

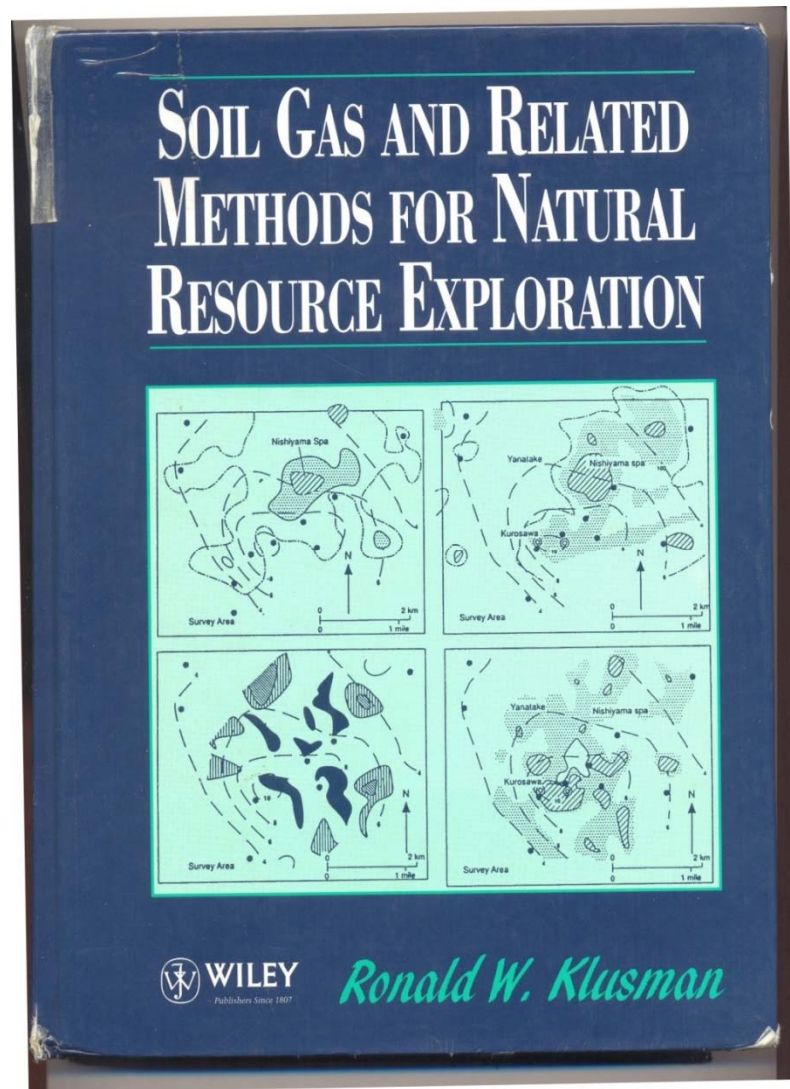
GAS SEEPAGE ON EARTH

**Experience with microseepage
measurements, flux detection and
indirect indicators**

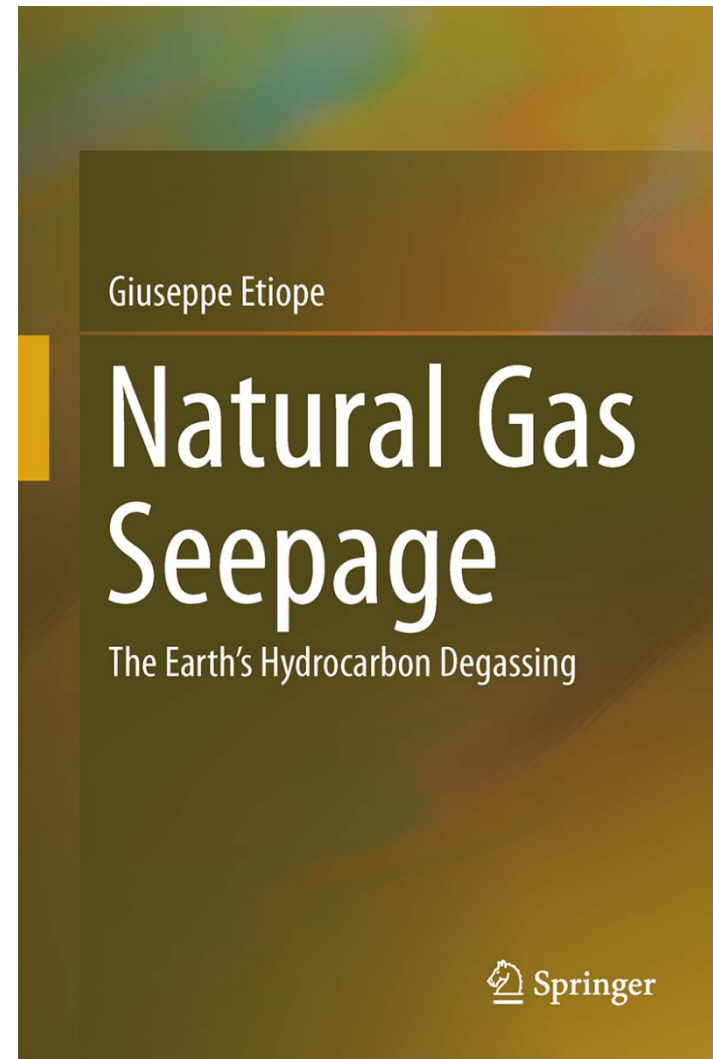
**Ronald W. Klusman
Emeritus Professor
Chemistry and Geochemistry
Colorado School of Mines**

rwklusman@earthlink.net

Klusman, 1993

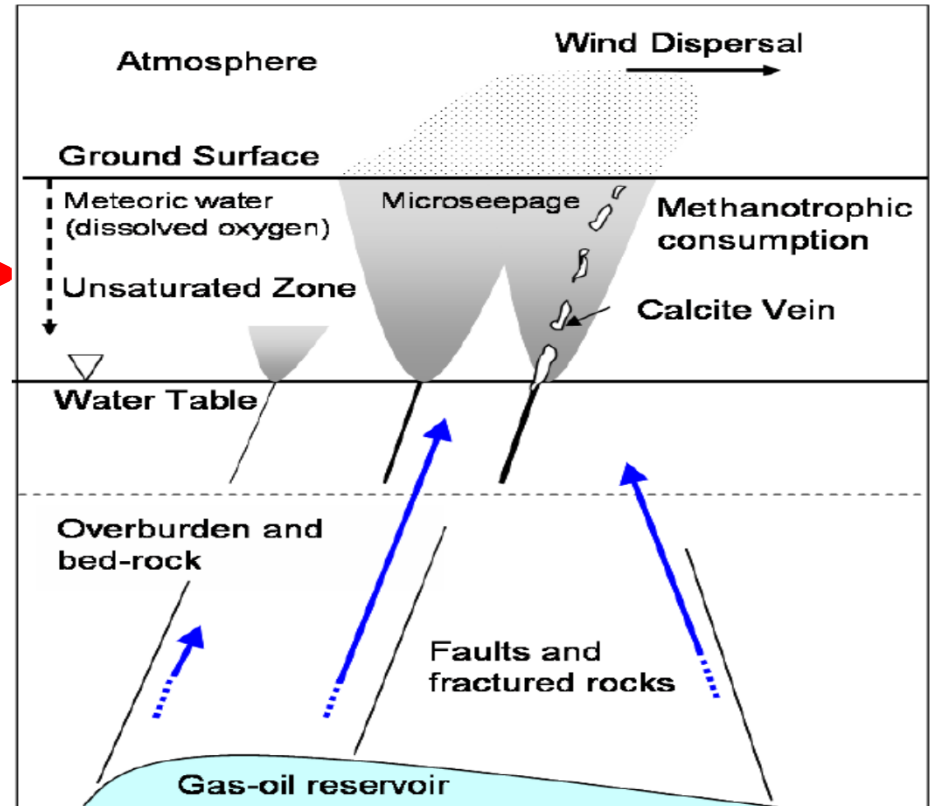
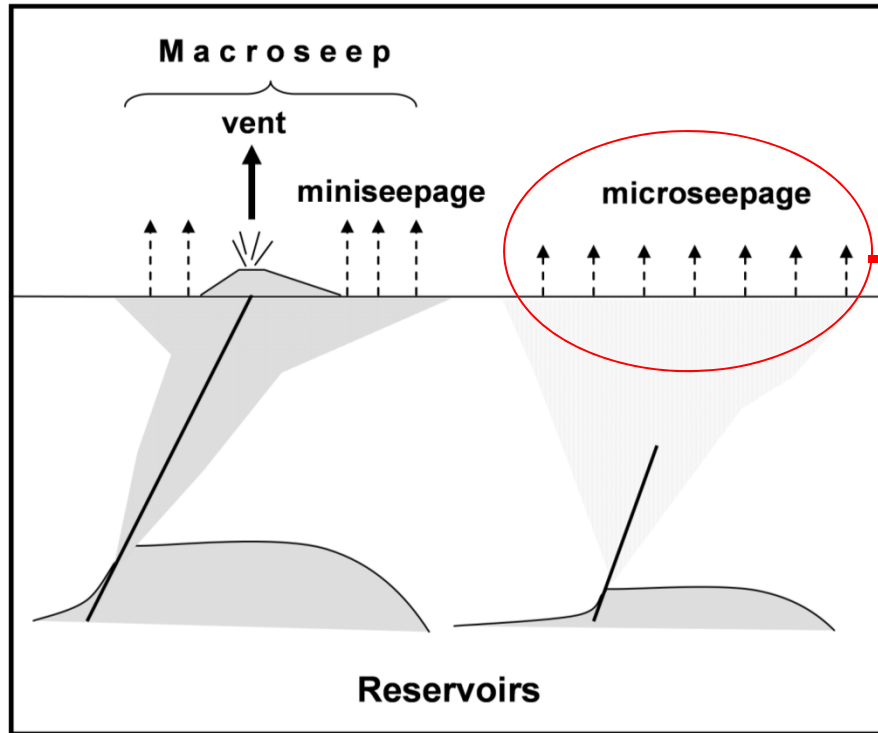


Etiope, 2015

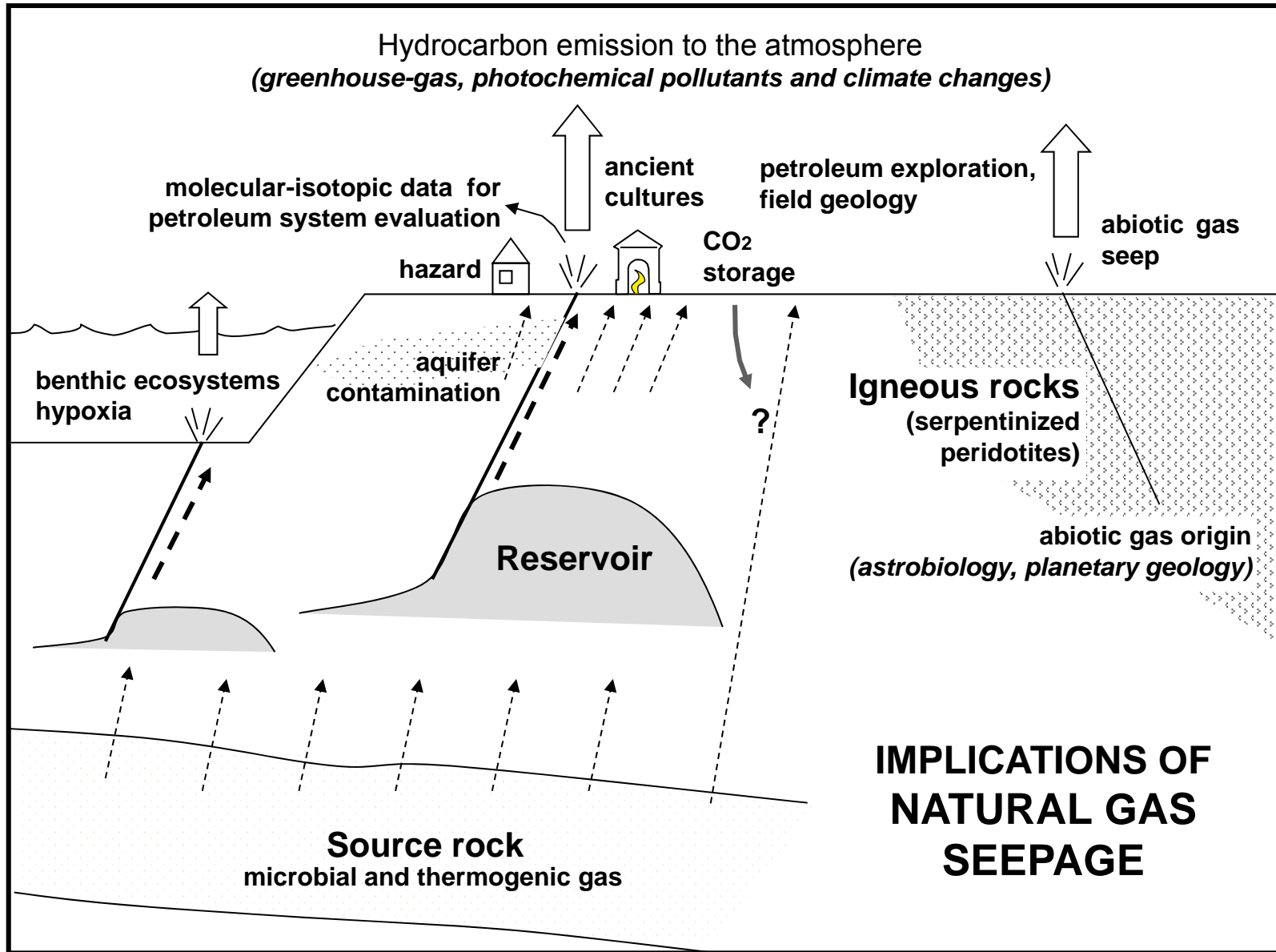


What is gas seepage

microseepage



Importance of gas seepage on Earth

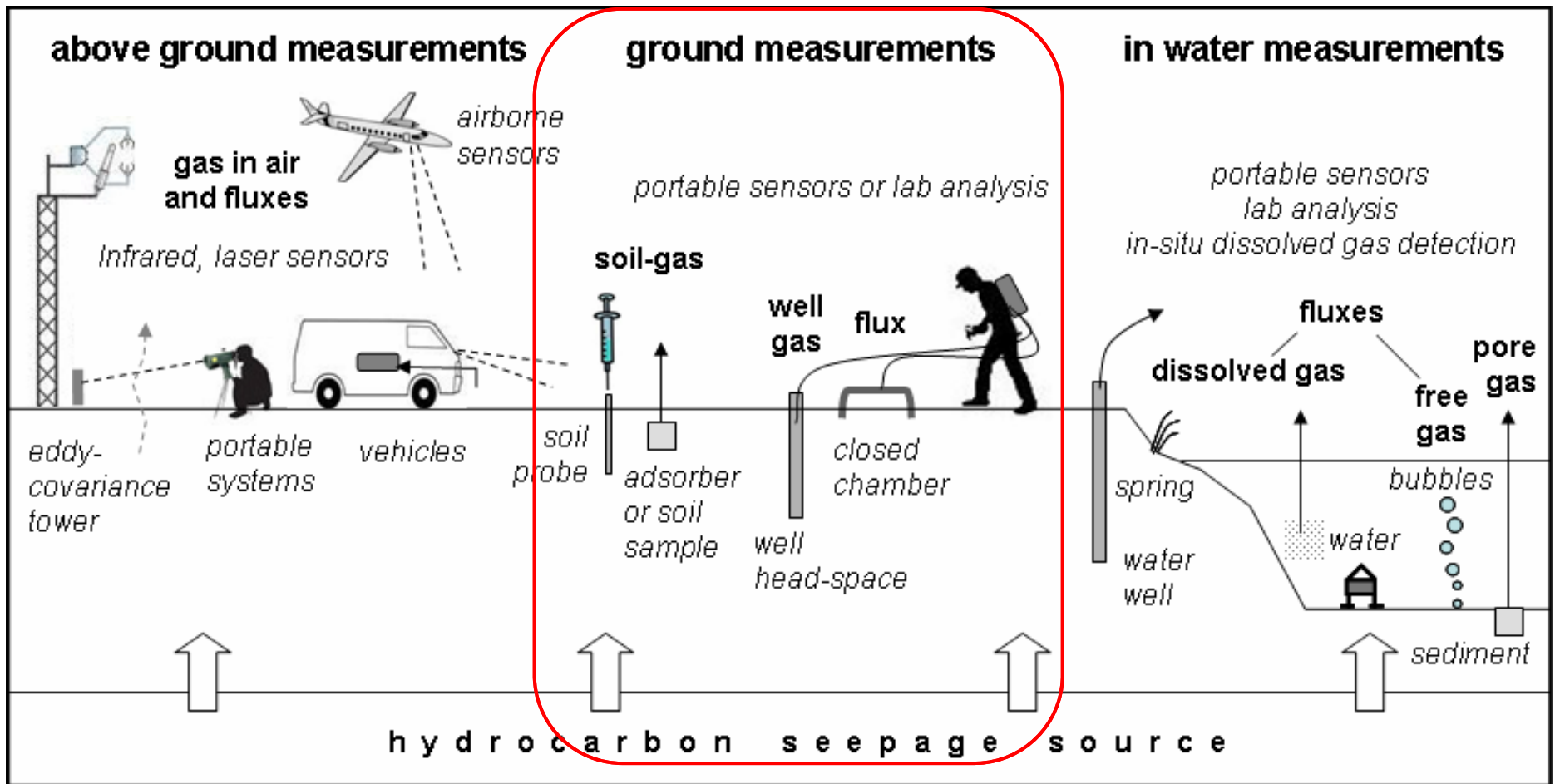


Etioppe (2015)

How to detect and measure gas seepage

Effective only for significant seepage

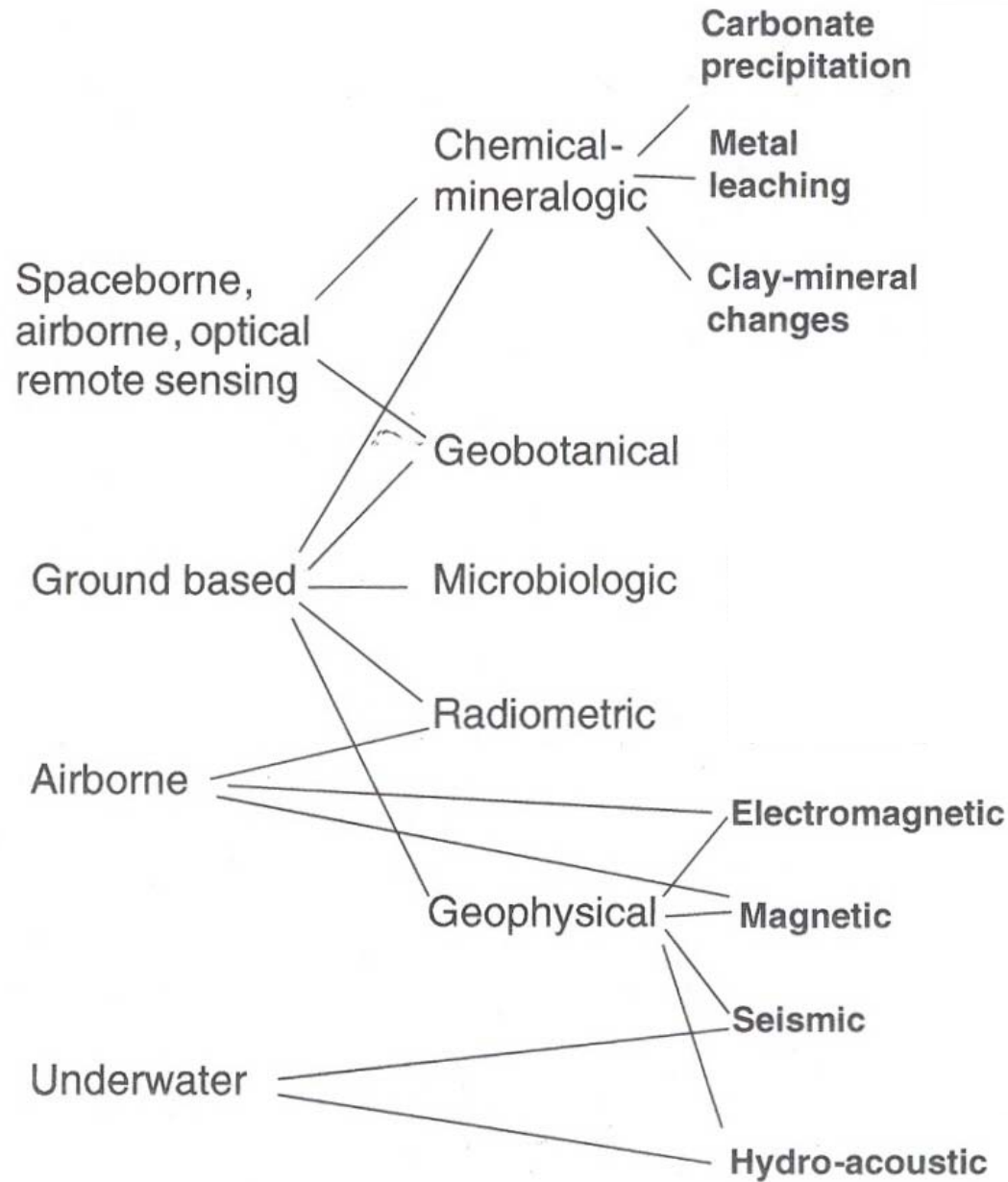
Effective also for very low seepage



approach to be adopted for Mars

Etiopo (2015)

Indirect Methods for Detection of Gas Seepage (Modified from Etiope , 2015, Figure 4.5)

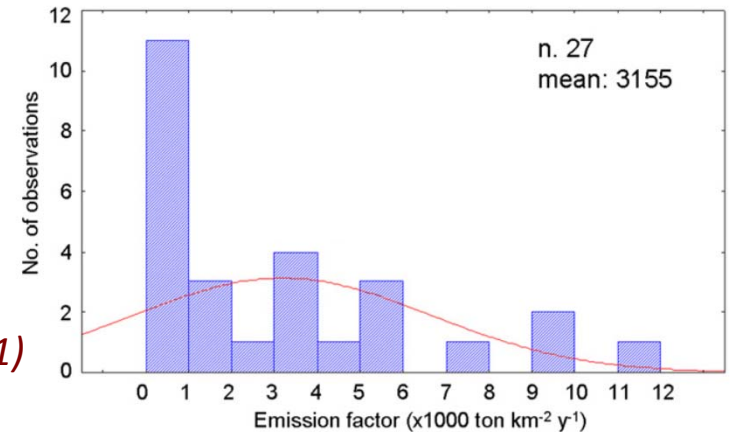


Typical methane fluxes from seepage on Earth

Gas seeps 0.1 – 100 ton/year (10^3 ton/year in large seeps)

Mud volcanoes *mean* 3100 ton km⁻² y⁻¹

Etiopie et al (2011)



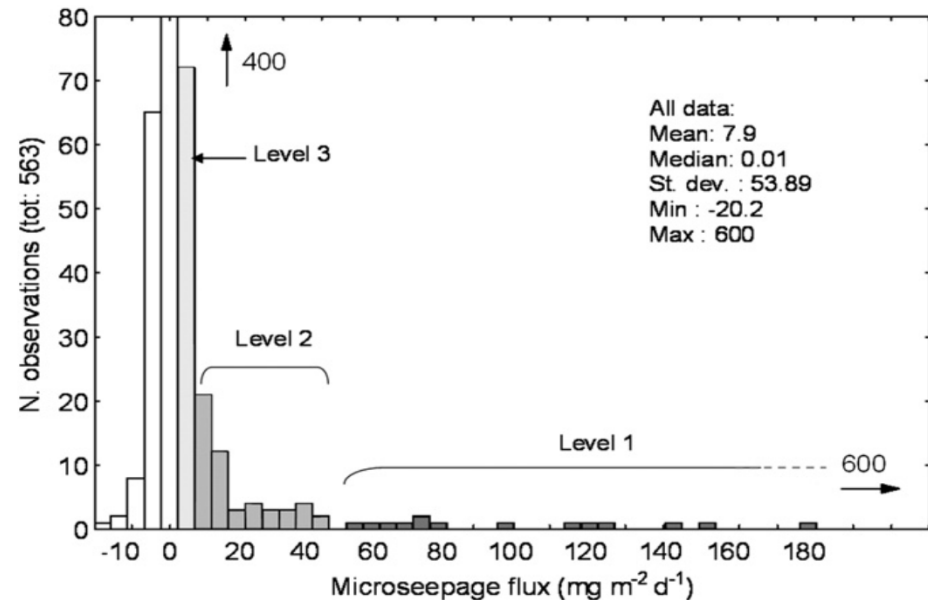
Microseepage

by definition >0 mg m⁻² day⁻¹

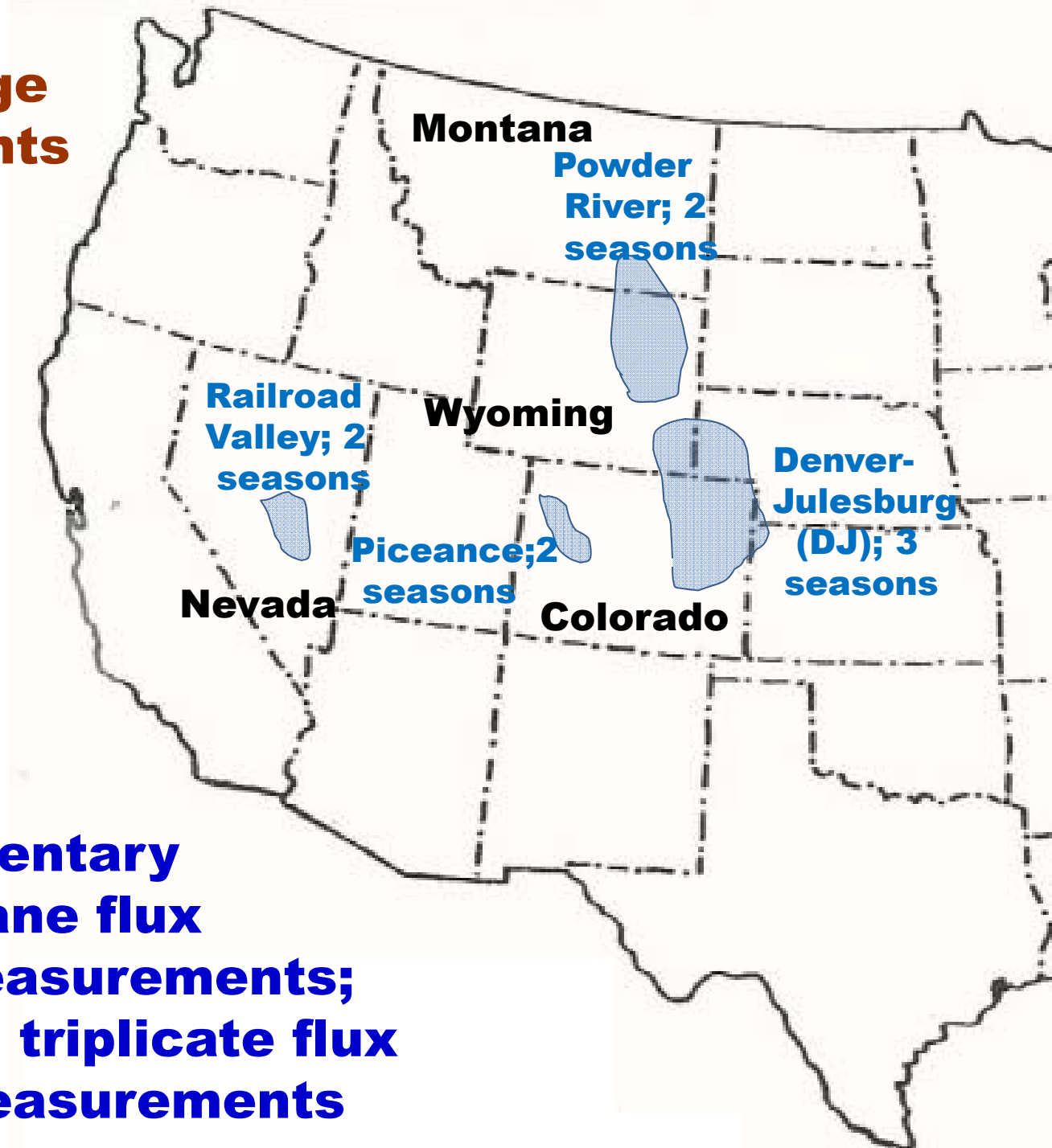
Methanotrophy

“negative” (downward flux)
drawing CH₄ from atm.

Etiopie and Klusman (2010)



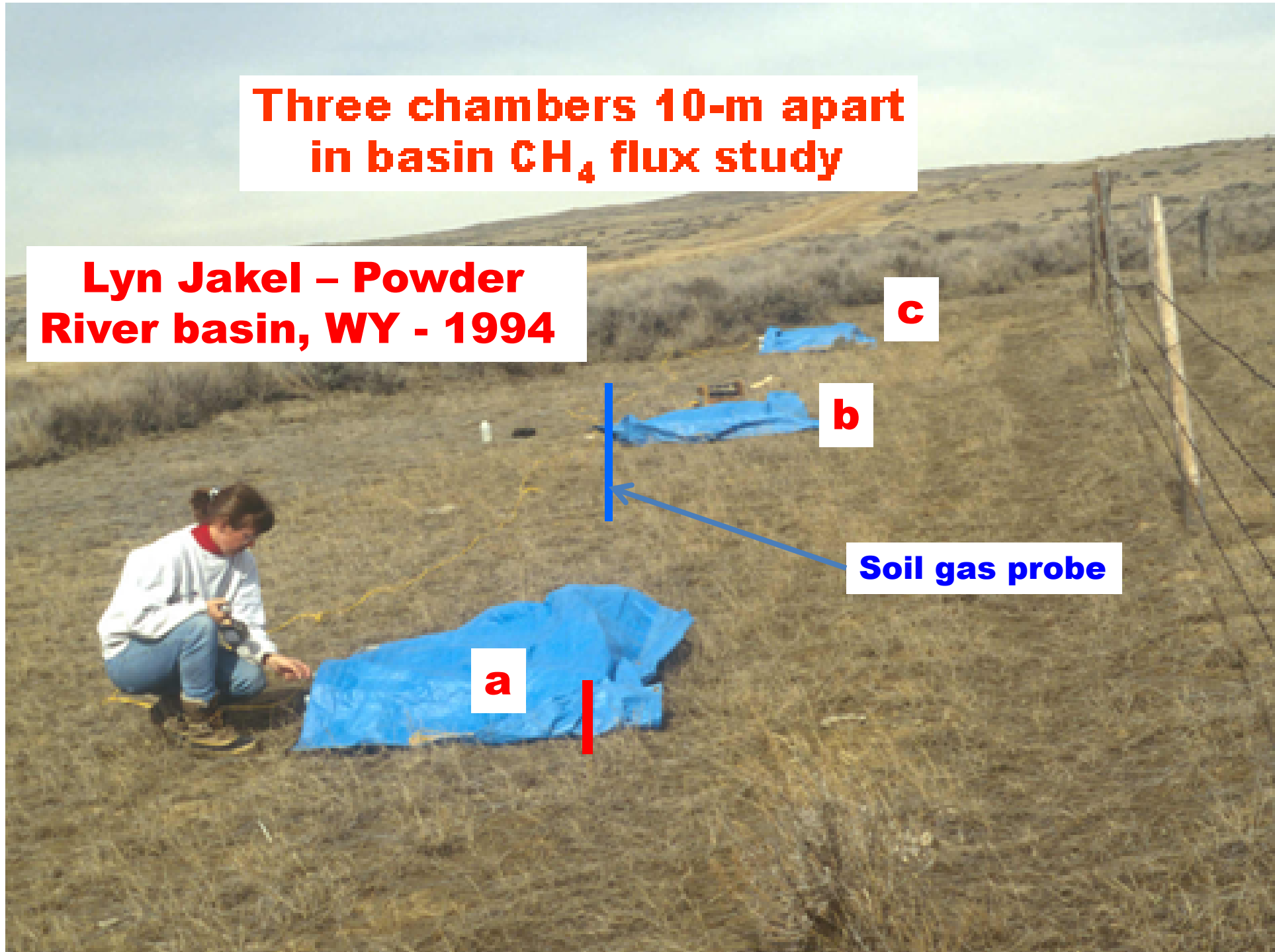
Microseepage measurements in USA



Early sedimentary basin methane flux baseline measurements; Total of 342 triplicate flux chamber measurements

**Three chambers 10-m apart
in basin CH₄ flux study**

**Lyn Jakel – Powder
River basin, WY - 1994**

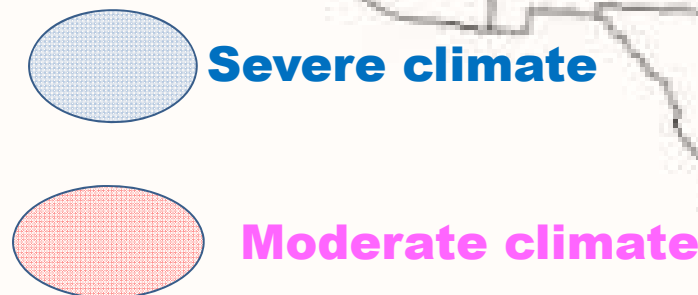
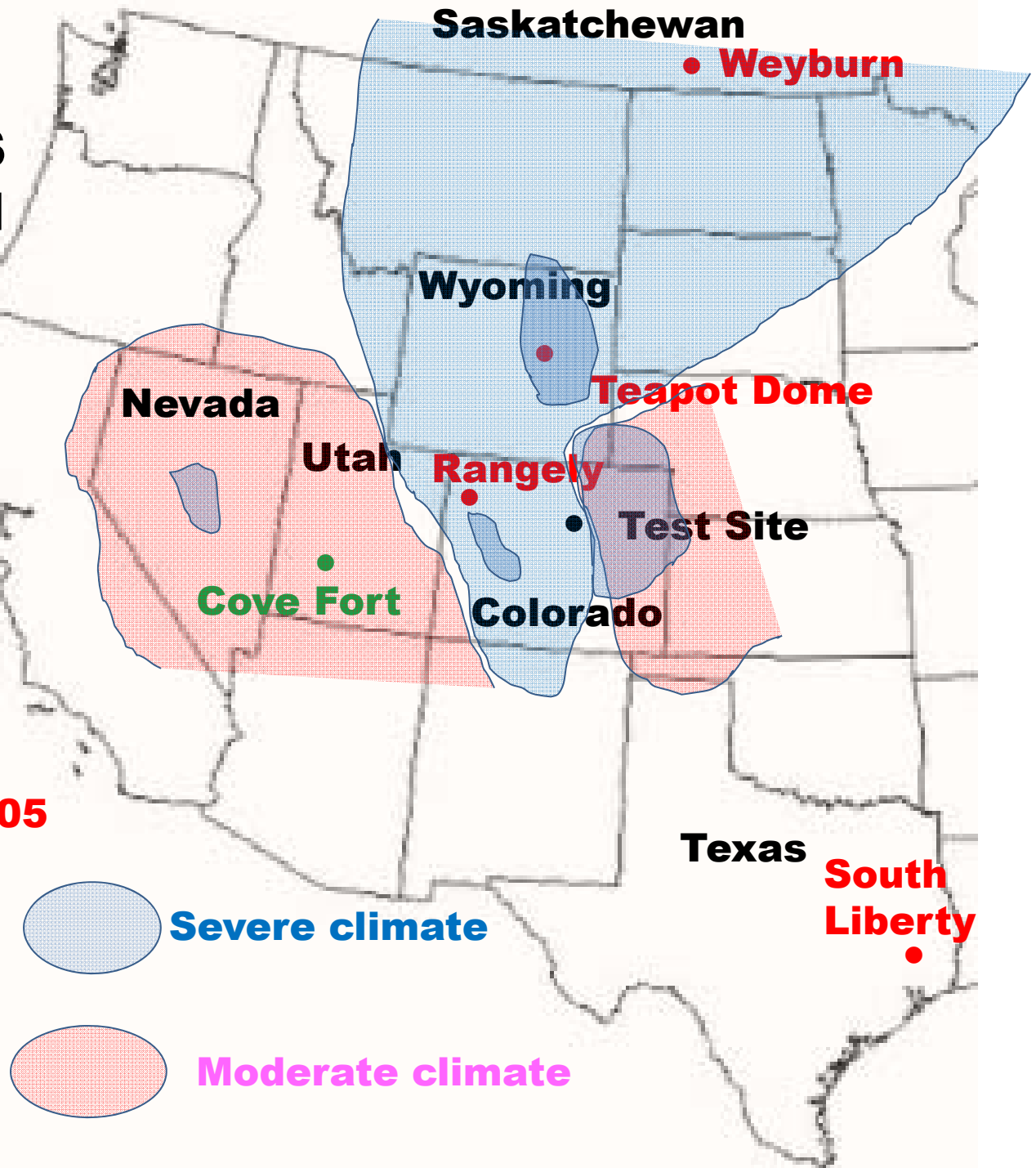


FLUX, SOIL GAS SITES WITH AN EMPHASIS ON SEASONALITY

Test site – early
measurements of
a variety of gases

CO₂-EOR sites;
CH₄, CO₂, light HCs;
Inert Gases -2000-07;
South Liberty – 2004-05
Weyburn -2011

Geothermal CH₄, CO₂,
N₂O -1998-99



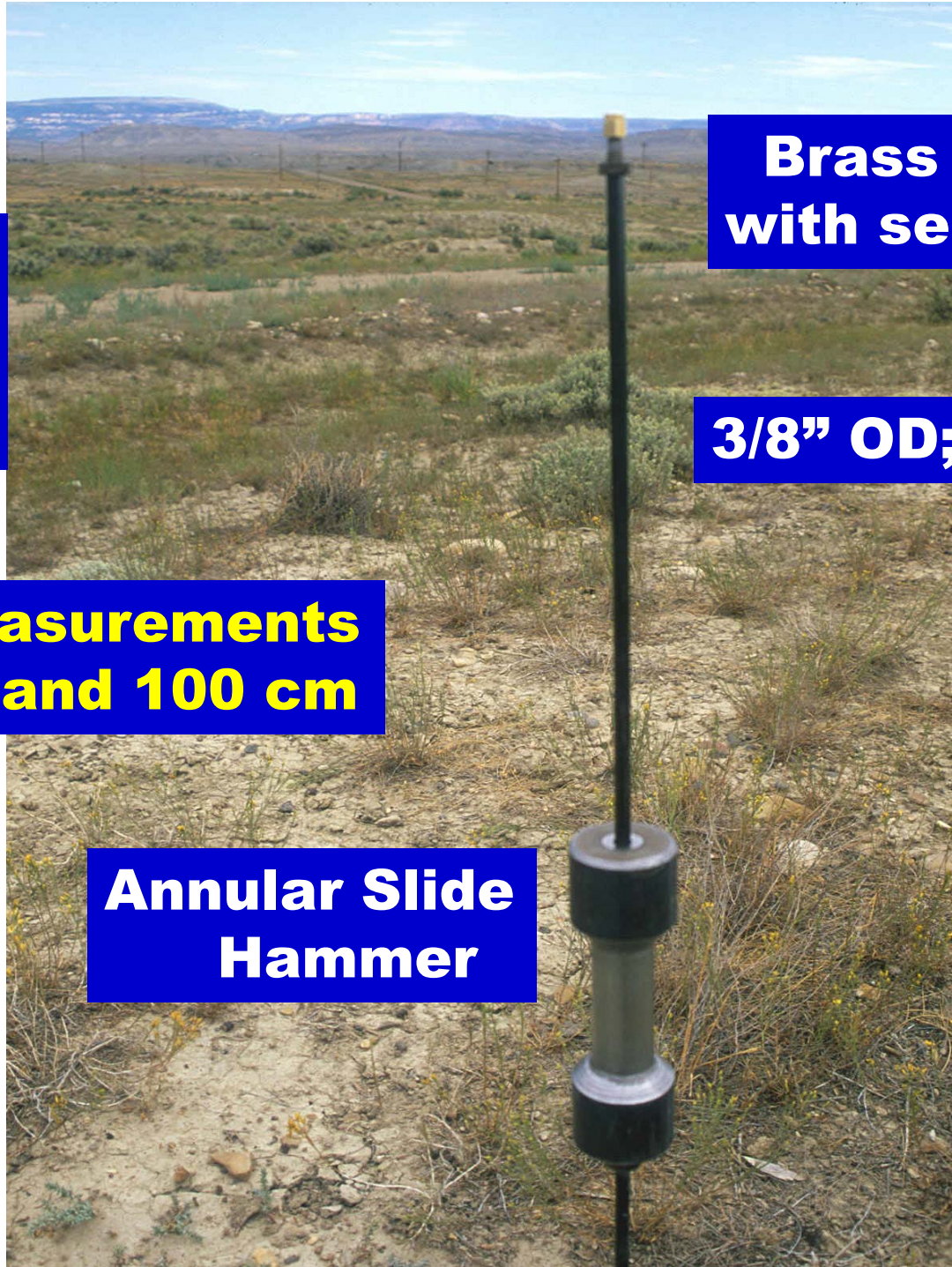
**GENERIC
SOIL GAS
PROBE**

**Soil gas measurements
at 30-, 60-, and 100 cm**

**Brass cap
with septum**

3/8" OD; 1/8" ID

**Annular Slide
Hammer**



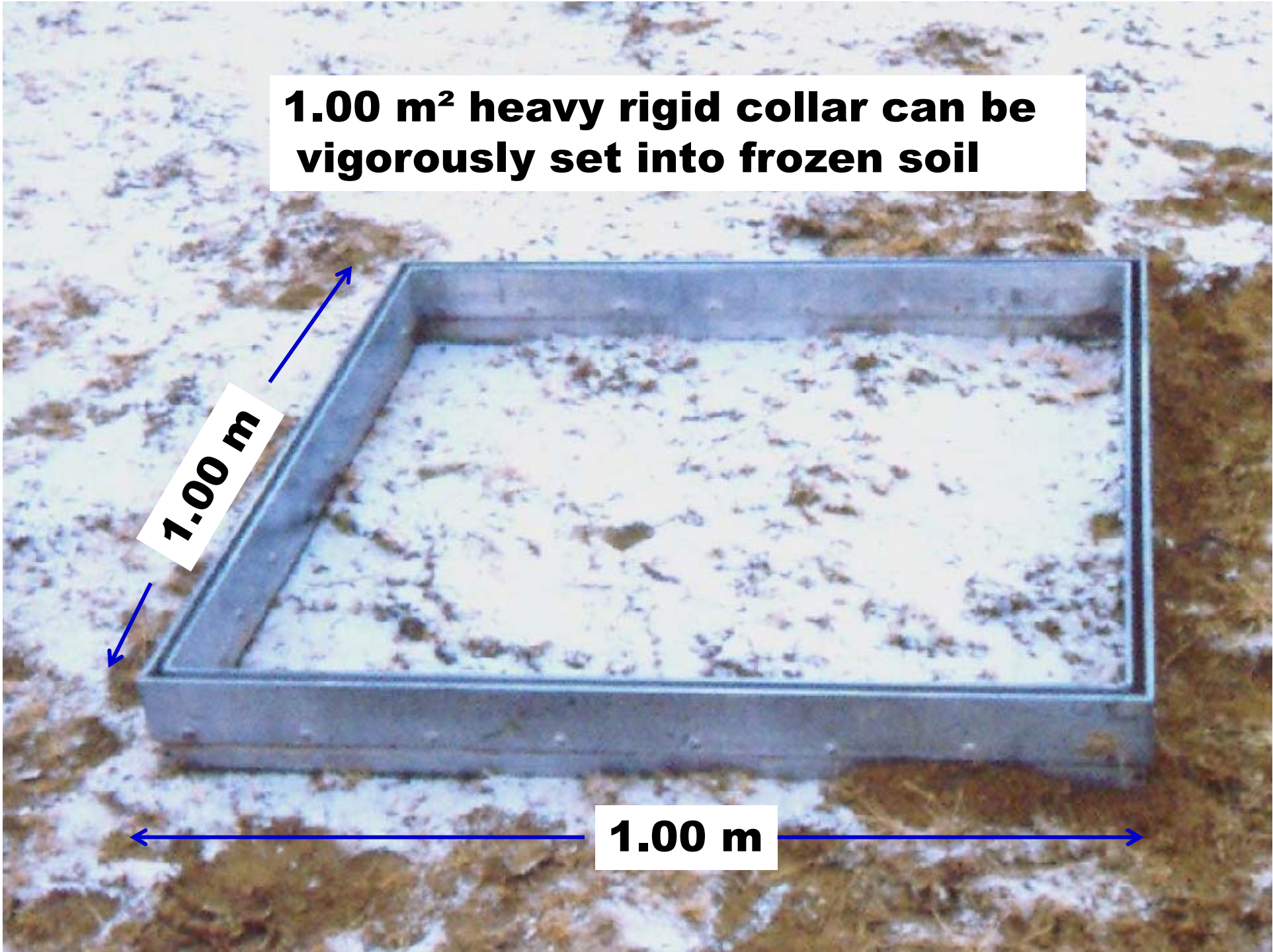
IMPROVEMENTS NEEDED FOR MONITORING, VERIFICATION AND ACCOUNTING (MVA) FOR APPLICATION IN CARBON CAPTURE AND GEOLOGIC STORAGE OF CO₂

- **Full seasonality needed in gas flux and soil gas measurements,**
- **Improved IR-based measurement of CO₂ in the 300-1000 ppmv range,**
- **More isotopic measurements of both CO₂ and CH₄ for evaluation of the role of methanotrophy,**
- **Focus measurements on faults and potential role as conduits for buoyant fluids,**
- **Seasonality, isotopic measurements, and faults as conduits will be particularly important on Mars. Large declining barometric gradients will draw gases upward.**

1.00 m² heavy rigid collar can be vigorously set into frozen soil

1.00 m

1.00 m



A photograph of a field setup for methane and light hydrocarbon sampling. A white Licor 7000 analyzer is mounted on a wooden table. A laptop computer is on a separate wooden stool. A blue metal flux chamber sits on the ground, connected to the analyzer by clear tubing. A red arrow points to a port on the chamber. The background shows a flat, open landscape under a cloudy sky.

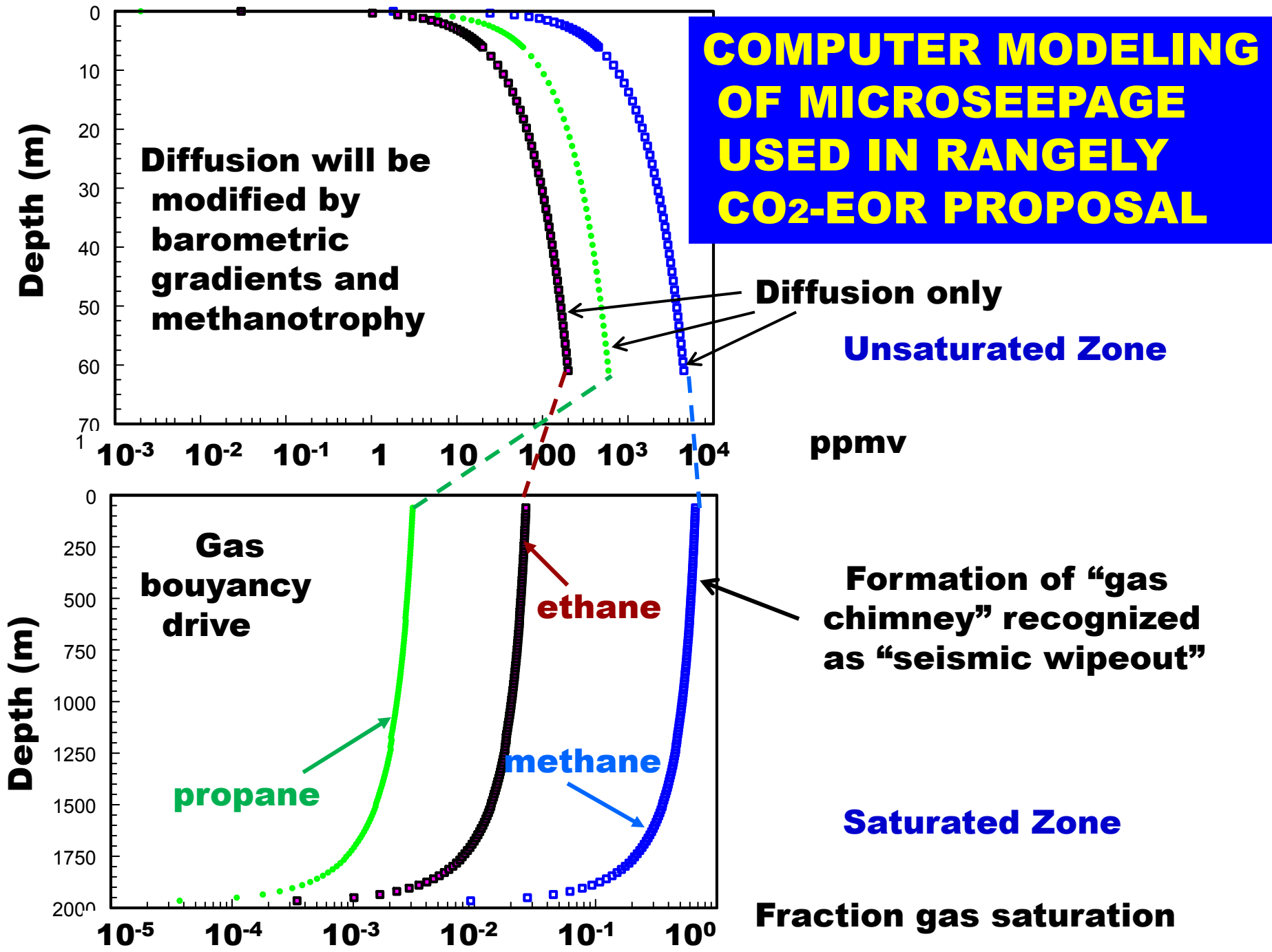
Licor 7000 inside insulating box

Tubing to and from flux chamber

Laptop computer

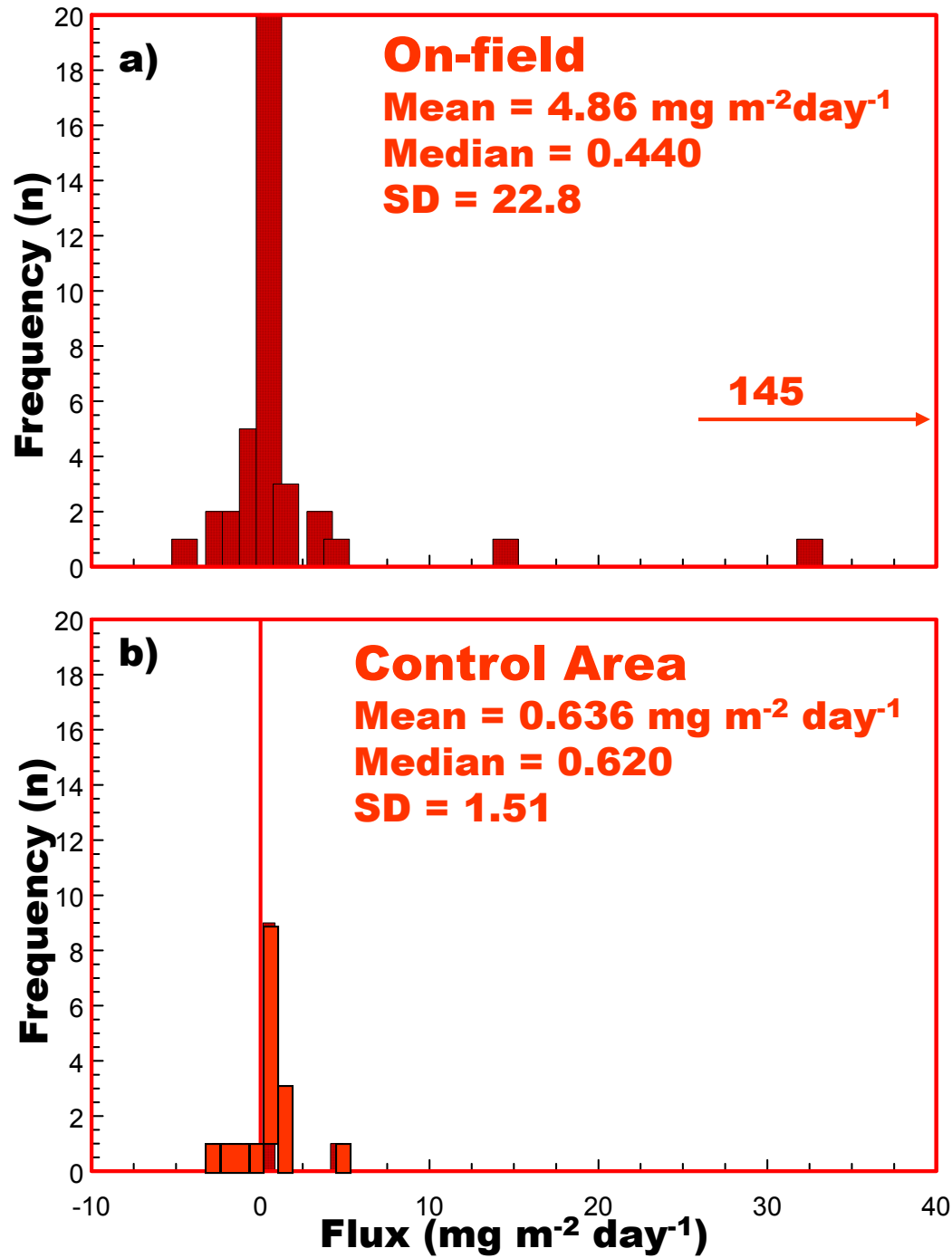
Port for methane and light hydrocarbon sampling using syringe

COMPUTER MODELING OF MICROSEEPAGE USED IN RANGELY CO₂-EOR PROPOSAL



Rangely CH₄ Flux

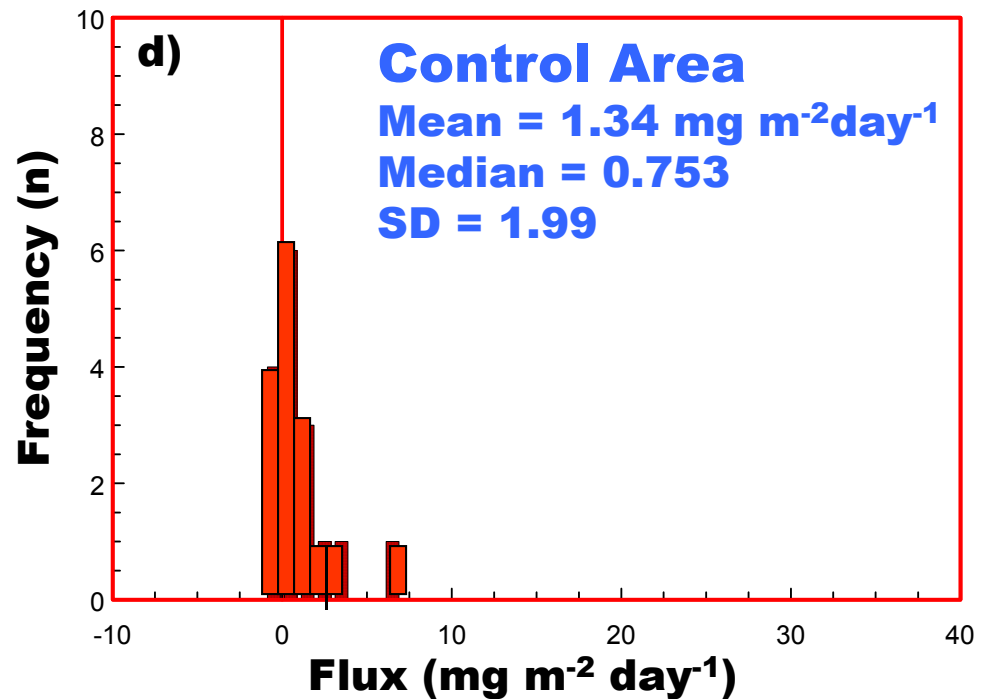
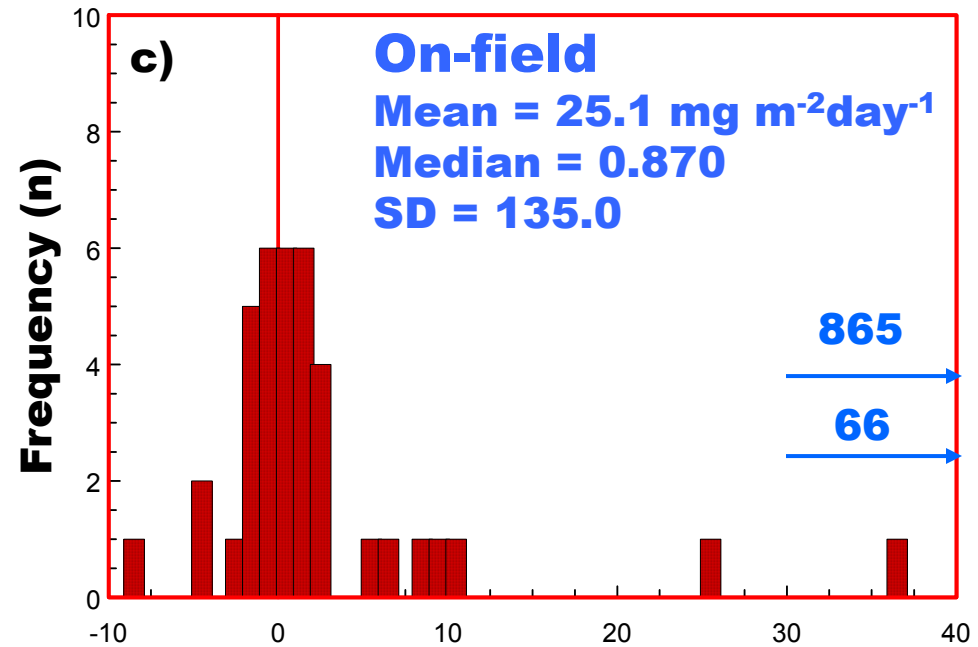
Summer, 2001



Rangely CH₄ Flux

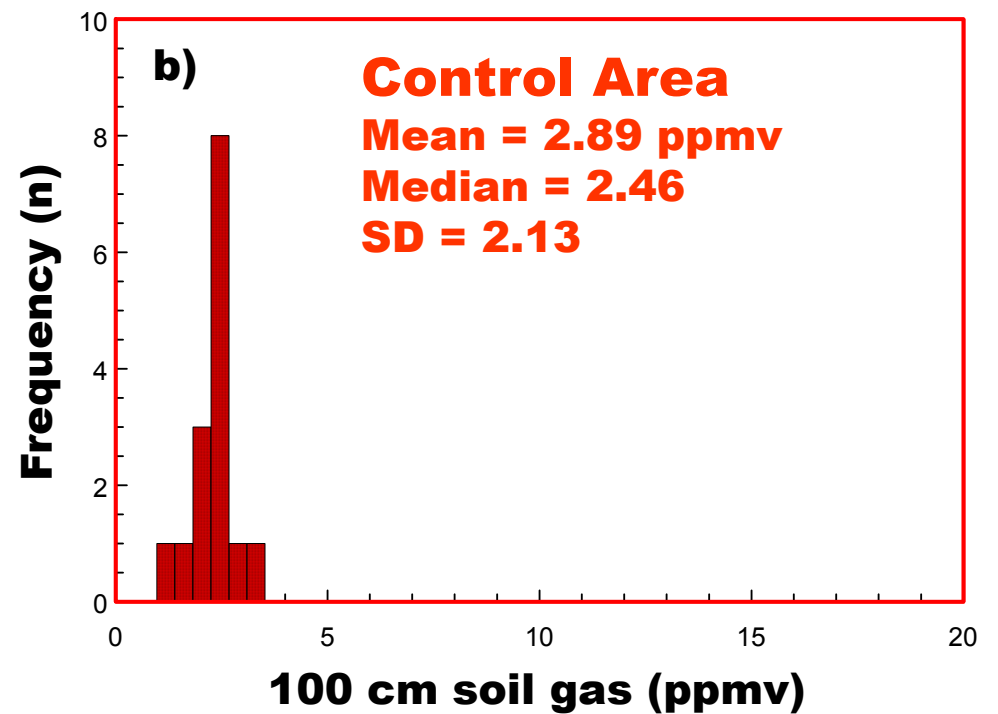
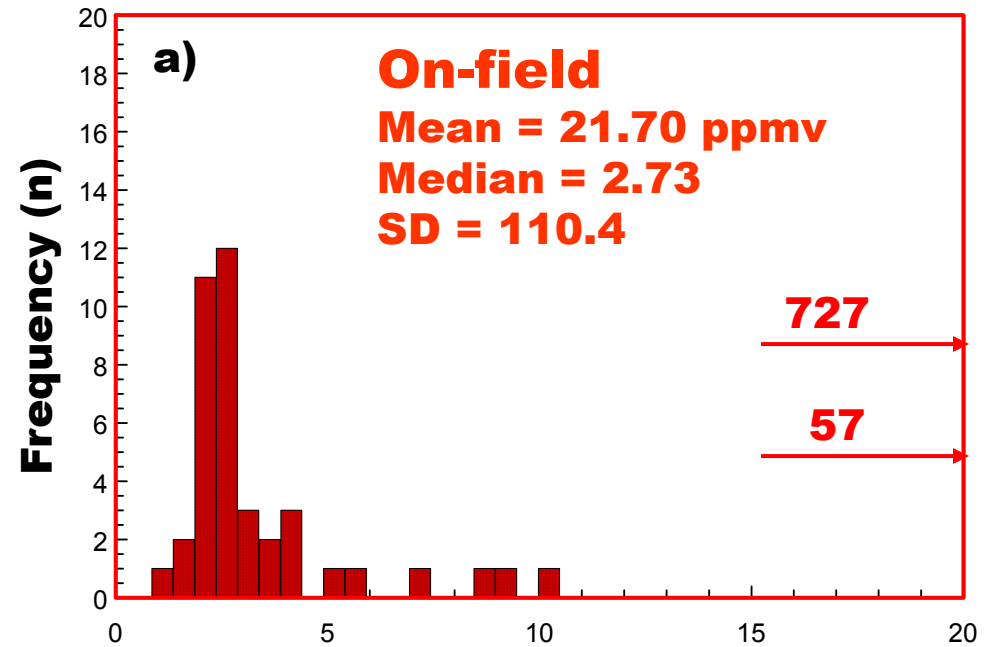
Winter 2001/02

Note that some negative fluxes still occur in winter



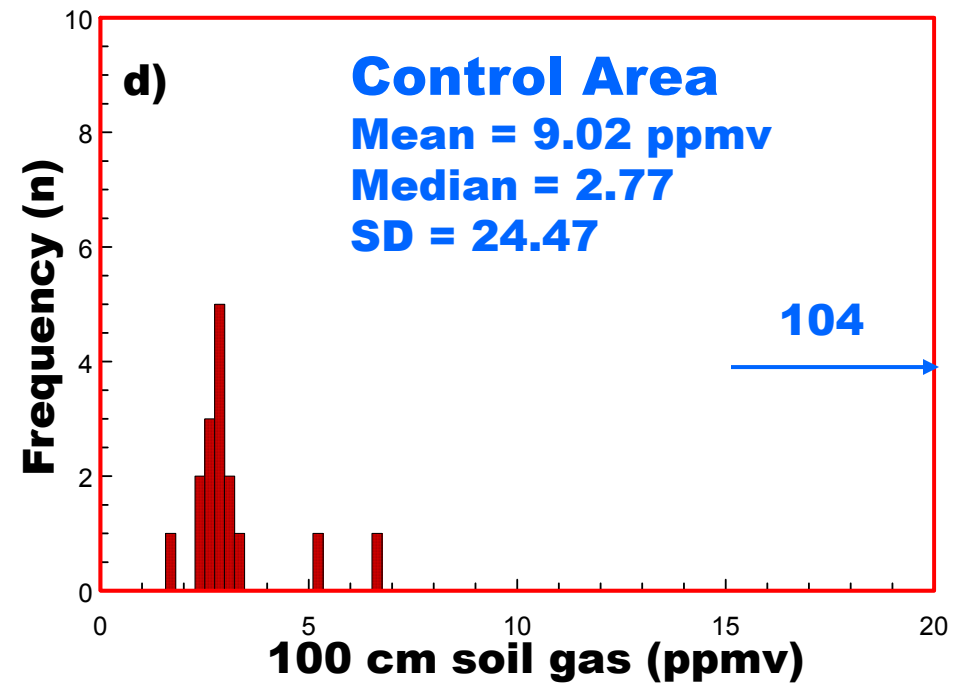
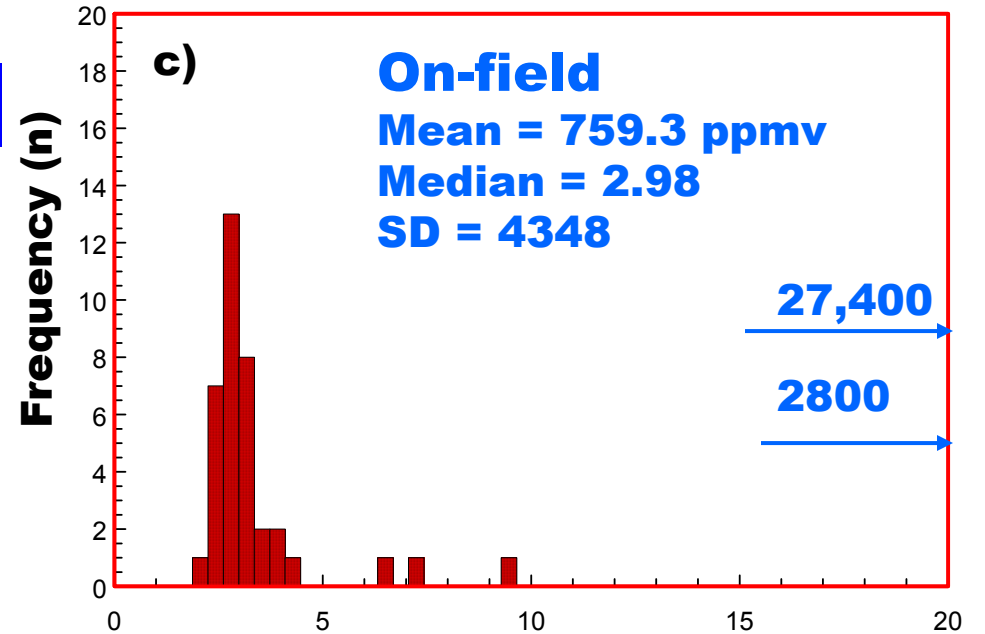
Rangely 100 cm soil gas CH₄

Summer 2001



Rangely 100 cm soil gas CH₄

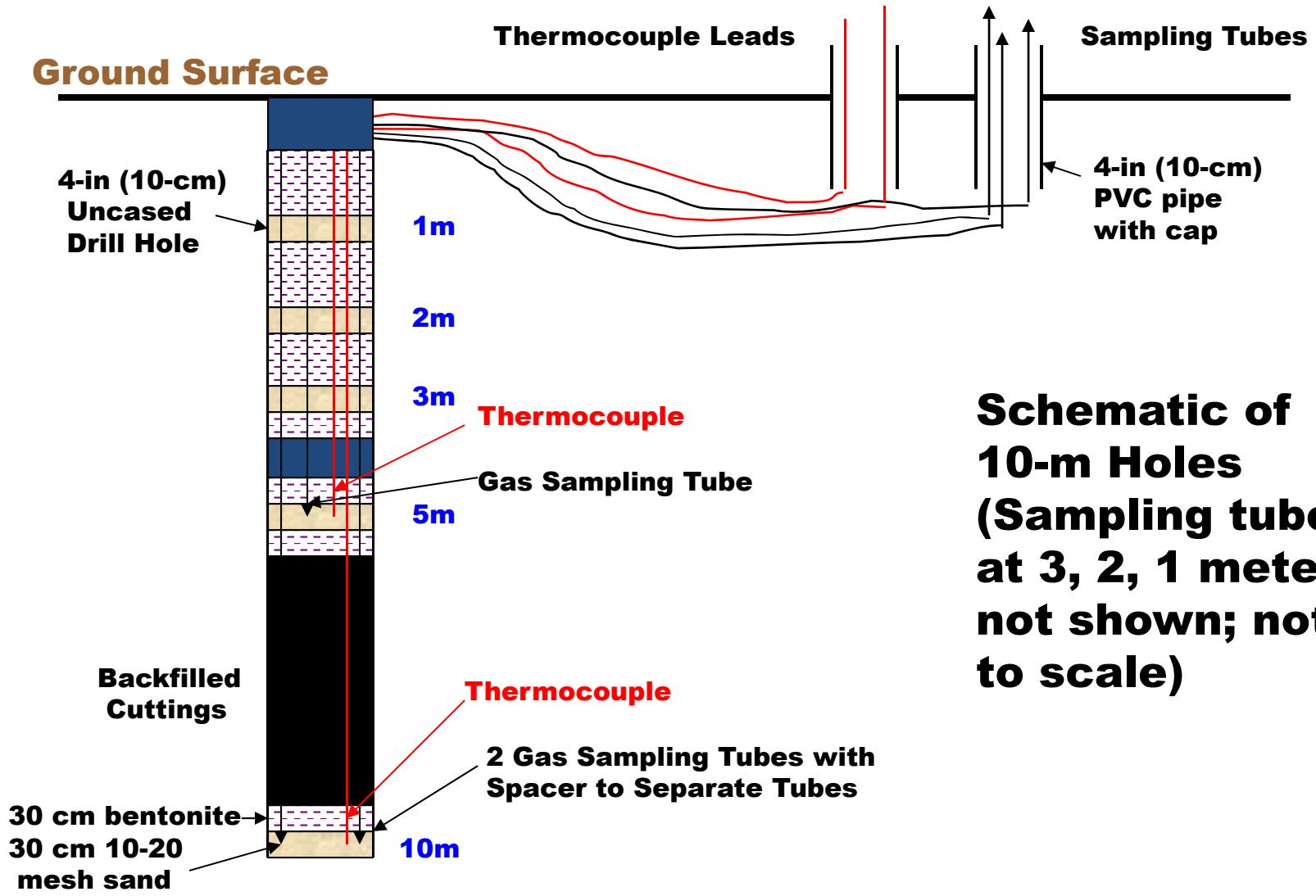
Winter 2001/02



SELECTION OF “INTERESTING” LOCATIONS FOR 10-M HOLES

- Magnitude and direction of both CO₂ and CH₄ fluxes,
- Magnitude and gradient of both CO₂ and CH₄ concentrations in soil gas profiles,
- Isotopic shift in 60-, and 100 cm soil gas CO₂ relative to atmospheric CO₂,
- Selected locations with microseepage evident, and with microseepage absent; **soil gas contributes more to the selection process than fluxes; shallow concentration gradients will be useful on Mars.**

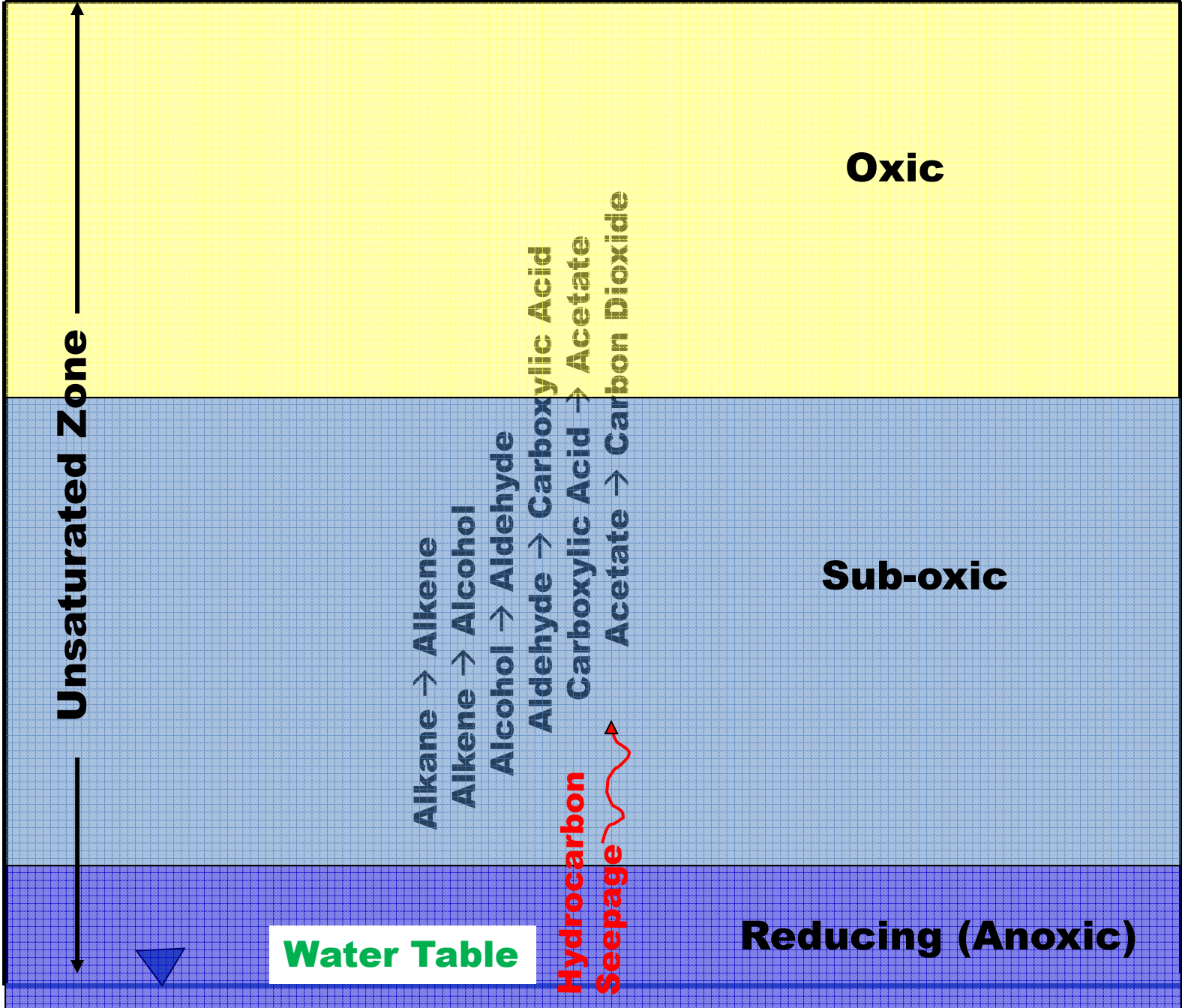




Schematic of 10-m Holes (Sampling tubes at 3, 2, 1 meters not shown; not to scale)

Depth

Surface



Unsaturated Zone

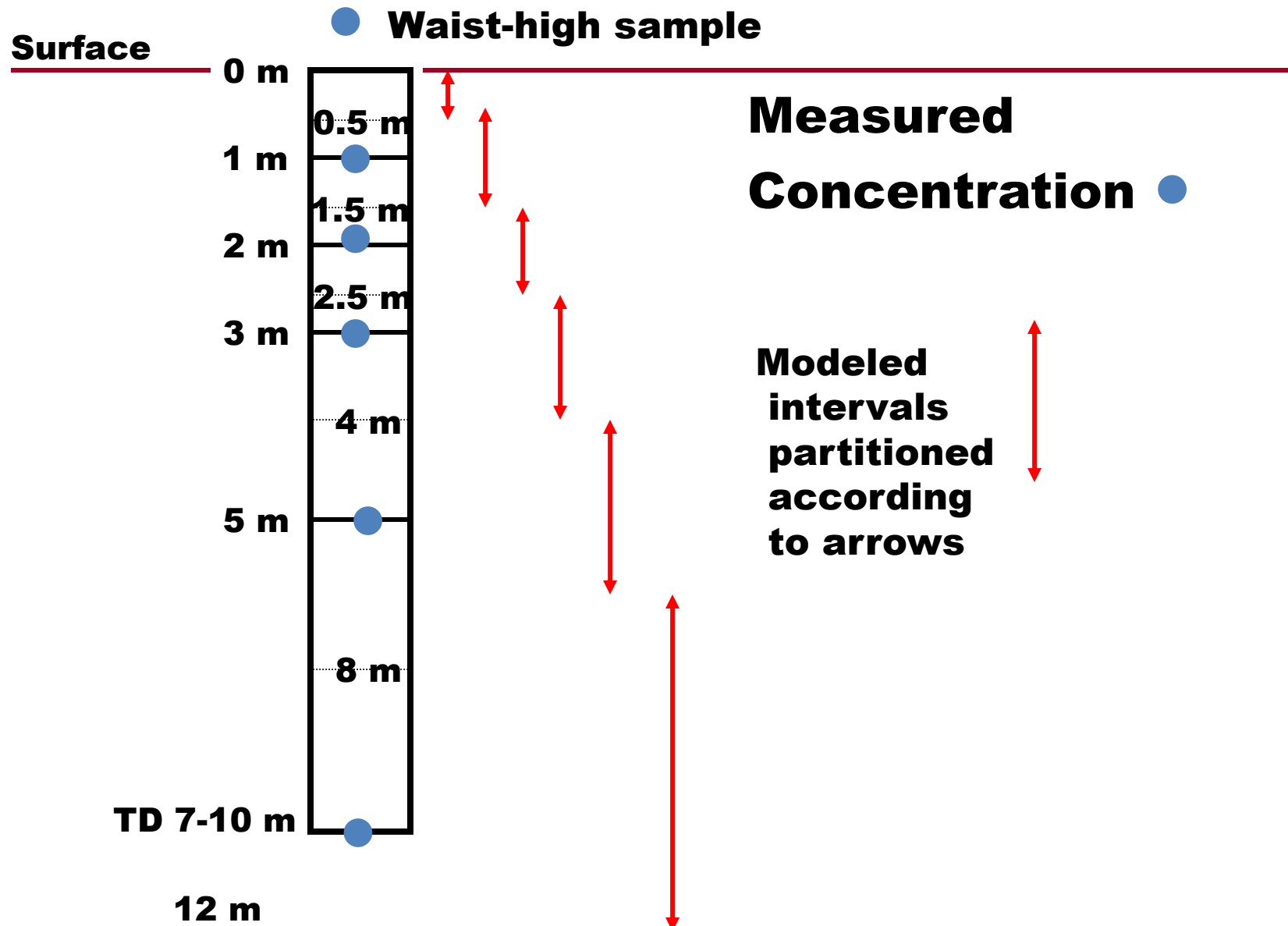
Oxic

Sub-oxic

Water Table

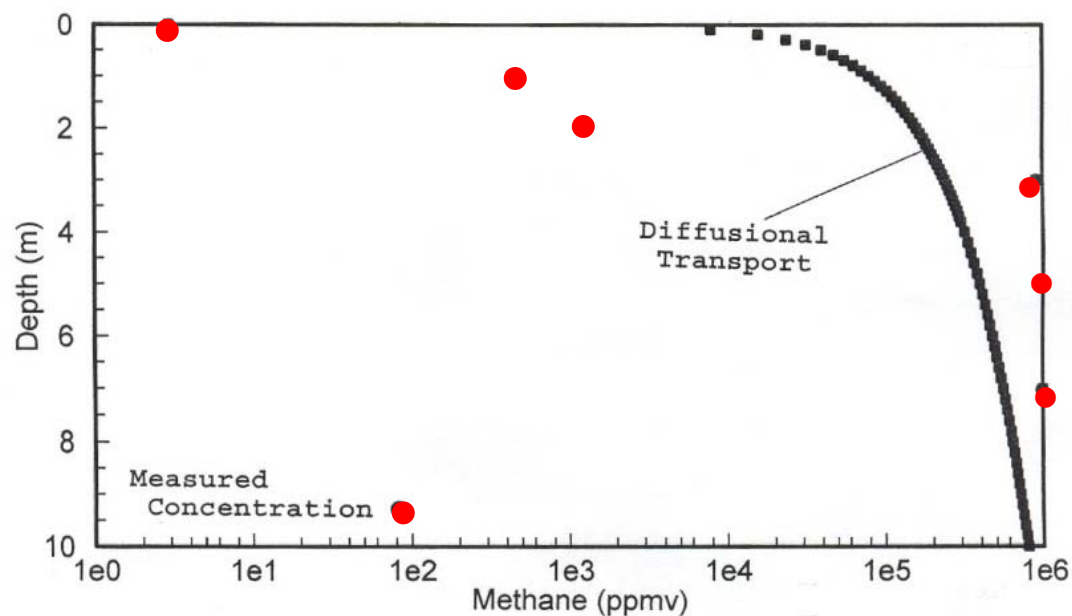
Reducing (Anoxic)

MODELING INTERVALS FOR “DEEP” (10-meter) HOLES

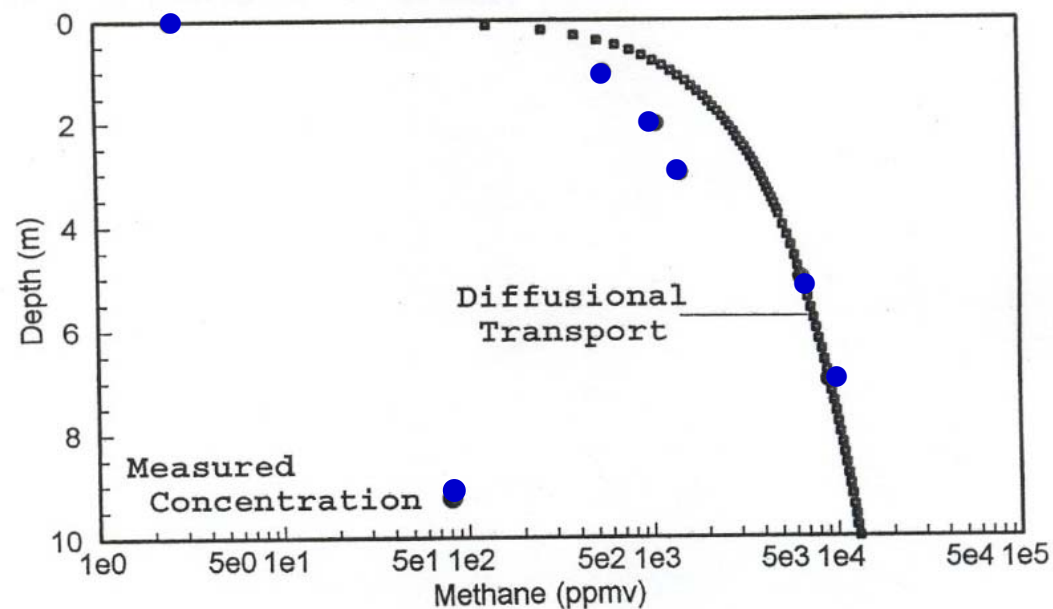


Rangley Measured and Modeled CH₄ Profile for 10-m Hole 01; Diffusion Only

Summer, 2002

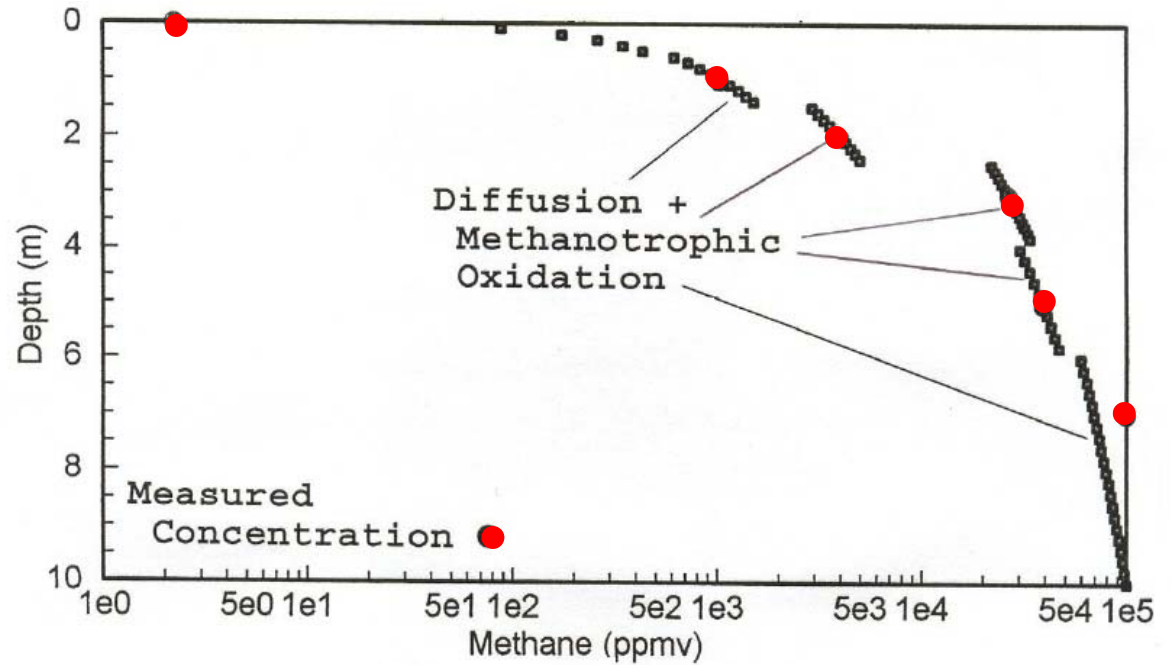


Winter, 2001/02

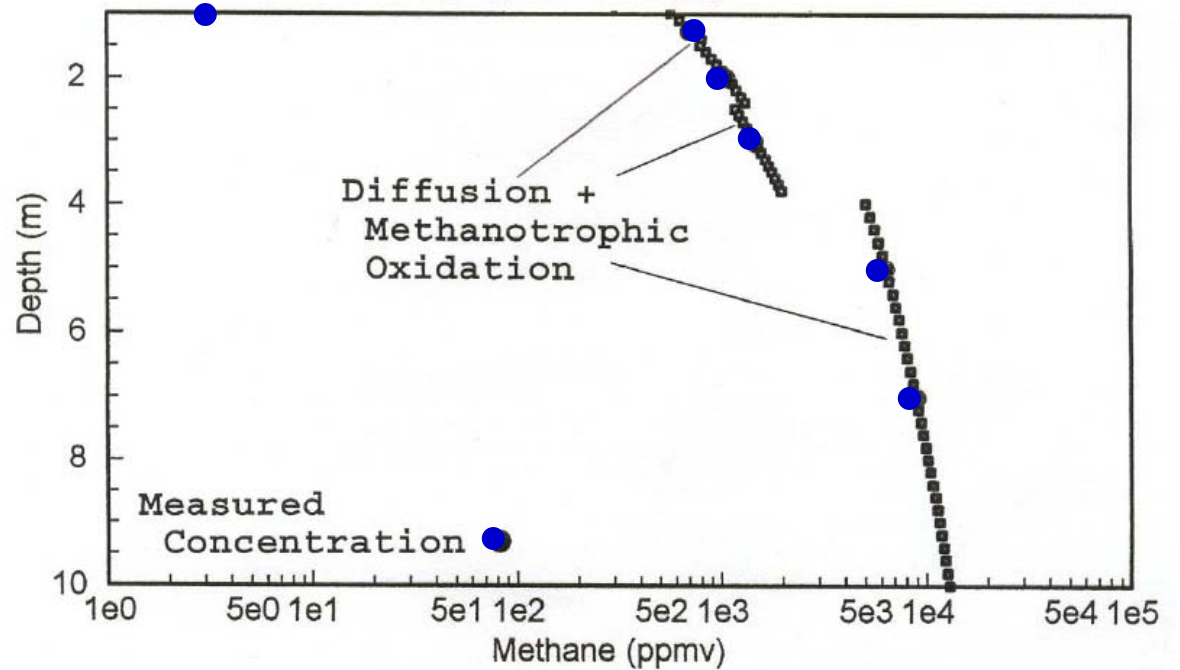


Rangely Measured and Modeled CH₄ Profile for 10-m Hole 01 Diffusion and Methanotrophic Oxidation

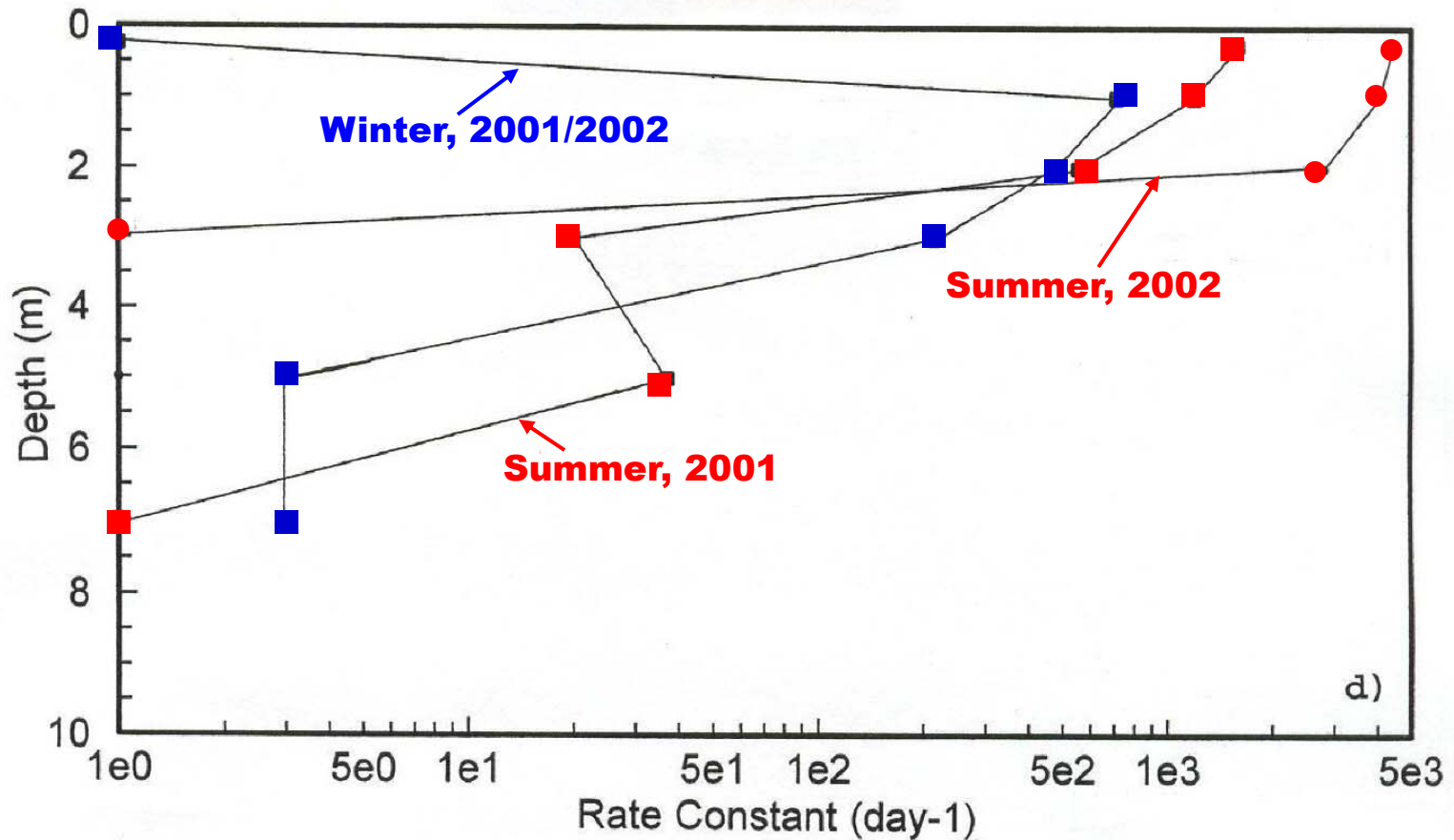
Summer, 2001



Winter, 2001/02

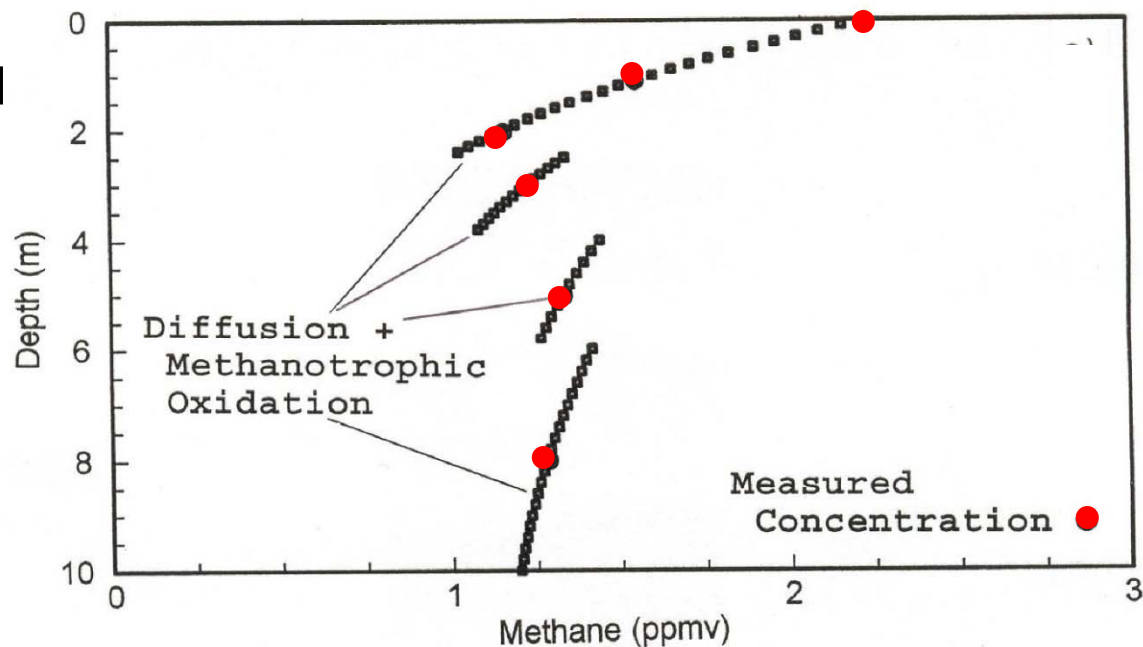


First-order Degradation (Methanotrophy) Rate Constants for CH₄; “Deep” Hole 01



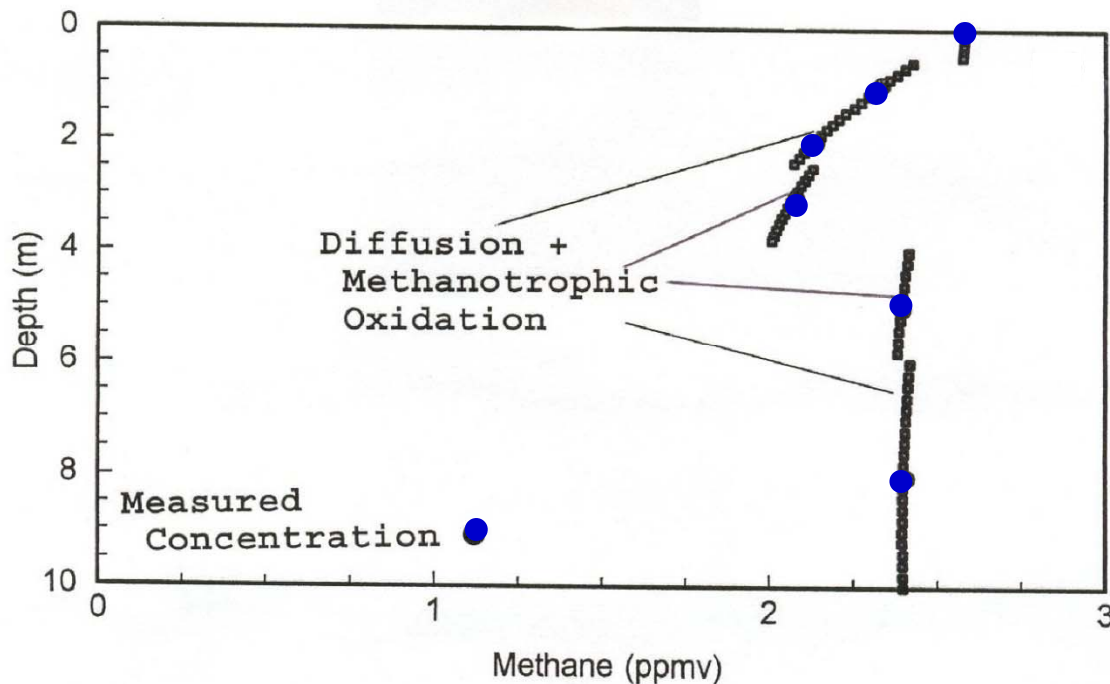
Rangely Measured and Modeled CH₄ for 10-m Hole 28; Diffusion and Methanotrophic Oxidation

Summer, 2001



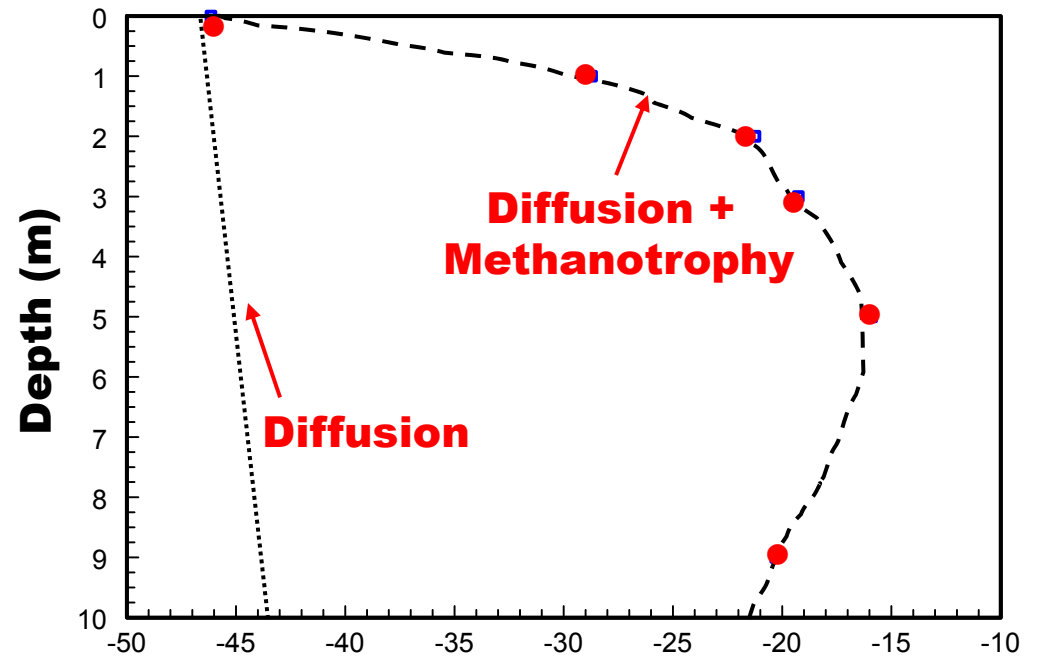
Winter, 2001/02

Note sub-atmospheric concentration of CH₄. A lower limit for methanotrophy not observed.

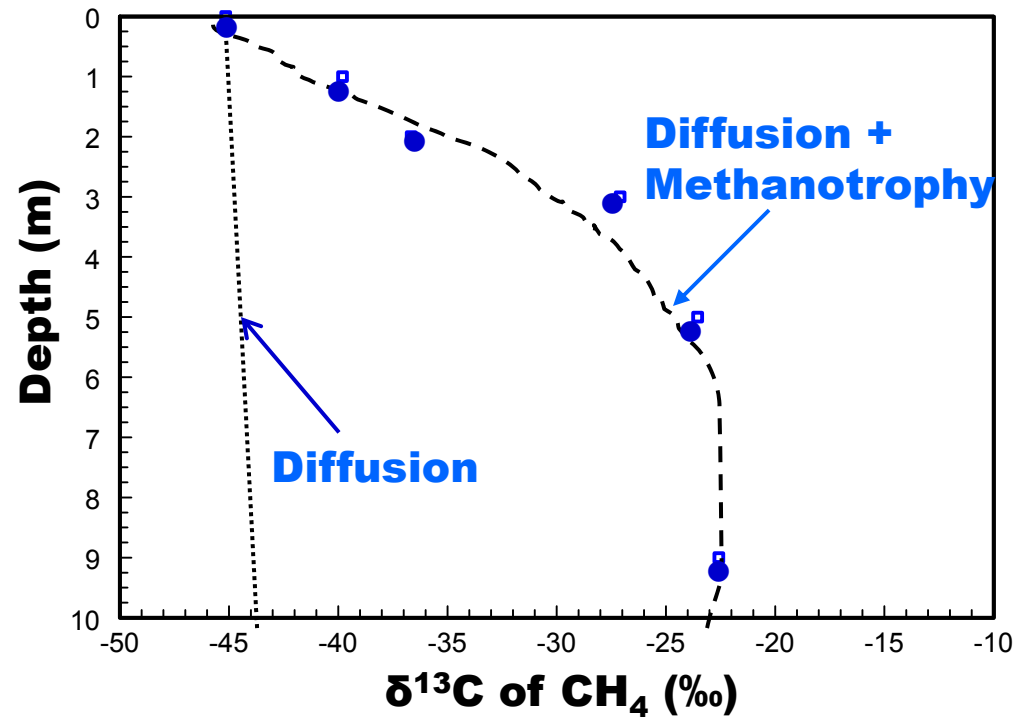


**Isotopic shift in $\delta^{13}\text{C}$ of CH_4
in anomalous 10-m Hole 03
at Rangely;
Reservoir = -40.71‰**

Summer, 2002

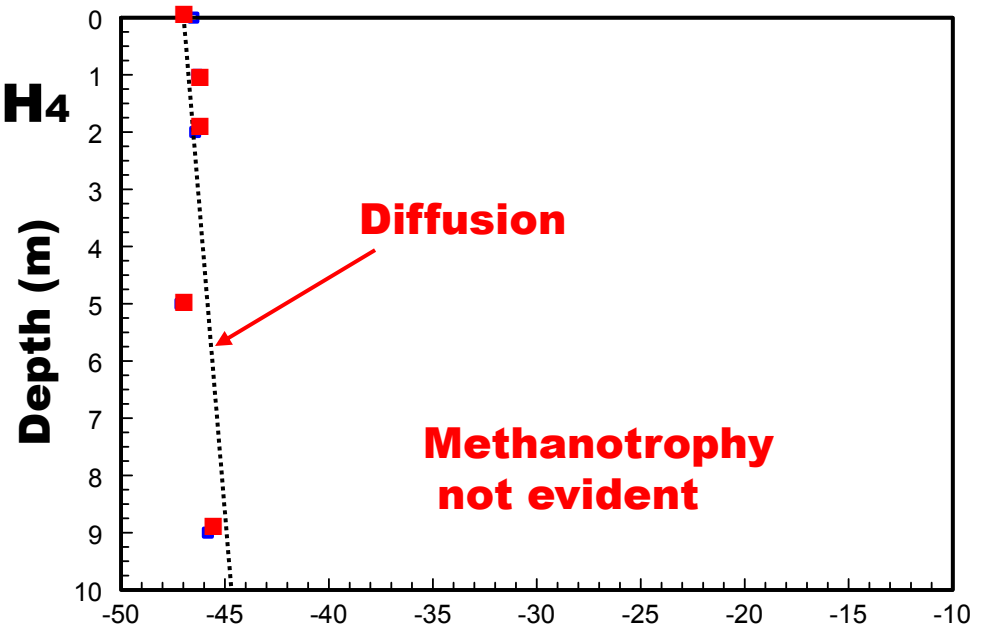


Winter, 2001/02

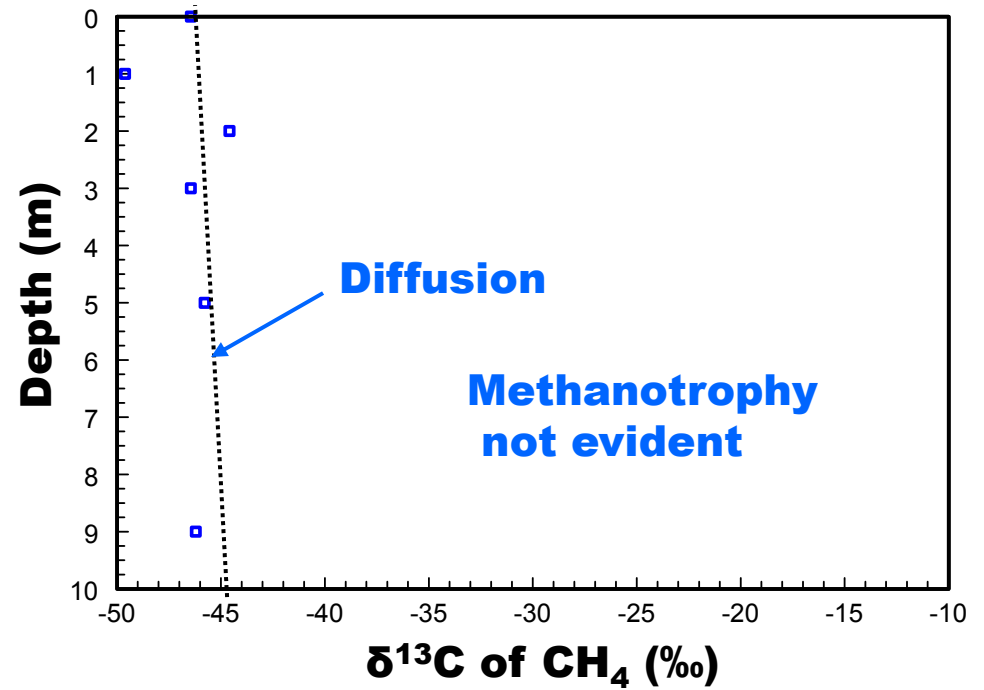


**Isotopic shift in $\delta^{13}\text{C}$ of CH_4
in non-anomalous 10-m
Hole 34 at Rangely
Reservoir = -40.71‰**

Summer, 2002



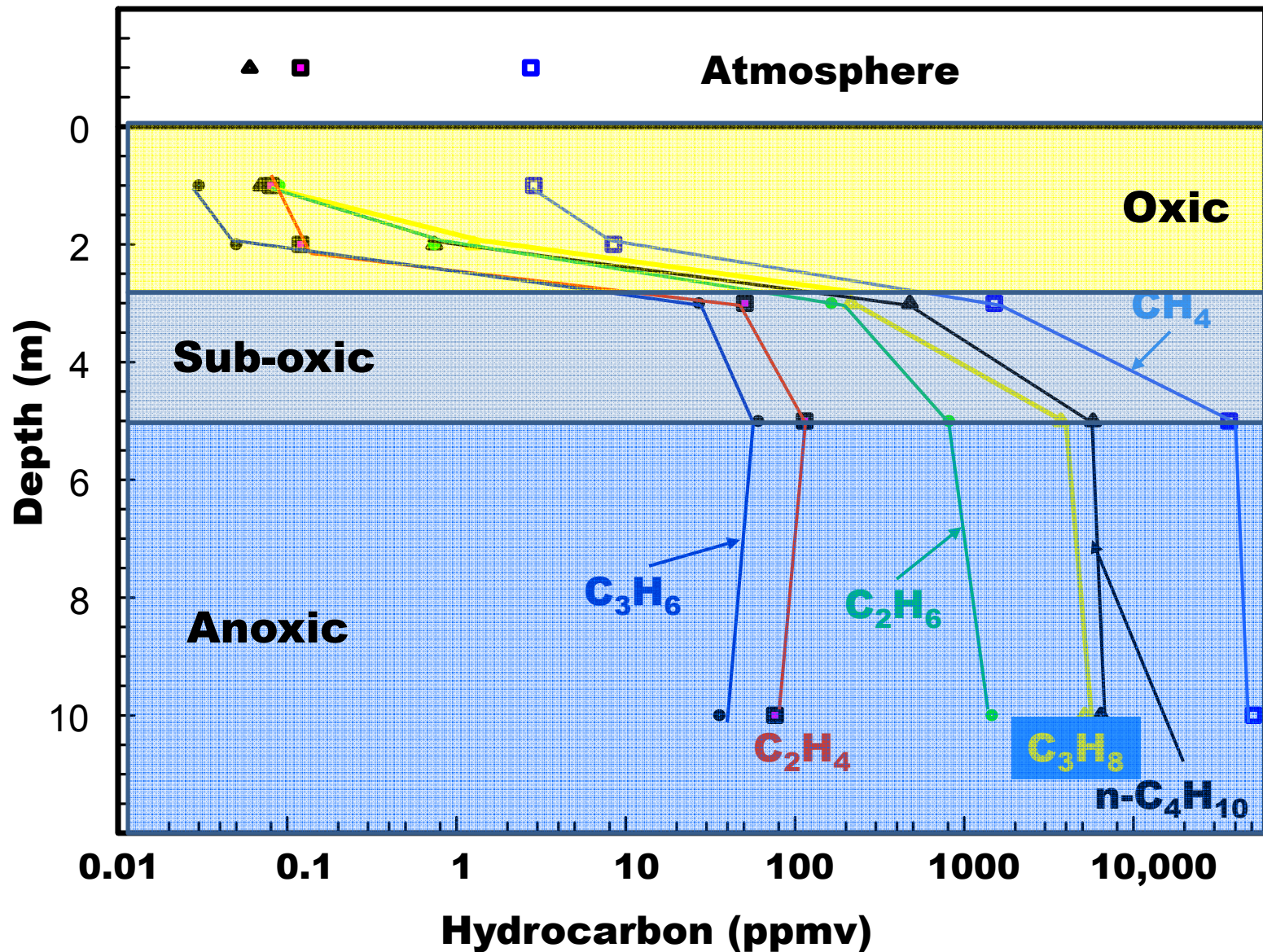
Winter, 2001/02



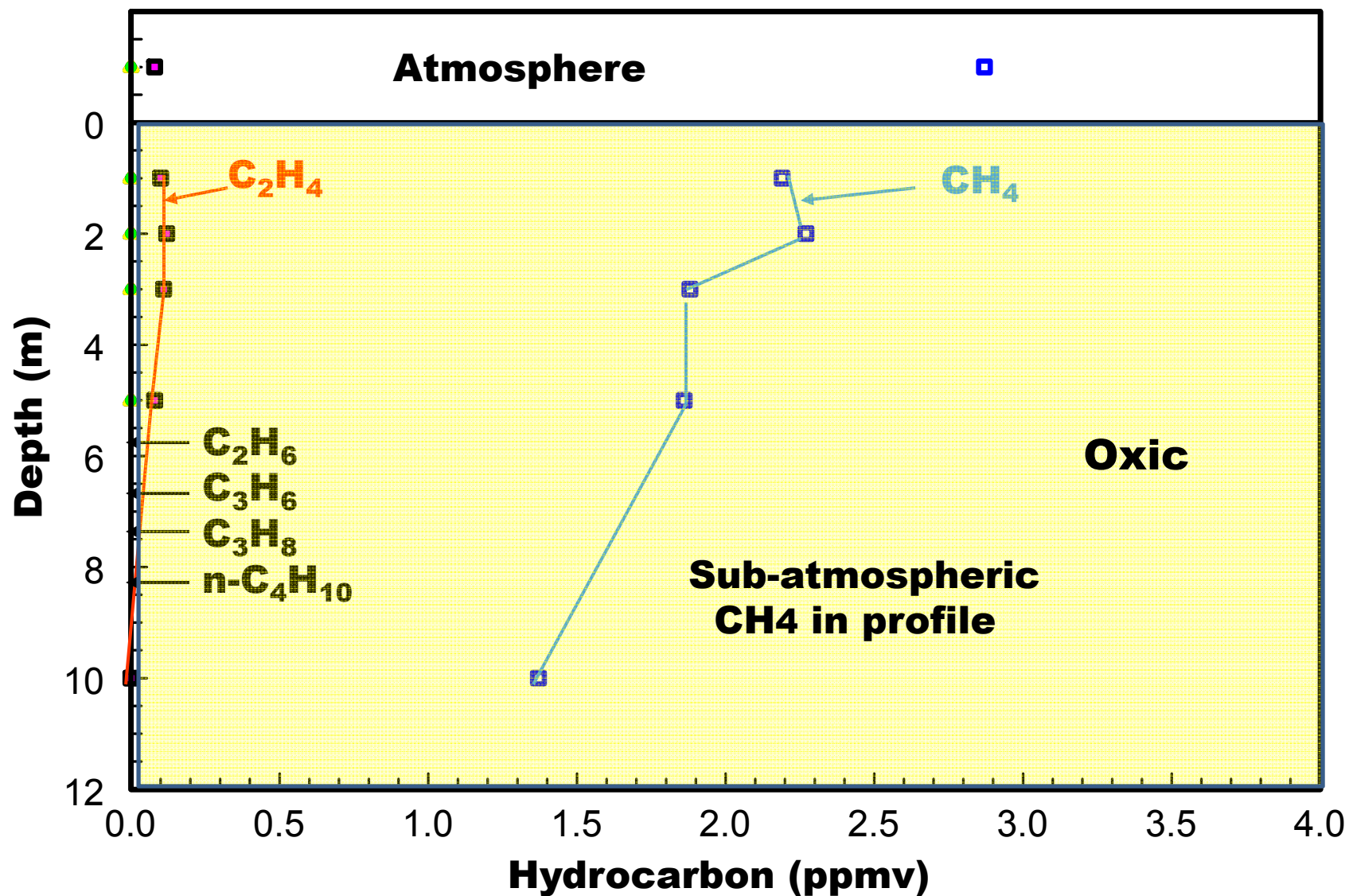
ESTIMATION OF CH₄ MICROSEEPAGE INTO THE ATMOSPHERE AT RANGELY (a start on Accounting)

- **The gross CH₄ microseepage into the atmosphere over 78 km² is 700±1200 tonnes year⁻¹ using the winter rate***
- **The net CH₄ 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 $\alpha = 0.015$.**

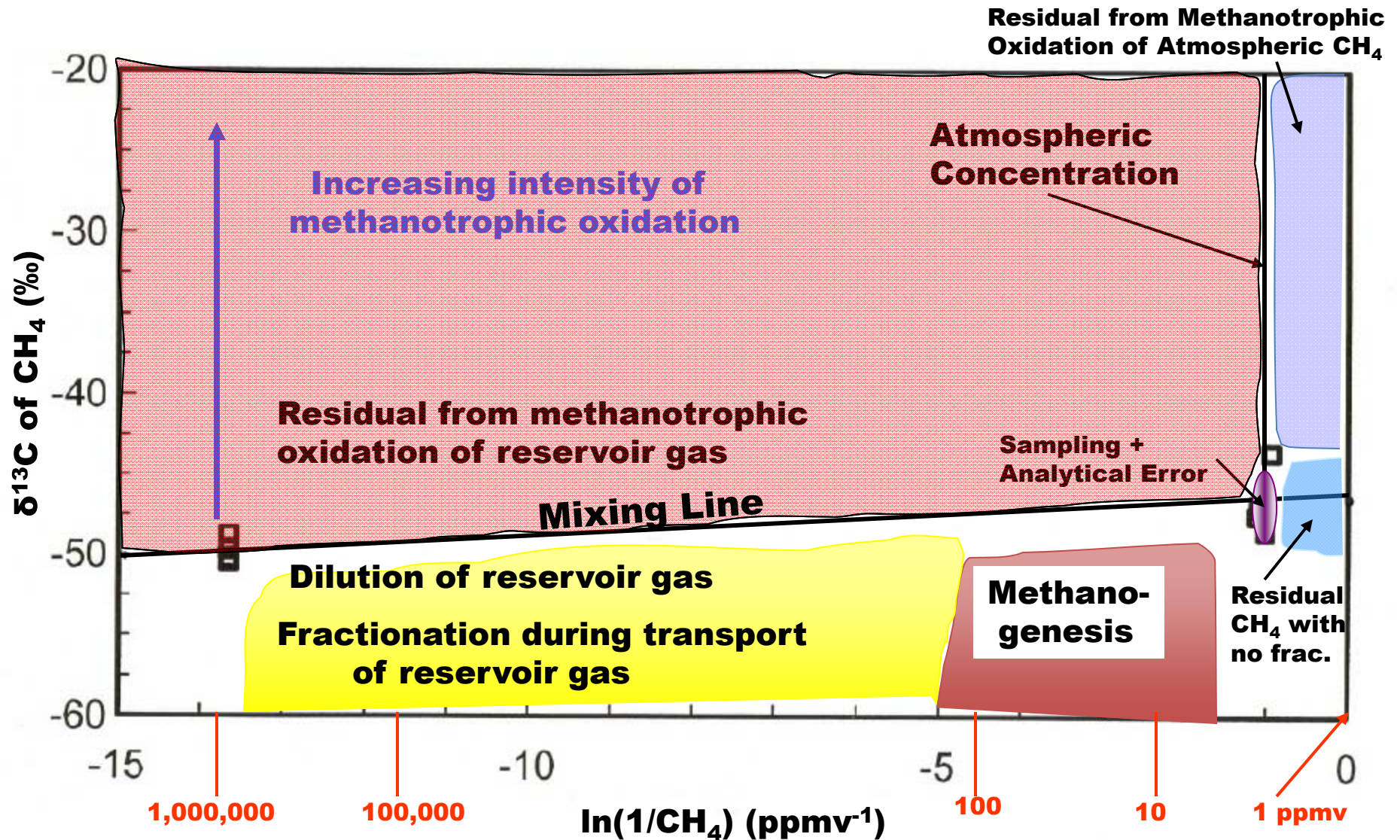
TEAPOT DOME – LIGHT HYDROCARBONS IN ANOMALOUS 10-m HOLE 17; JANUARY, 2005



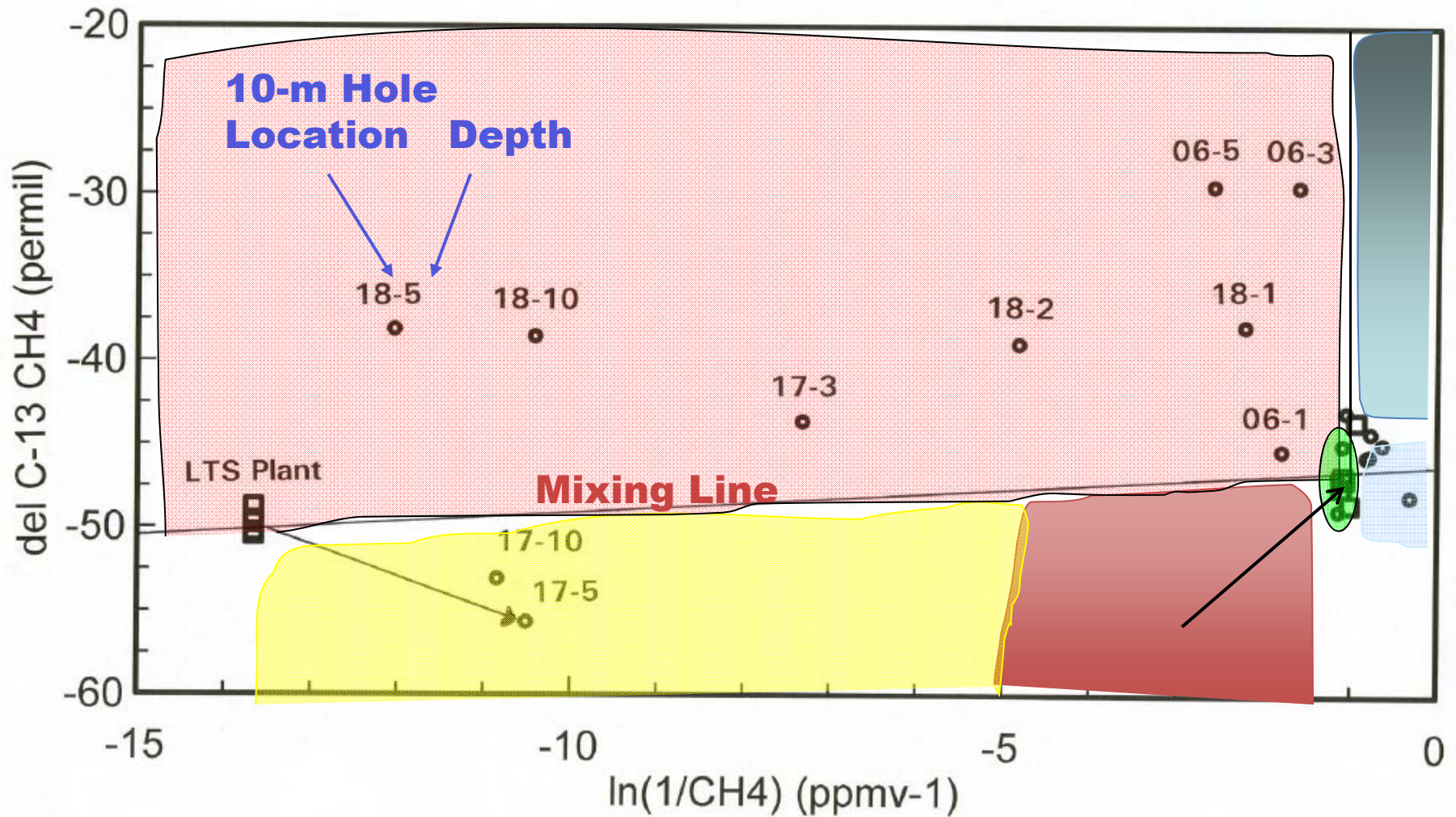
TEAPOT DOME – LIGHT HYDROCARBONS IN NON-ANOM.10-m HOLE 02; JANUARY, 2005



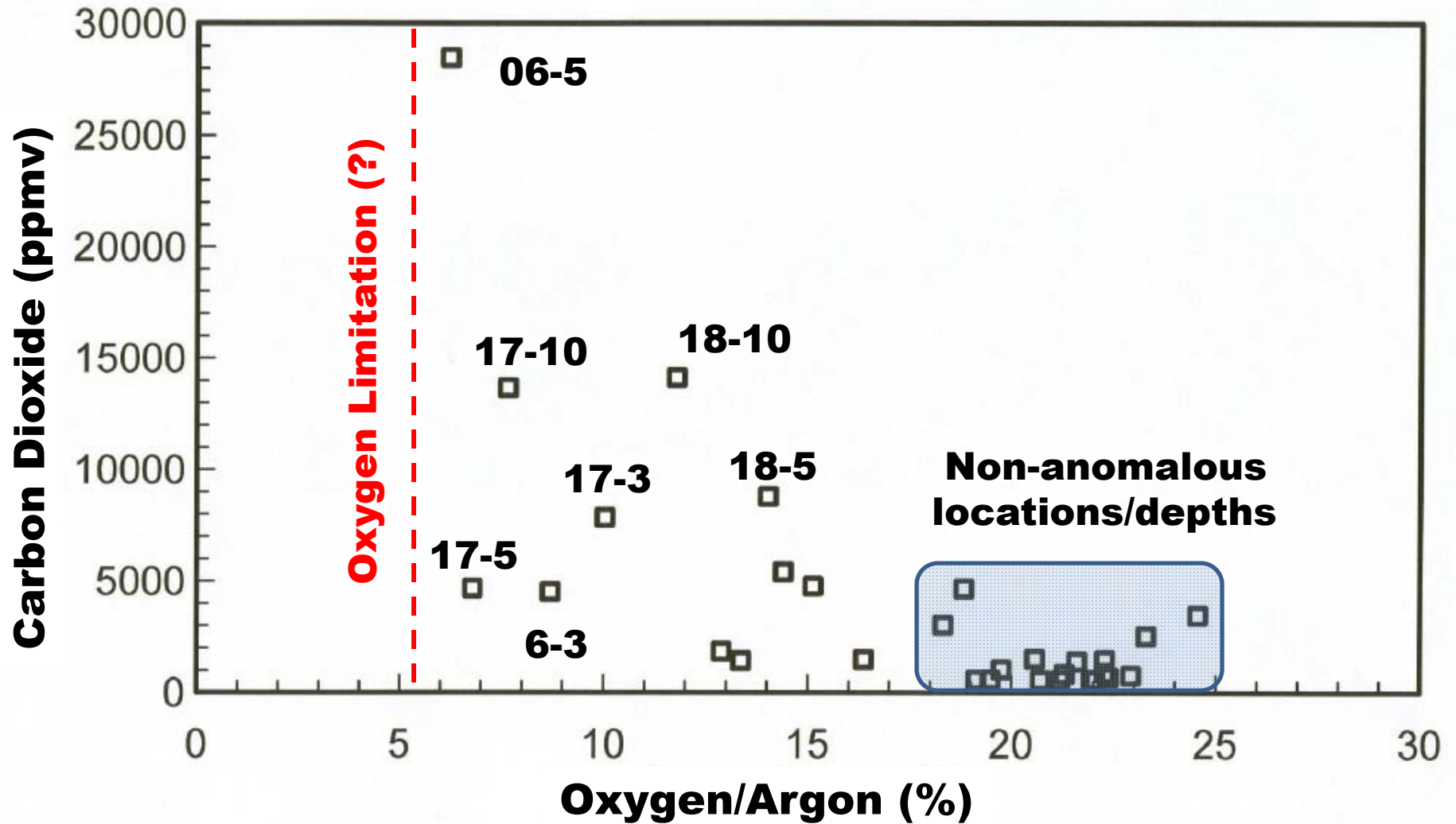
Generic $\delta^{13}\text{C}$ of CH_4 vs. $\ln(1/\text{CH}_4)$ Diagram



TEAPOT DOME – 10-m HOLES JANUARY, 2005

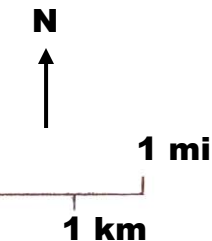
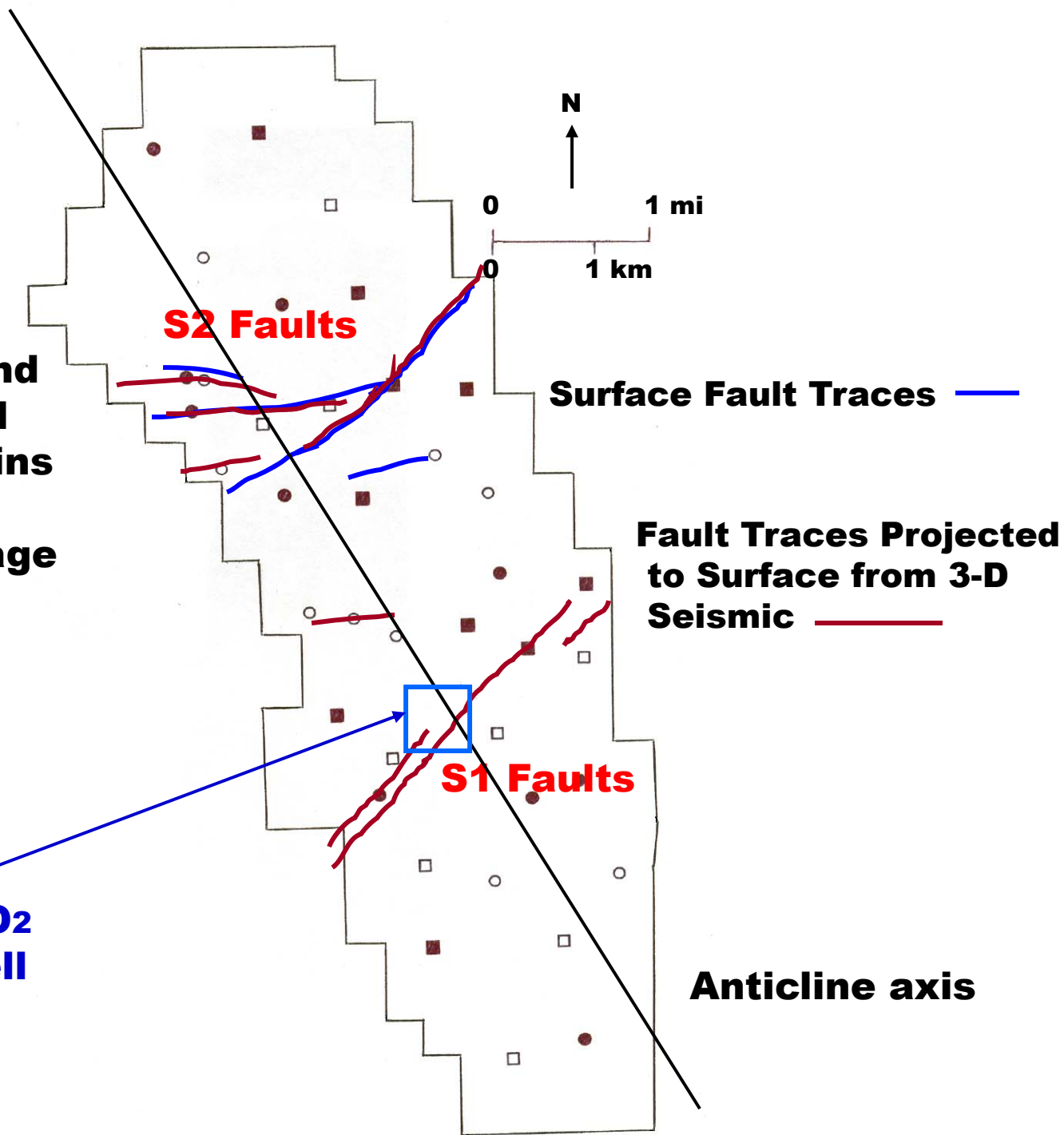


Teapot Dome – Winter, 2005 10-m Holes



Tensional faults and fractures form and fill with calcite veins as a function of hydrocarbon leakage

**Section 10;
Proposed CO₂
Injection Well**



S2 Faults

Surface Fault Traces —

Fault Traces Projected to Surface from 3-D Seismic —

S1 Faults

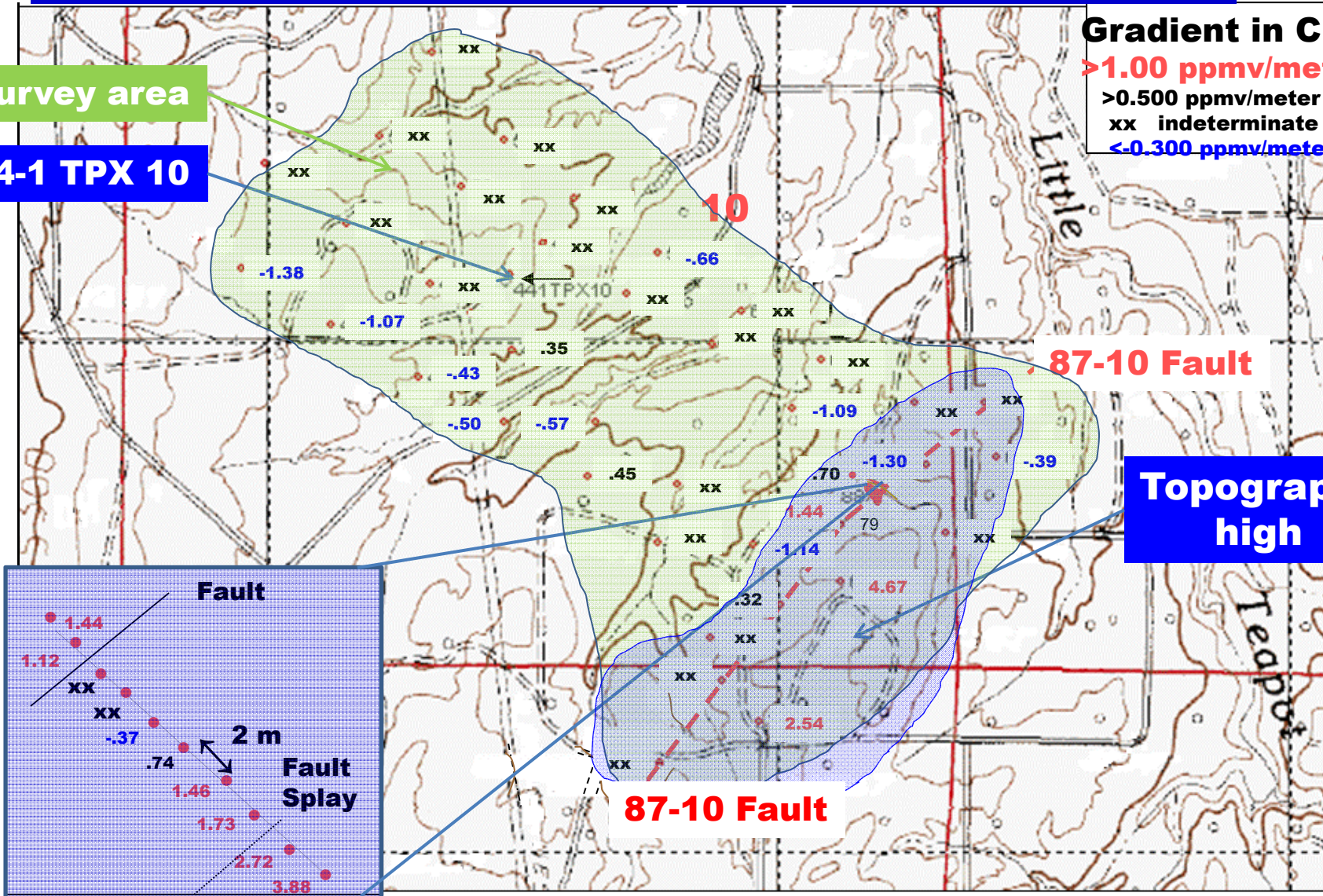
Anticline axis

Teapot Dome – Section 10 Soil Gas Survey

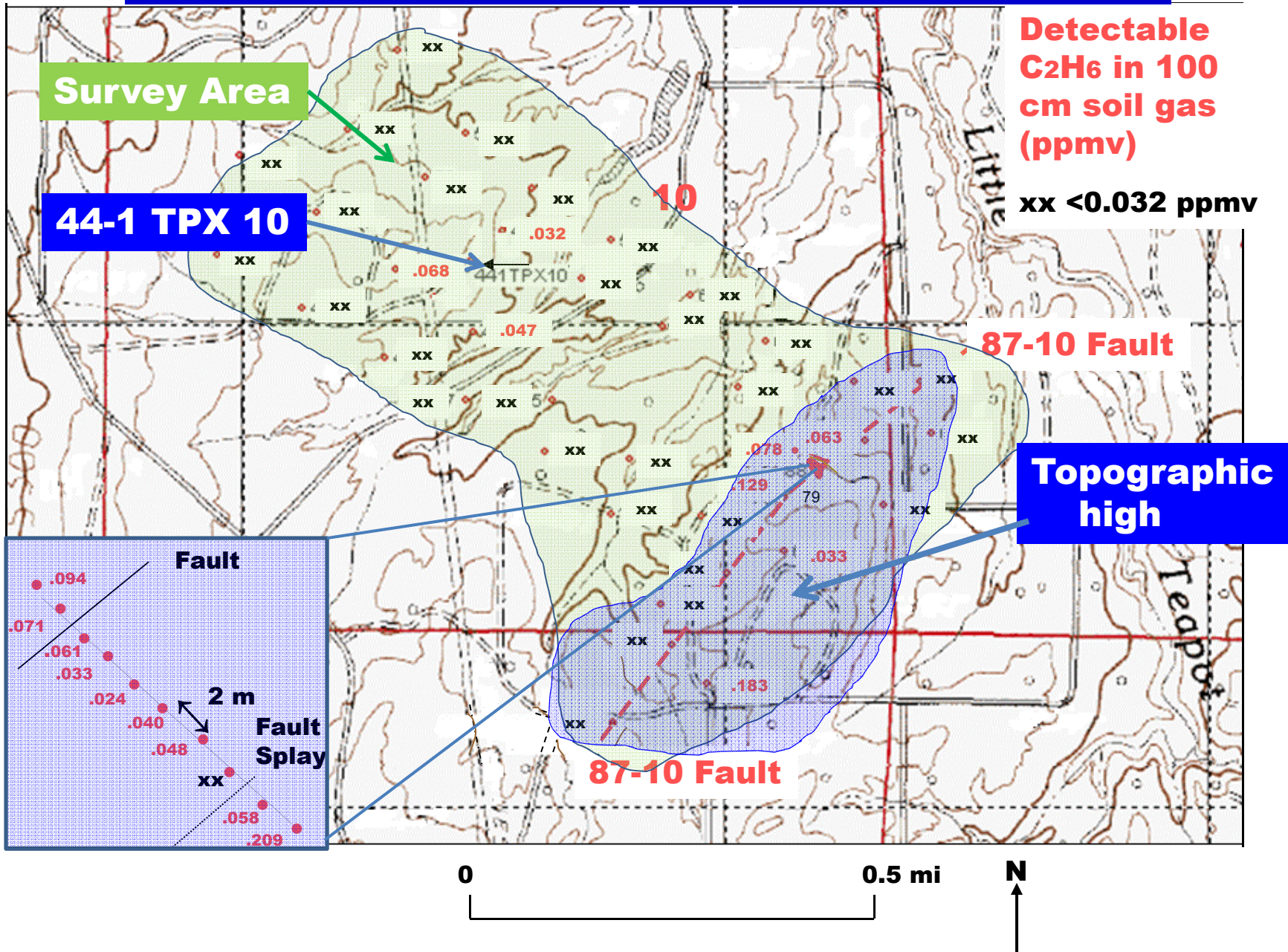
Gradient in CH₄
>1.00 ppmv/meter
>0.500 ppmv/meter
xx indeterminate
<0.300 ppmv/meter

Survey area

44-1 TPX 10



Teapot Dome – Section 10 Survey Area

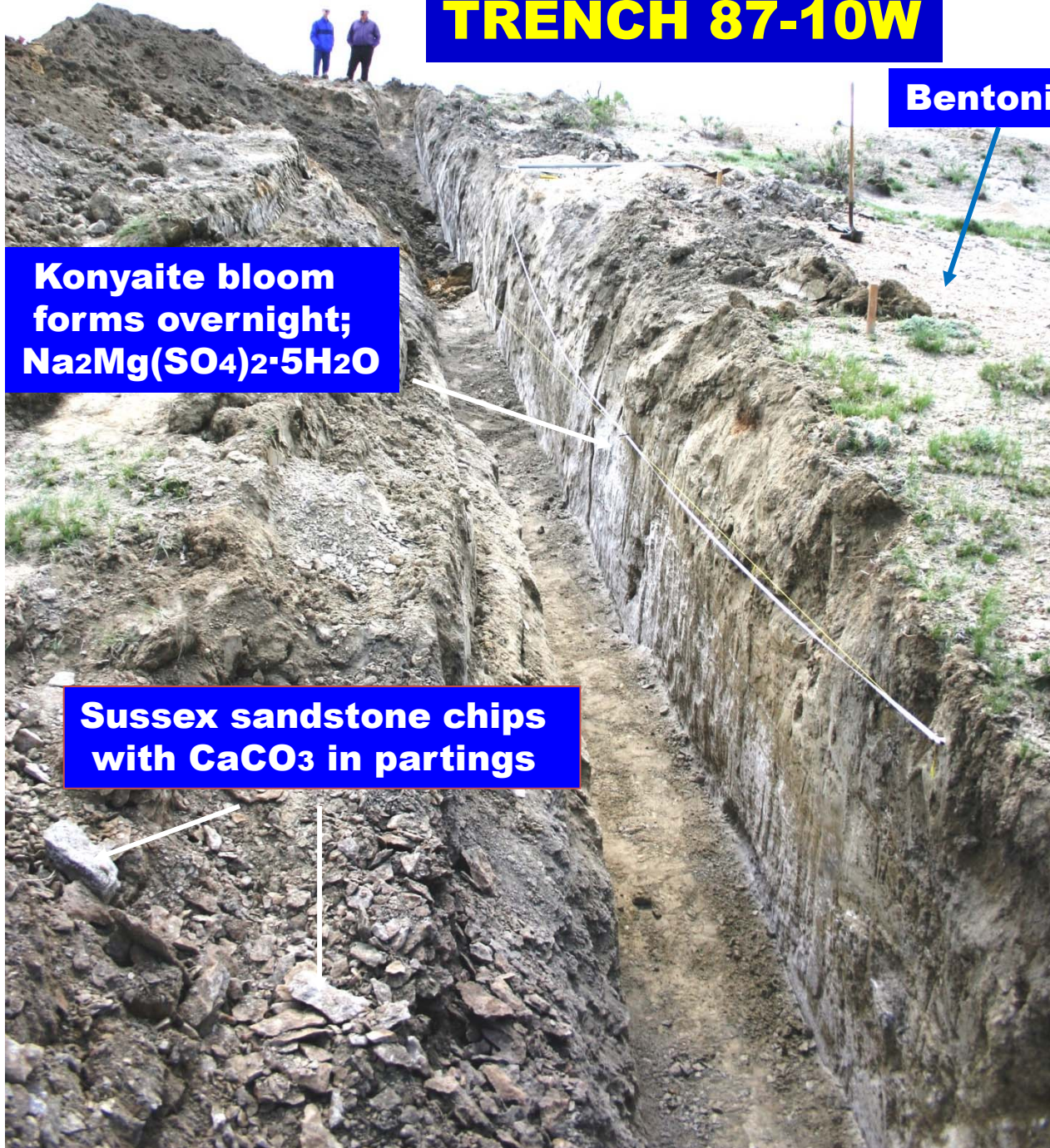


TRENCH 87-10W

Bentonite-rich "soil"

Konyaite bloom
forms overnight;
 $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$

Sussex sandstone chips
with CaCO_3 in partings

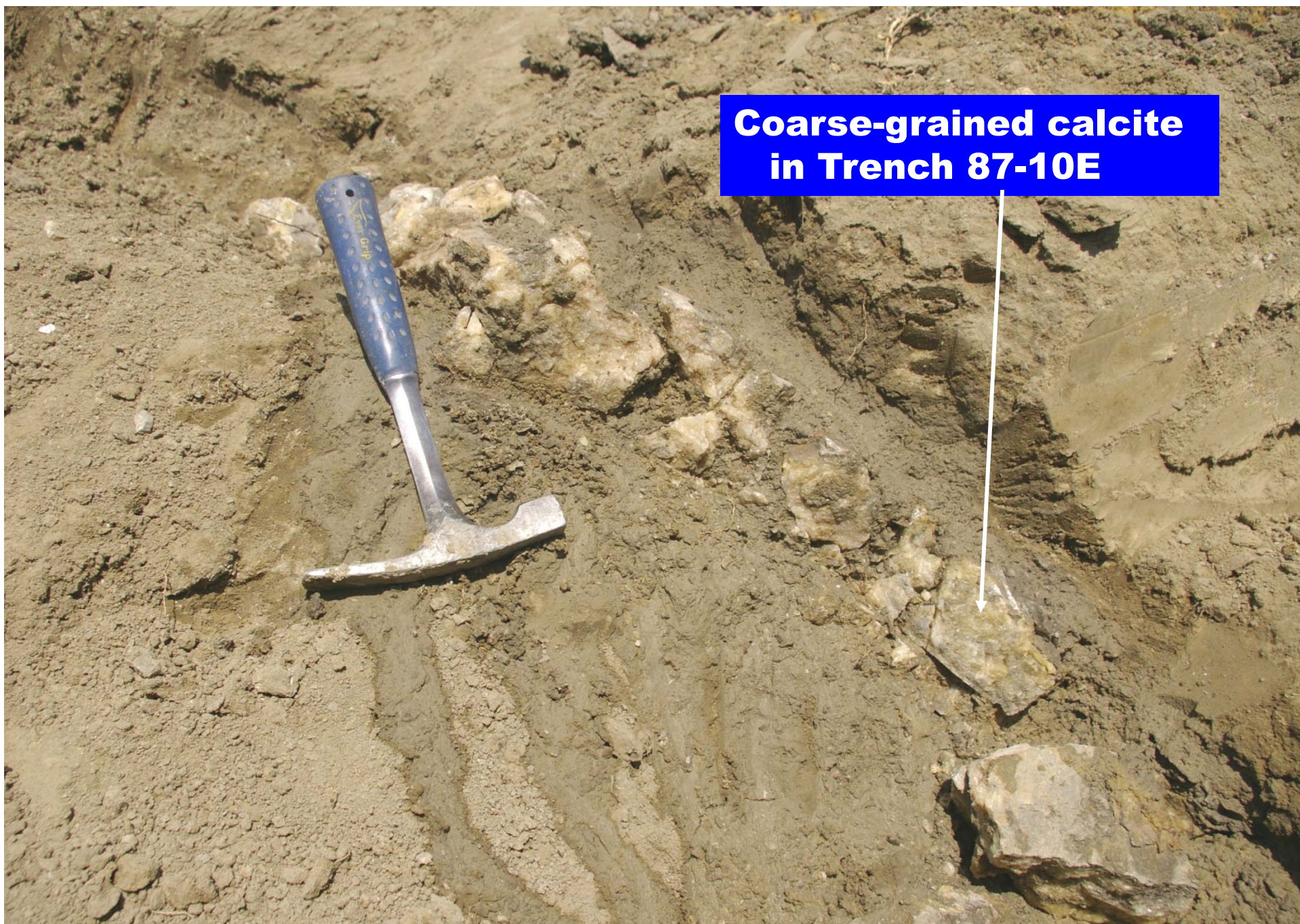


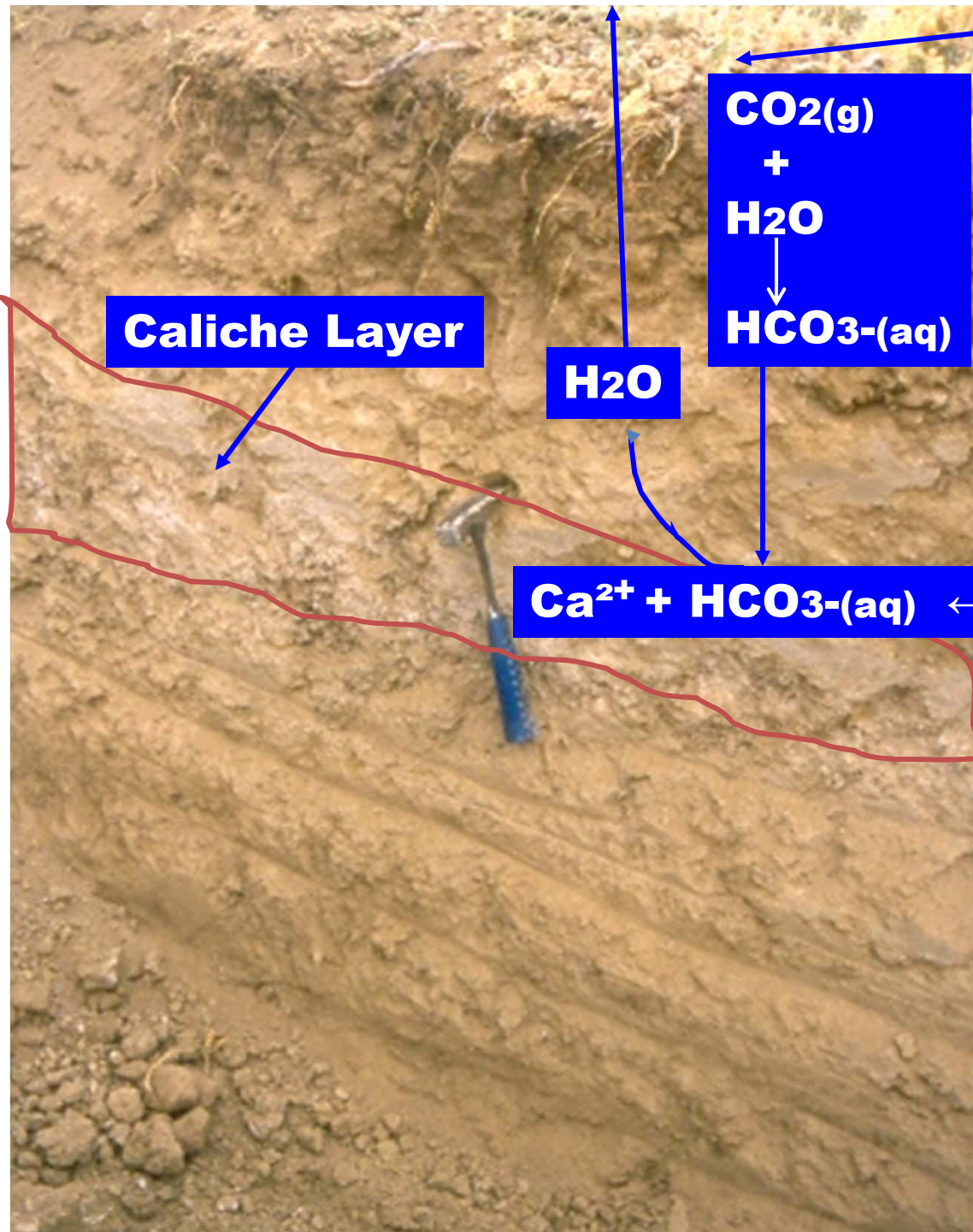
An aerial photograph of a vast, flat, and extremely dry landscape. The ground is covered in a dense network of polygonal cracks, characteristic of evaporite deposits. The color of the ground is a mix of light grey and dark brown, indicating different mineral compositions. Sparse, low-lying green and brown shrubs are scattered across the cracked surface. A blue banner with yellow text is overlaid on the upper portion of the image, and another blue banner with white text is overlaid on the lower portion.

Surface Evaporite on Marine Shales

Konyaite has a bitter taste; nahcolite more alkaline

**Coarse-grained calcite
in Trench 87-10E**





$\delta^{13}\text{C} = -11.48\text{‰}$

Caliche Layer

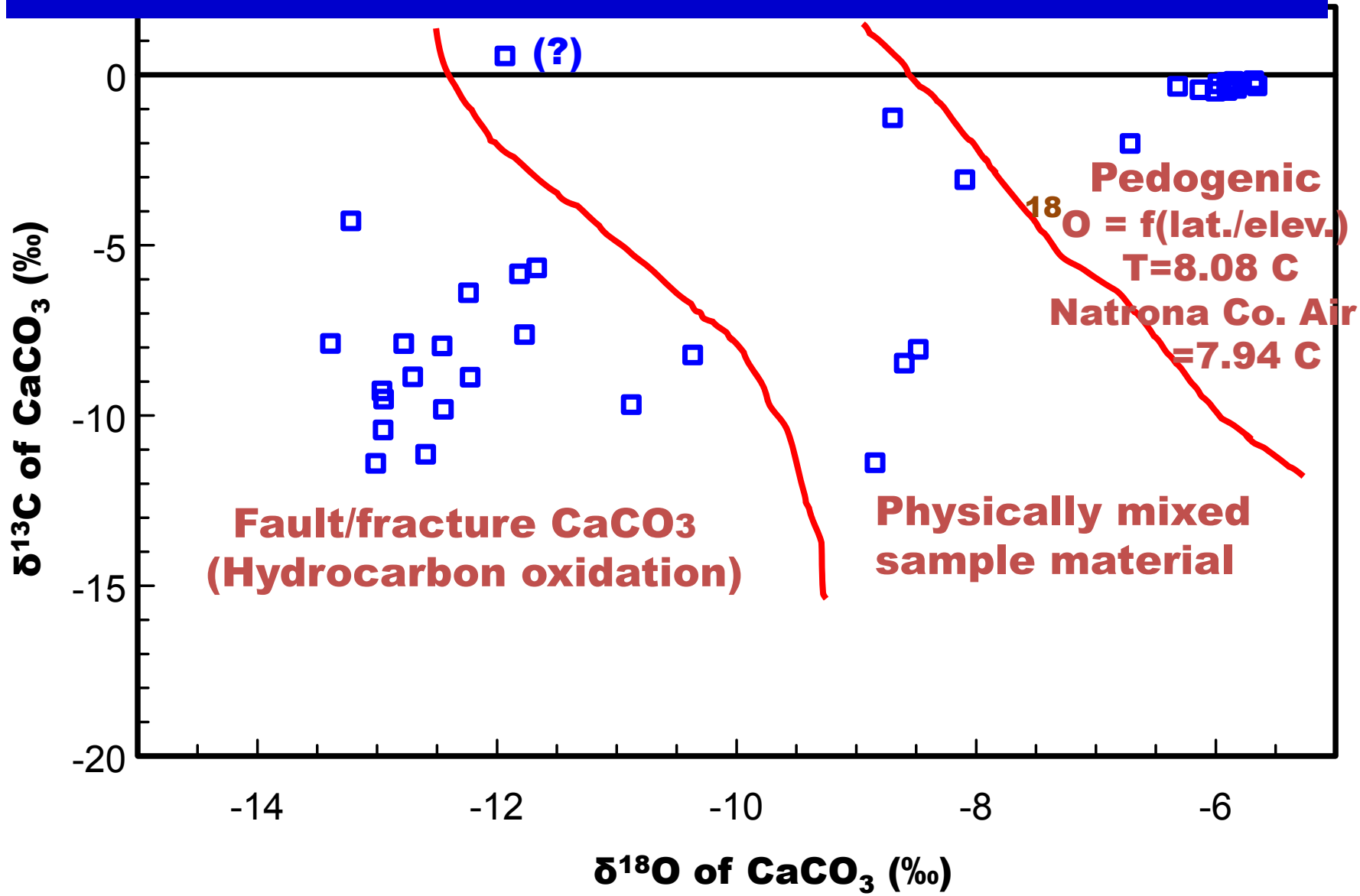
H_2O

**$\text{CO}_2(\text{g})$
+
 H_2O
↓
 $\text{HCO}_3^-(\text{aq})$**

$\text{Ca}^{2+} + \text{HCO}_3^-(\text{aq}) \leftrightarrow \text{CaCO}_3(\text{s})$

$\delta^{13}\text{C} = -1.95\text{‰}$

TEAPOT DOME - SECTION 10 - TRENCHES 87-10W and 87-10E



INDIRECT INDICATORS OF GAS SEEPAGE

(from Klusman, 1993, Chapter 7)

Applicability to Mars

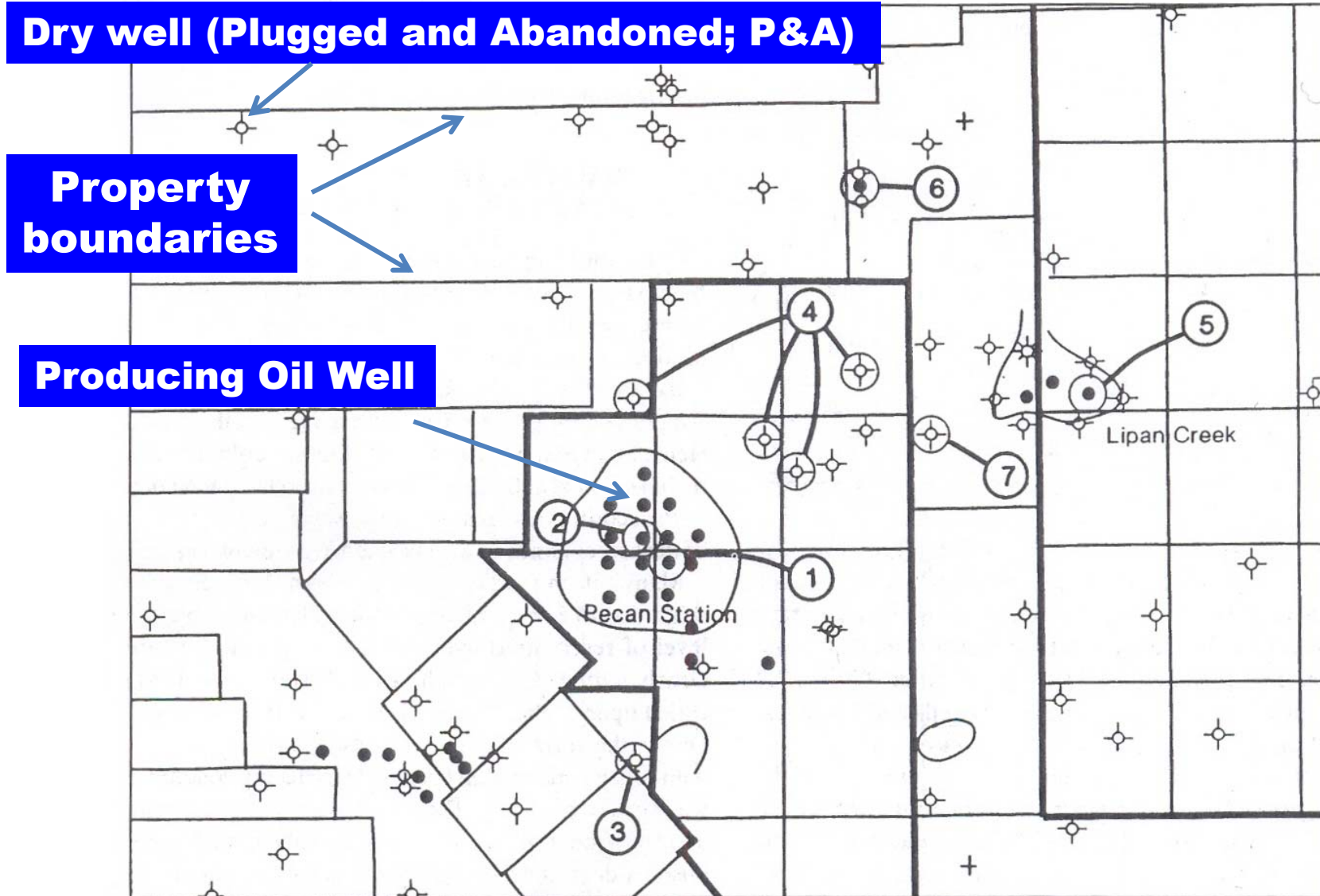
- Yes** Satellite imagery – Linear and circular features, topographic highs, color shifts indicative of alteration
- Yes** Secondary carbonate and sulphate minerals
- Yes** $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of cements and vein materials
- Yes** Electrical resistivity of shallow subsurface
- Yes** Horizontal gradient magnetic intensity indicative of iron reduction producing magnetite and sulphides
- Yes** Radiometric – redox processes inhibiting migration of uranium and potassium-40 in near-surface
- Yes** Gradients in temperature with depth – Heat flow related to mass flow because of poor thermal conductivity of rocks
- ?** Selected trace elements in soils – iodine, strontium, ratioed to iron as indicators of redox conditions

INDIRECT INDICATORS OF GAS SEEPAGE

Applicability to Mars

- ? Gradients in inert gases with depth – variable results because of high mobility of helium, high concentrations of neon and argon in the Earth atmosphere overwhelming a signal from depth**
- ? UV fluorescence of organics extracted from soil indicative of multi-ring structures**
- No Geobotany and biogeochemistry – Natural selection processes indicative of unusual soil chemistry**
- No Satellite radar – detection of oil film on sea surface**
- No Microbiological – Specific organisms tolerant of alcohols produced by stepwise oxidation**
- No Ground radar – indicative of polar molecules; water vapor as a “carrier gas.”**

Oil Production in Tom Green County, Texas (from Foote, 1986)

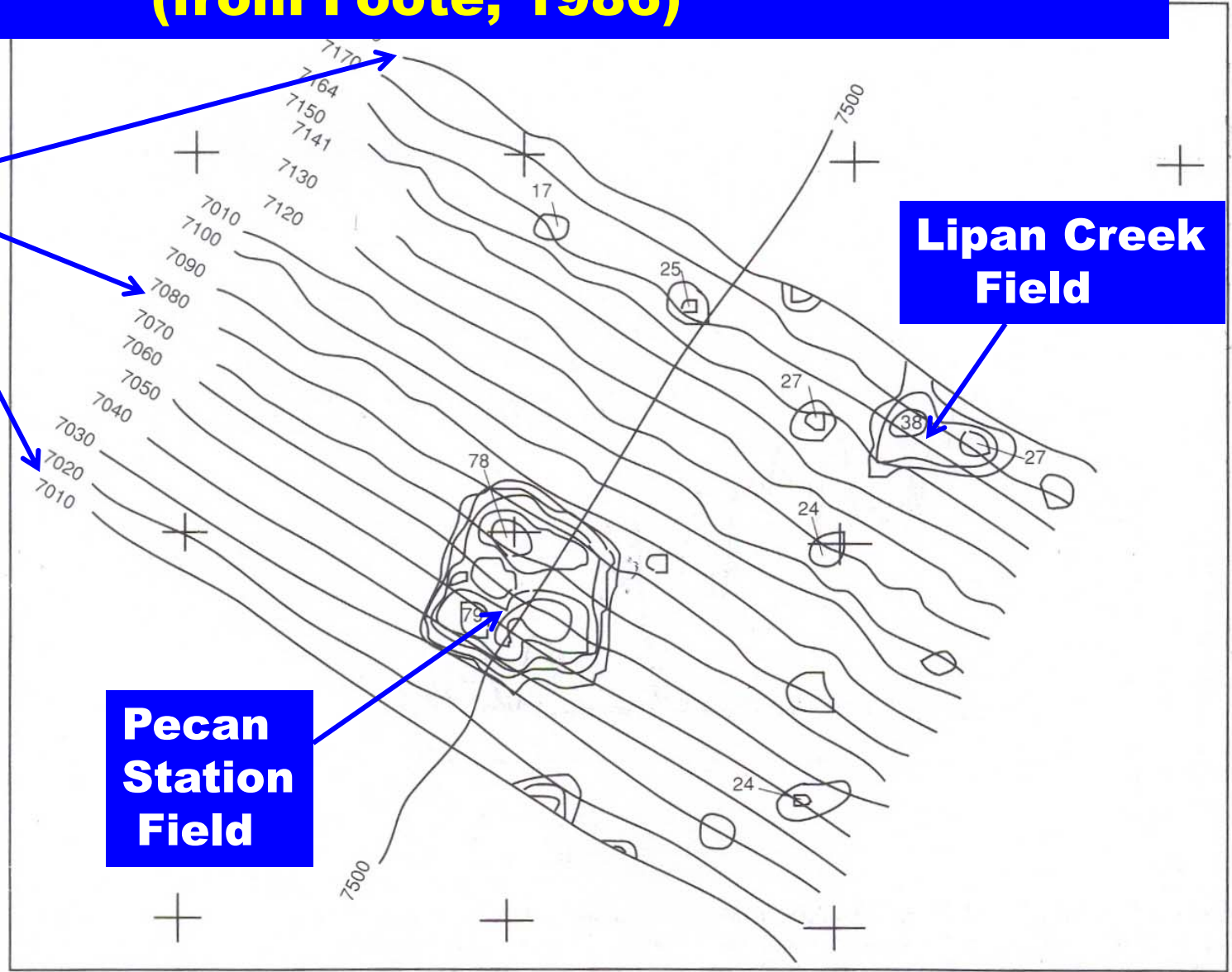


Horizontal Gradient Magnetometer Survey in Tom Green County, Texas (from Foote, 1986)

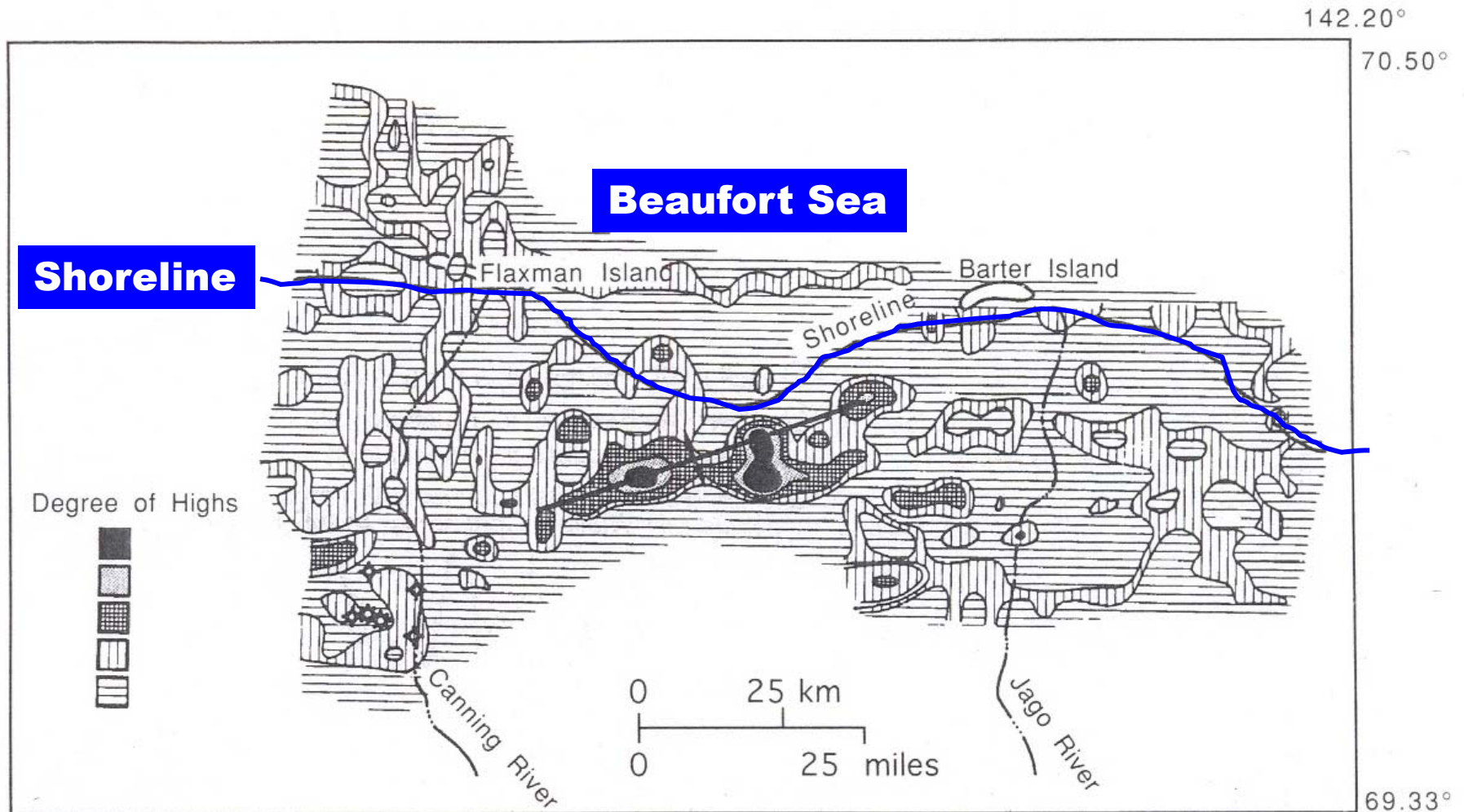
Flight lines

Lipan Creek Field

Pecan Station Field

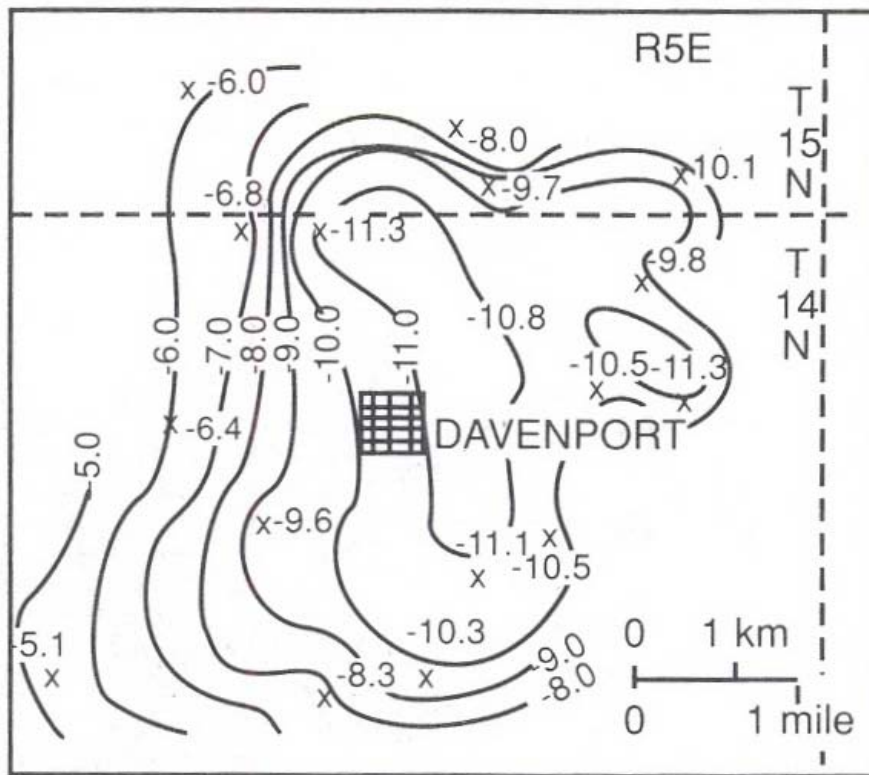


Magnetic Anomalies over Marsh Creek Anticline in Arctic National Wildlife Refuge, Alaska (from Donovan et al., 1984)

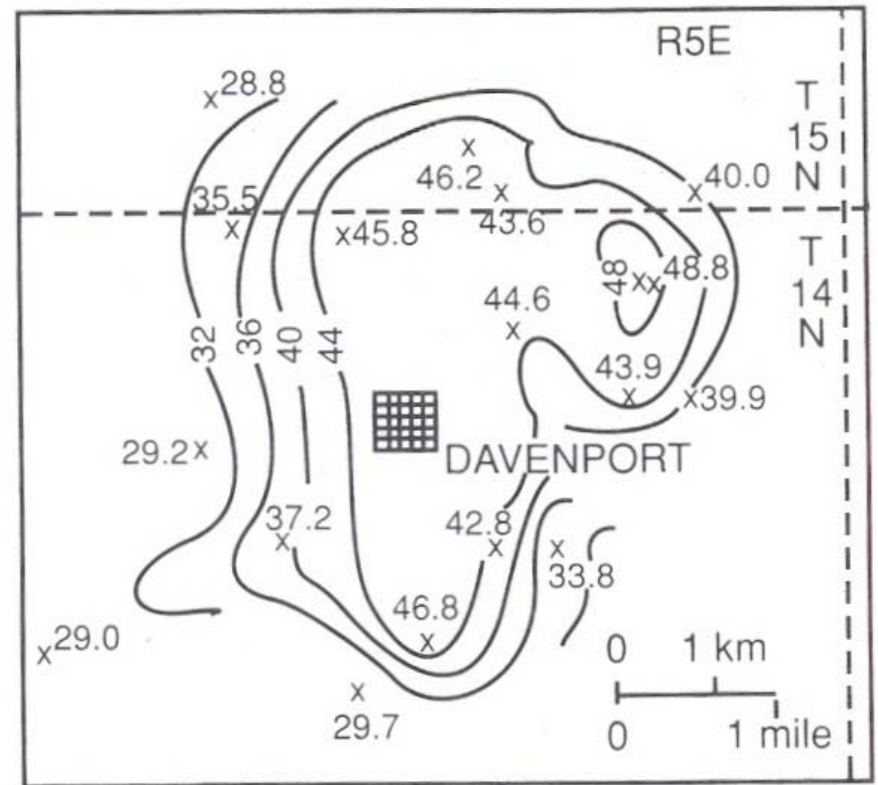


Isotopic Shift of Carbonate Cement Above Seepage at Davenport Field, OK (from Donovan et al., 1979)
≈ 210 shallow dolomite cement samples on a grid

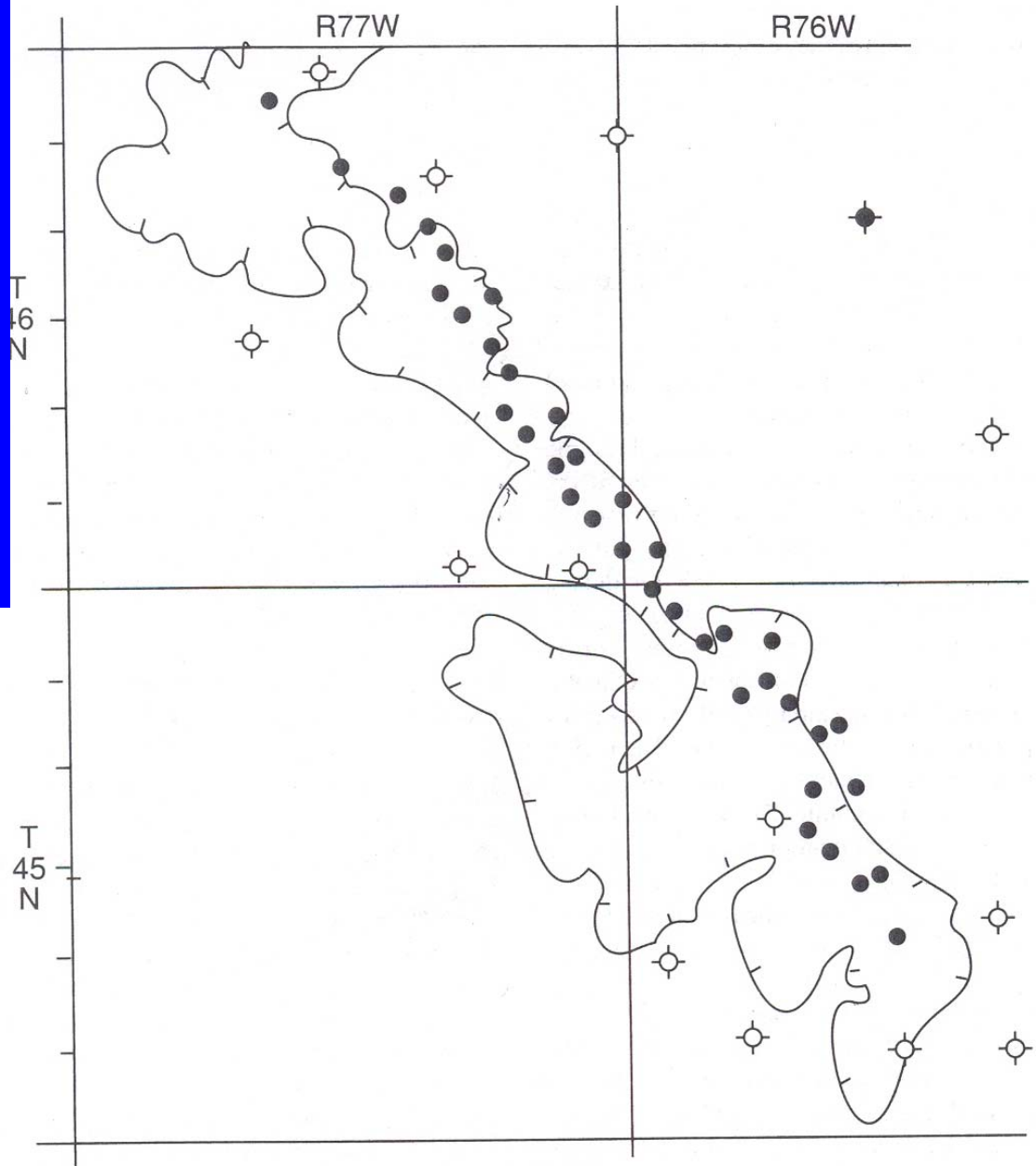
$\delta^{13}\text{C}$ of $(\text{Ca},\text{Mg})(\text{CO}_3)_2$



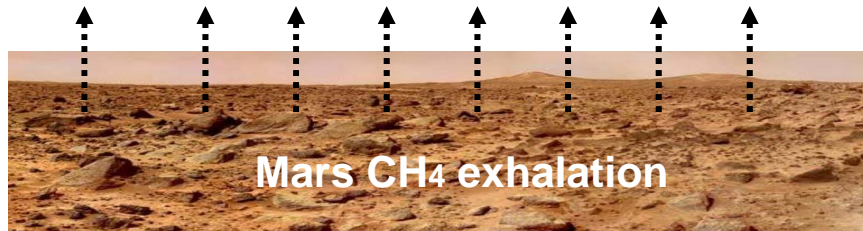
$\delta^{18}\text{O}$ of $(\text{Ca}, \text{Mg})(\text{CO}_3)_2$



**In-fill Drilling by
December, 1981
Superimposed
Over 1974 Gamma
Radiation Survey
at Heldt Draw Oil
Field, Powder
River, WY (from
Curry, 1984)**



A FEW MARTIAN SEEPS or WEAK MICROSEEPAGE CAN SUSTAIN THE ATMOSPHERIC CH₄ LEVEL (and the Mumma's plume)



the CH₄ plume on Mars reflects an episodic emission of
~19,000 t CH₄ yr⁻¹ (Mischna et al., 2011) or
~150,000 t CH₄ yr⁻¹ (Lefevre and Forget, 2009)

equivalent to a diffuse microseepage of ~10-100 mg m⁻²d⁻¹ from an area of 500 to 5000 km²

If the whole 30000 km² olivine outcrop at the Nili Fossae (Hoefen et al., 2003) is assumed to exhale, a microseepage of 2 mg m⁻²d⁻¹ (the lowest level detected in terrestrial peridotites) would be sufficient to support the plume

If a global Martian CH₄ source of around 100-300 t yr⁻¹ is required to maintain the 10 ppb atmospheric level (Atreya et al, 2007), one large mud volcano or a few small mud volcanoes, or just a very weak microseepage, sparse in different zones of Mars, would be sufficient.

Etioppe, Oehler, Allen (2011)
Etioppe, Ehlmann, Schoell (2013)

SPECULATIONS ABOUT EXPERIMENTS ON MARS

- **Slim coring device needed on rover**
- **Locations for coring visually selected based on surface geology**
- **Cores drilled to practical depth and inserted into incubation chamber that can subsequently be sealed and warmed to slightly above freezing**
- **Spike chamber with minor hydrogen and trace of water, CO₂ indigenous in atmosphere**
- **Monitor pressure and atmospheric composition and isotopy daily with TLS; two weeks enough(?); can be done while traveling, **DETECTION OF METHANOGENESIS (?)****
- **Pressure can detect adsorption/desorption and/or leakage**
- **Purge gas from chamber, spike chamber with minor oxygen and a trace of water, methane, CO₂ indigenous in atmosphere**
- **Monitor pressure and atmospheric composition and isotopy; two weeks enough(?); can be done while moving, **DETECTION OF METHANOTROPHY (?)****
- **Expel core from chamber; drill next core.**

Main final messages

Observations of terrestrial gas seepage can be used to infer forms and magnitude of potential seepage on Mars, and perhaps where to look

Seasonality on Earth is important

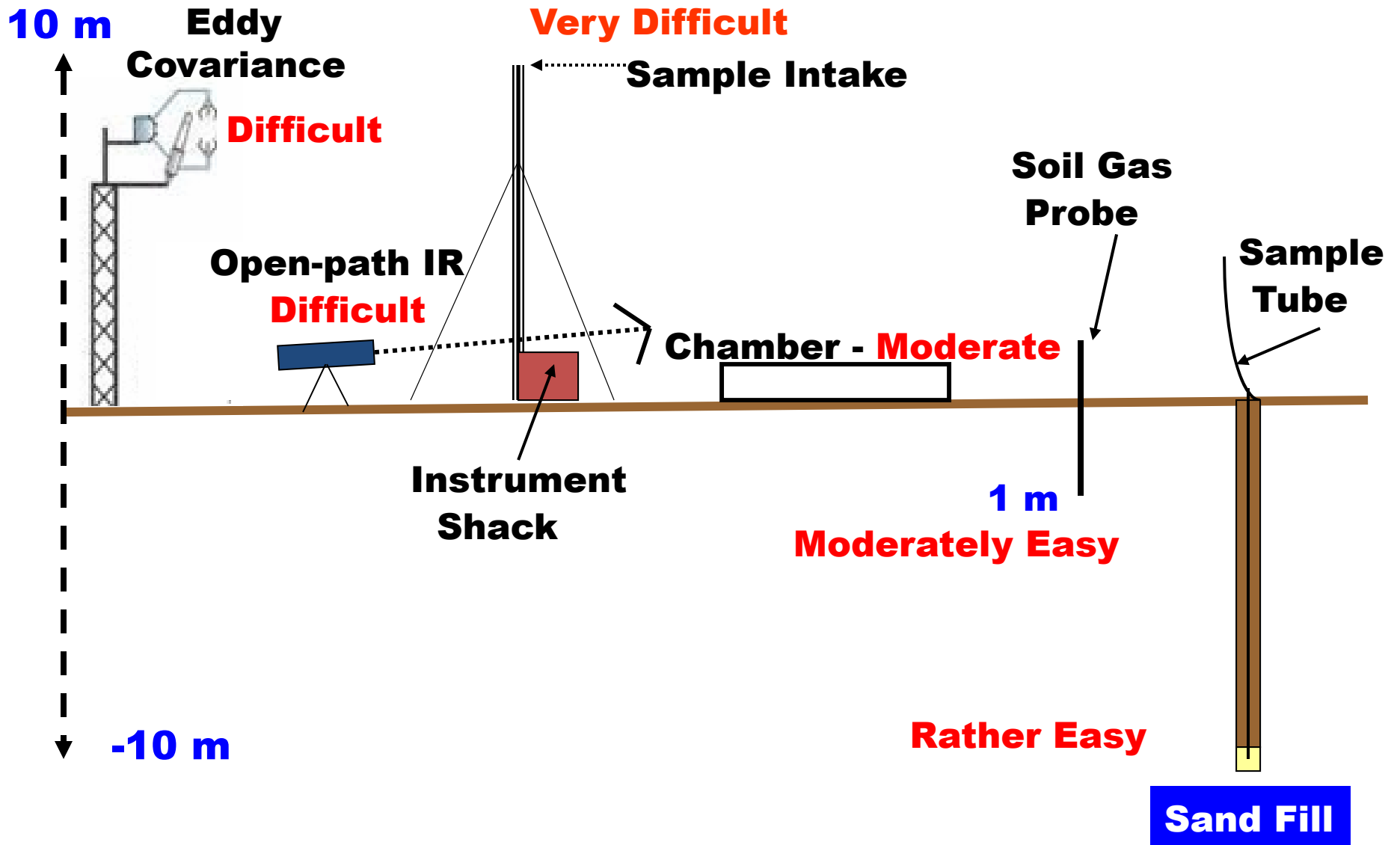
Low microseepage, sparse in different zones of Mars, would be sufficient to sustain methane observed in the atmosphere

BUT, as on Earth, CH₄ microseeping on Mars cannot be detected a few cm above the soil, because of winds and dilution of the leaking gas

Recommendation

Geologic CH₄ on Mars should be searched preferably above or near faults or at apparent mud volcanoes, by **drilling** into the soil or using **accumulation chambers** on the ground

DETECTION OF MICROSEEPAGE



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