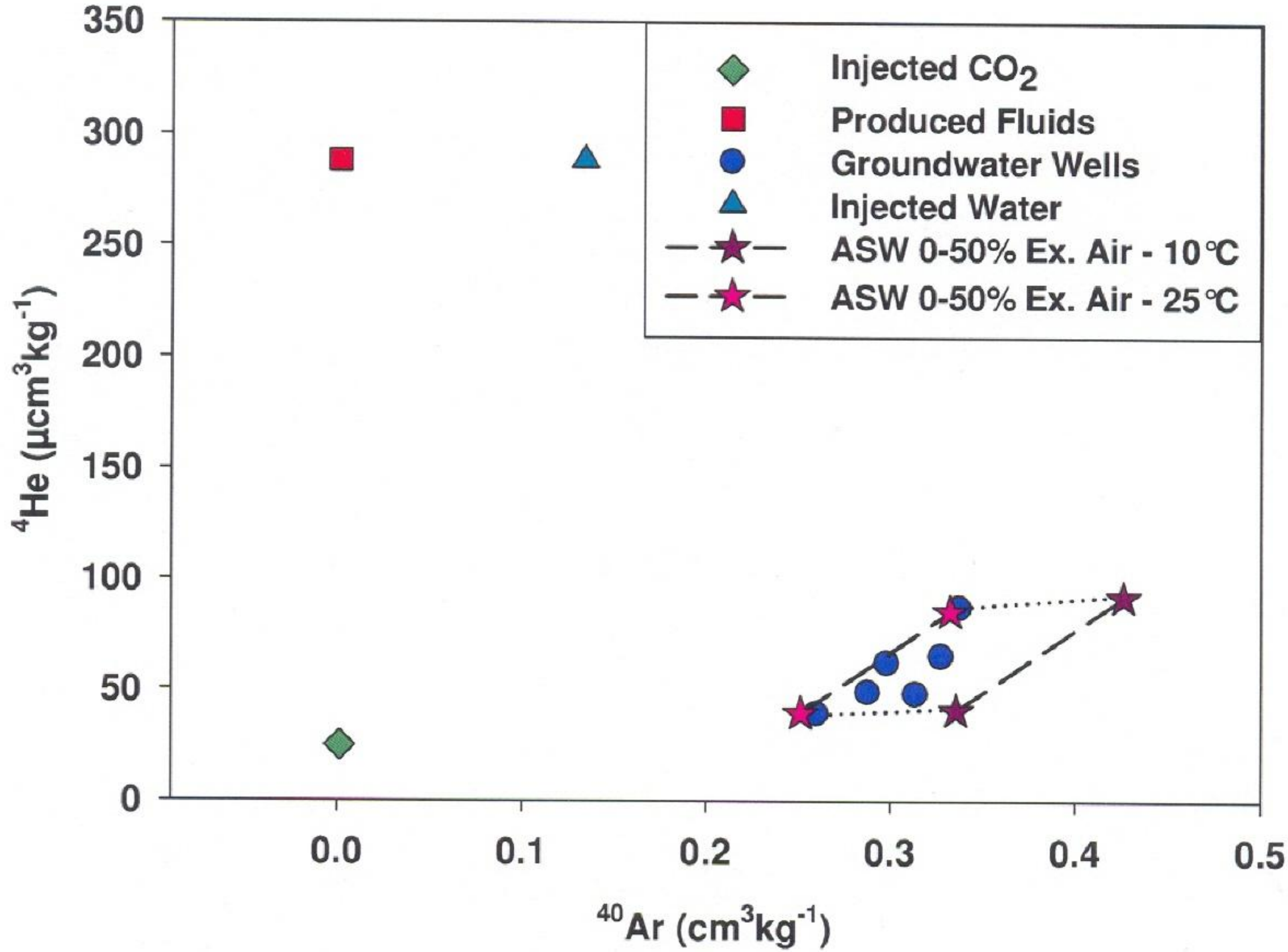
CO_2-N_2/O_2 at Kerr Farm (from Romanak, 2011)



He – Ne Isotopic Ratios (from Gilfillan and Haszeldine, 2011) VERIFICATION



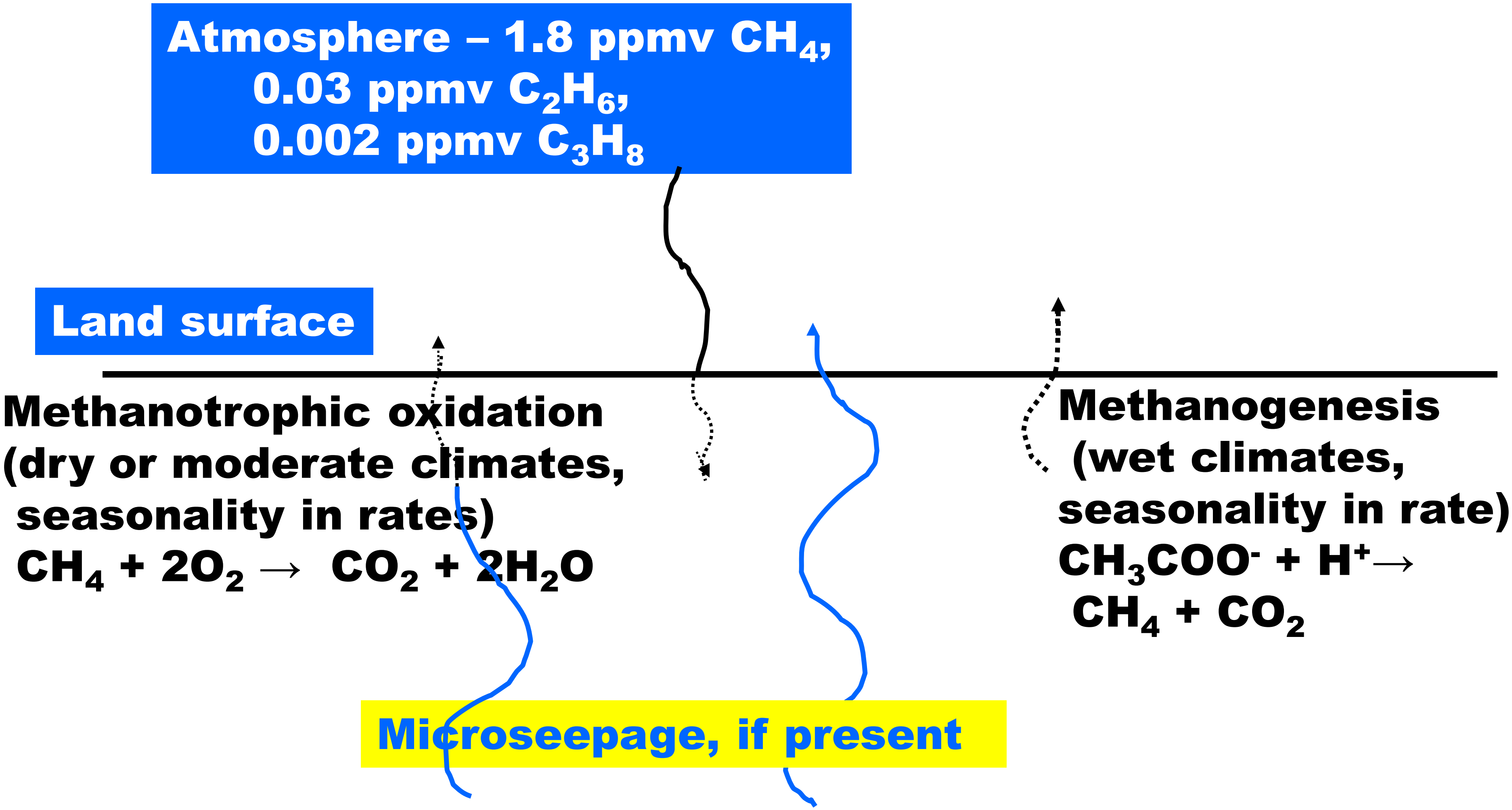
He – Ar Isotopic Ratios (from Gilfillan and Haszeldine, 2011) VERIFICATION

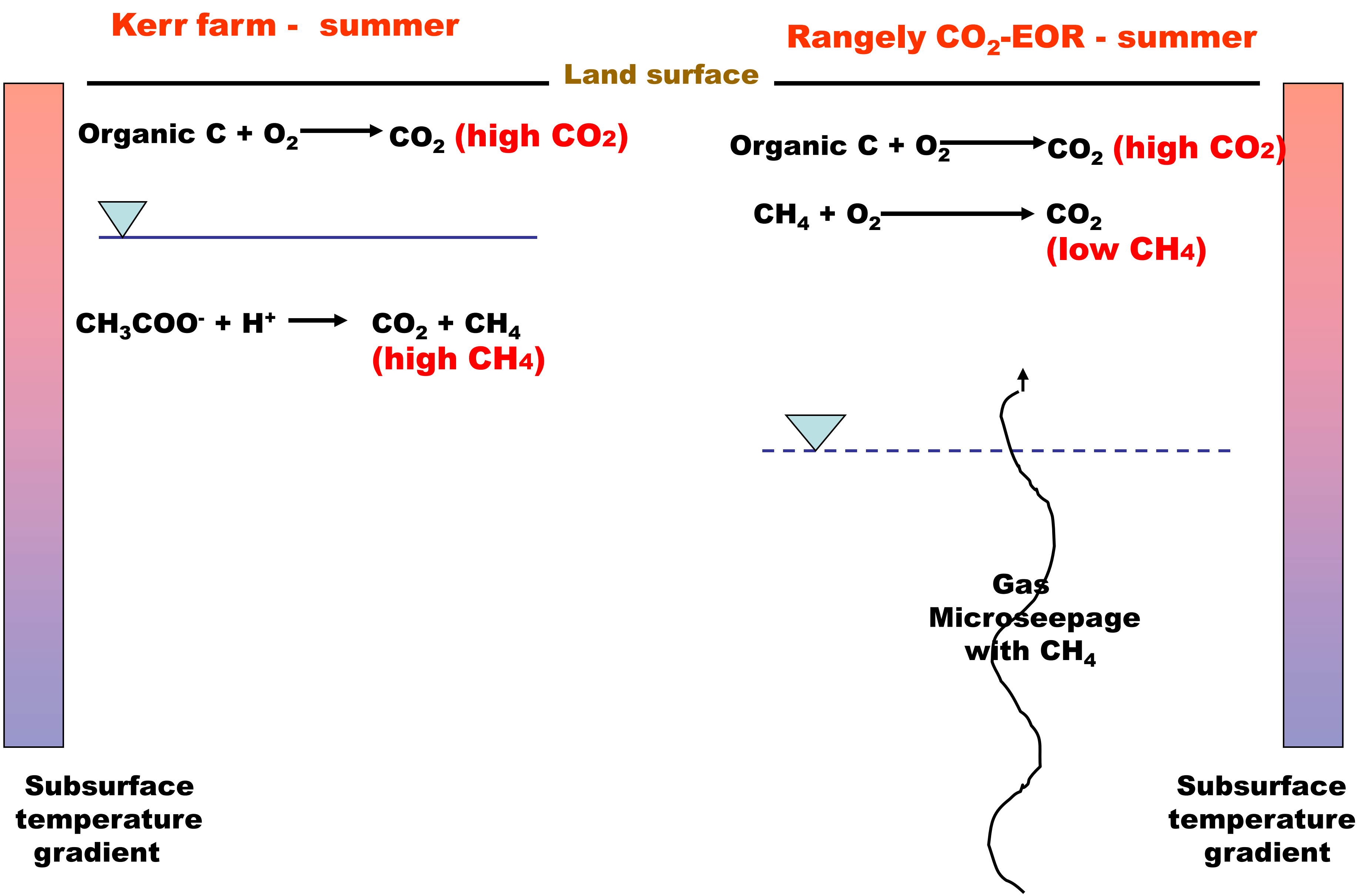


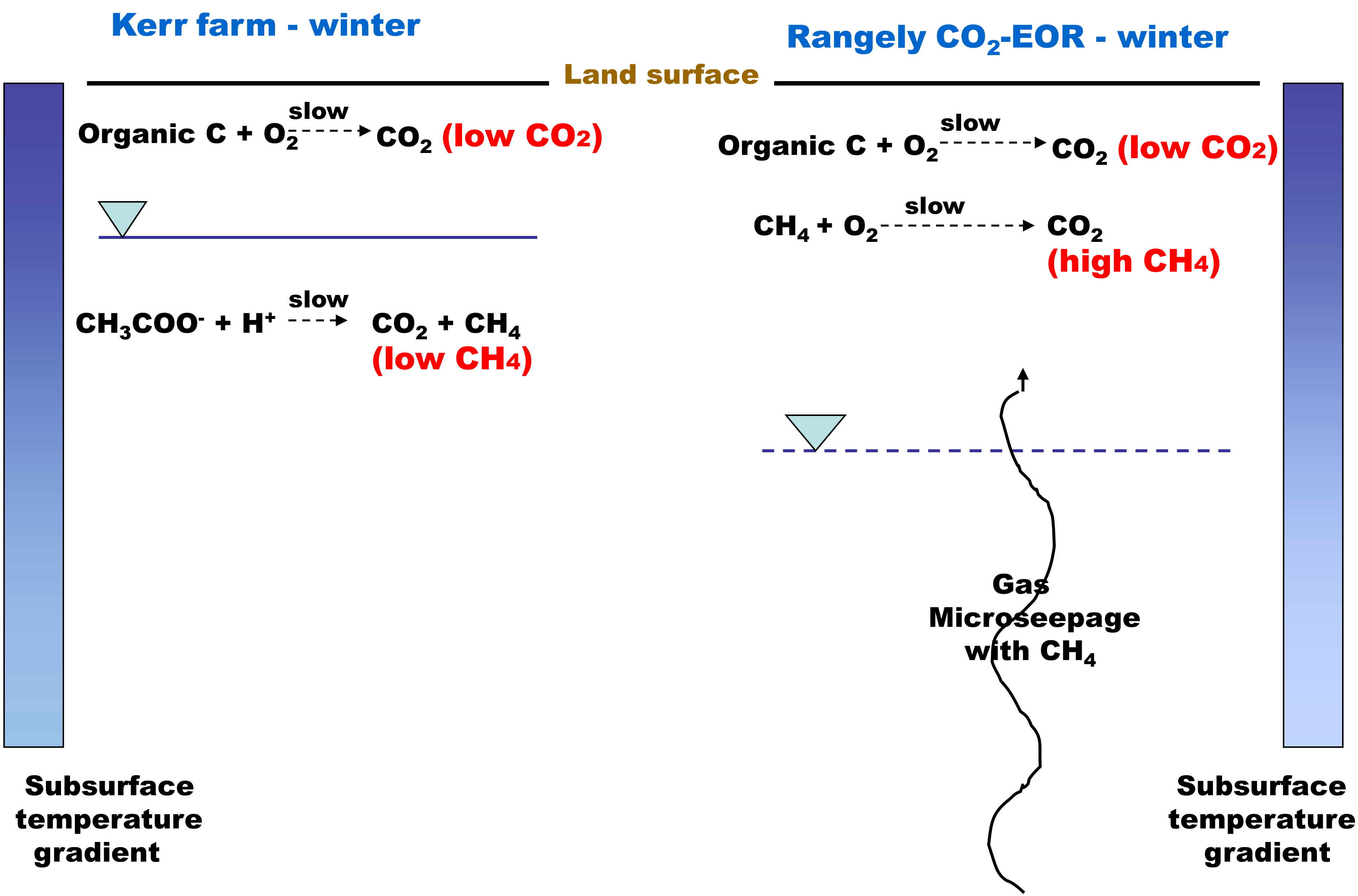
Romanak (2011),
Gilfillan and Haszeldine (2011),
Beaubien et al. (2013)

CONCLUSION: NO LEAKAGE ON THE KERR FARM

SOIL PROCESSES OPERATING WITH RESPECT TO METHANE




Kerr farm - summer
Rangely CO_2-EOR - summer
Land surface
Organic C + O_2 → CO_2 (high CO2)
CH_3COO^- + H^+ → CO_2 + CH_4
(high CH4)
Organic C + O_2 → CO_2 (high CO2)
CH_4 + O_2 → CO_2
(low CH4)
Gas Microseepage with CH_4
Subsurface temperature gradient
Subsurface temperature gradient


Kerr farm - winter
Rangely CO_2-EOR - winter
Land surface
Organic C + O_2 --slow--> CO_2 (low CO2)
CH_3COO^- + H^+ --slow--> CO_2 + CH_4 (low CH4)
Organic C + O_2 --slow--> CO_2 (low CO2)
CH_4 + O_2 --slow--> CO_2 (high CH4)
Gas Microseepage with CH_4
Subsurface temperature gradient
Subsurface temperature gradient

Klusman, 2011- Alternative Interpretation of Lefleur, 2010, 2011 Data

- Injected CO_2 from Buelah, ND reacts with reservoir carbonate rock with $\delta^{13}C$ of ≈ 0‰ to produce a produced fluid of -10 to -12‰. The soil gas $\delta^{13}C$ of -23‰ is consistent with normal soil respiration, not leakage.

- The relative concentrations of CO_2 and CH_4 in summer and winter are consistent with a methanogenic source for CH_4. Slowing of microbiological processes in winter reduces the CH_4 concentration. If there was leakage, there would be increased CH_4 in winter due to slowing of methanotrophic oxidation.

CONCLUSION: Lefleur data is also consistent with a conclusion of "No Leakage" on Kerr farm.

CONCLUSIONS

- **Monitoring protocols will need to be developed for each project that reflects climate, geology, and accommodates cultural interferences,**
- **Methanotrophic oxidation (methanotrophy) will be important in the attenuation of hydrocarbon microseepage at CO_2-EOR projects,**
- **Measurement of carbon-containing gases will require liberal use of isotopes and possibly C-14,**
- **It is possible to make estimates of gas microseepage over CO_2-EOR fields and presumably over future pure sequestration projects,**
- **Measurement of carbon-containing gases will require liberal use of isotopes and possibly C-14.**

ACKNOWLEDGEMENTS

Rangely – U.S. Dept. of Energy-Basic Energy Sciences for funding;

- Chevron Production USA for access to confidential reservoir characterization documents, reservoir water quality data, reservoir pressure data, and backhoe for soil characterization in trenches.

Teapot Dome – Rocky Mountain Oilfield Testing Center (RMOTC) for funding;

- Naval Petroleum Reserve No. 3 for field access and data, and backhoe for soil profile characterization, fault trenching.