

# FUGITIVE METHANE FORENSICS

Alan Jeffrey, Ph.D.  
NEMC Meeting  
Chicago, July 14 , 2015



# Ross Store, Fairfax District

**Los Angeles Times**

Monday, March 25, 1991

## Blast Shatters Store; 23 Hurt

Explosion May Be Tied to Abandoned Oil Field




More than seven hours after the original explosion, flames continue to seep up from cracks in pavement.

**Wider Use Ahead**  
**Heart Pump:**

**Regan Sees Close Vote in House on MX Funds**

**U.S. Presses for Allied Support**



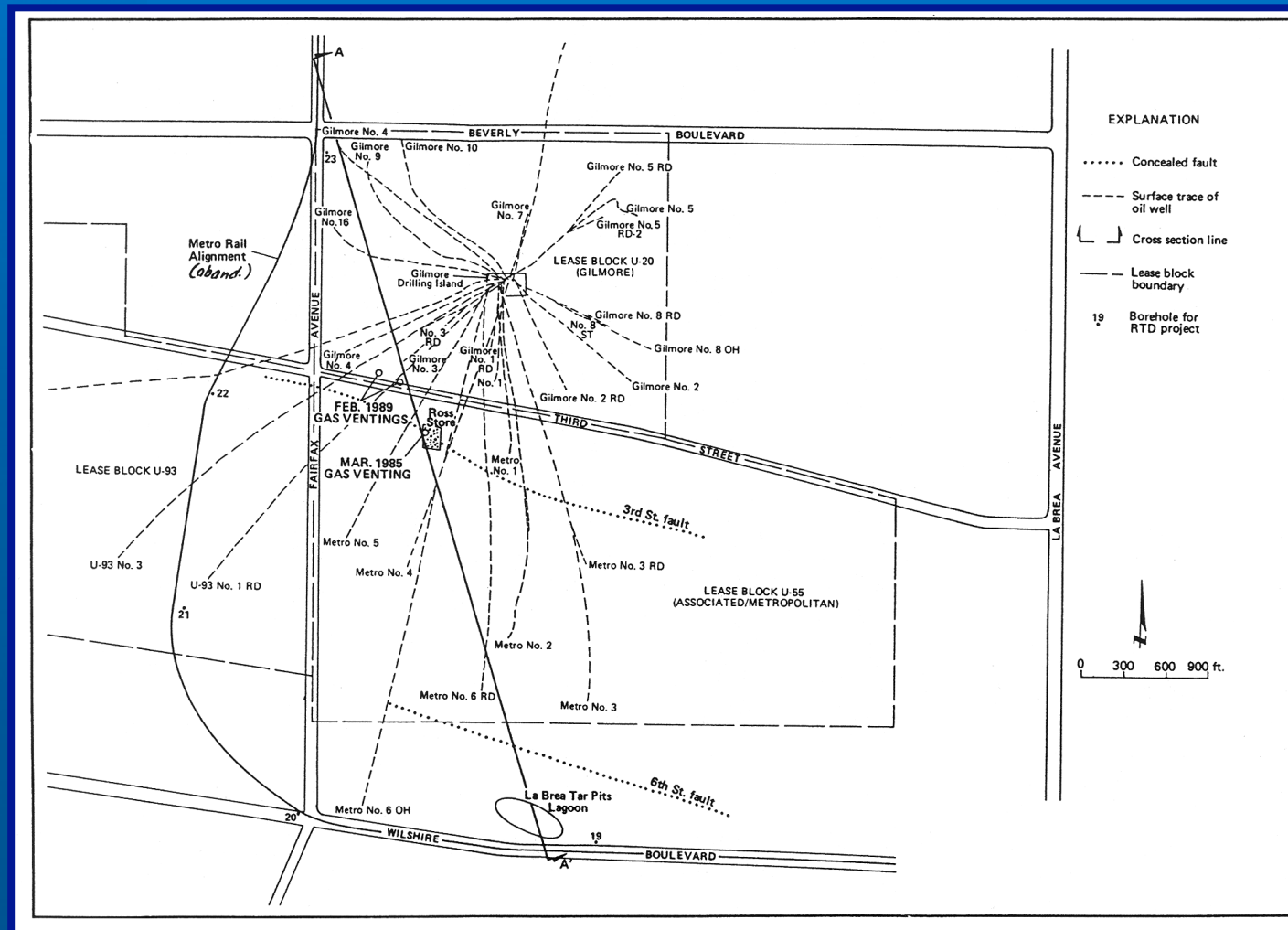
More than seven hours after original explosion, flames continue to seep up from cracks in pavement.

## BLAST: 23 Injured; Burnoff of Gas Could Take Months, Fire Dept. Says

# Fairfax District, Los Angeles

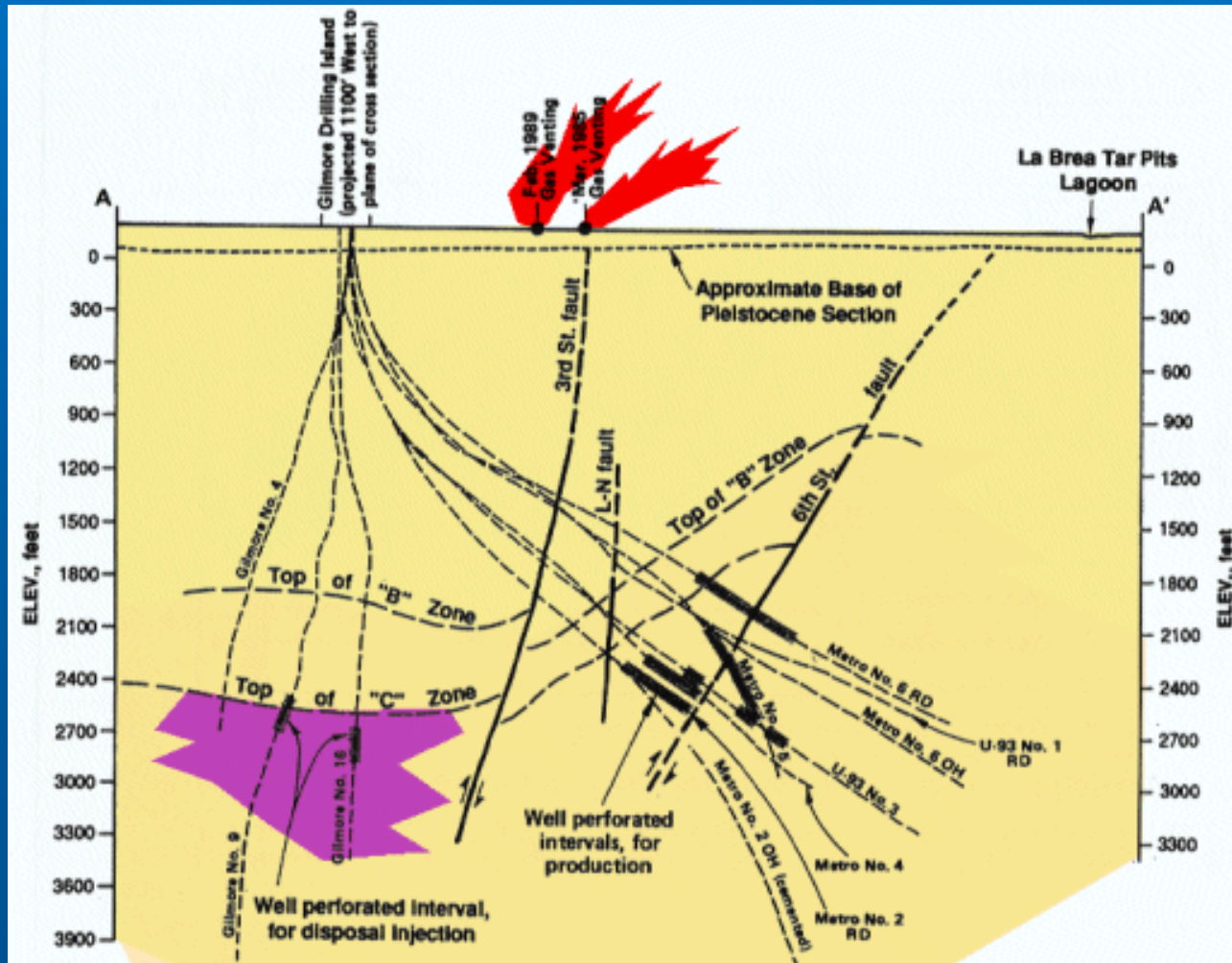


# Ross Store, Fairfax District





# Ross Store, Fairfax District



# Sources of Methane

- **BIOGENIC METHANE**
  - Marsh gas, methane hydrates
  - Landfill gas
  - Degradation of petroleum products
- **THERMOGENIC METHANE**
  - Pipeline gas
  - Migrated petroleum gas

# Biogenic Methane Formation

## CO<sub>2</sub> Reduction



## Fermentation

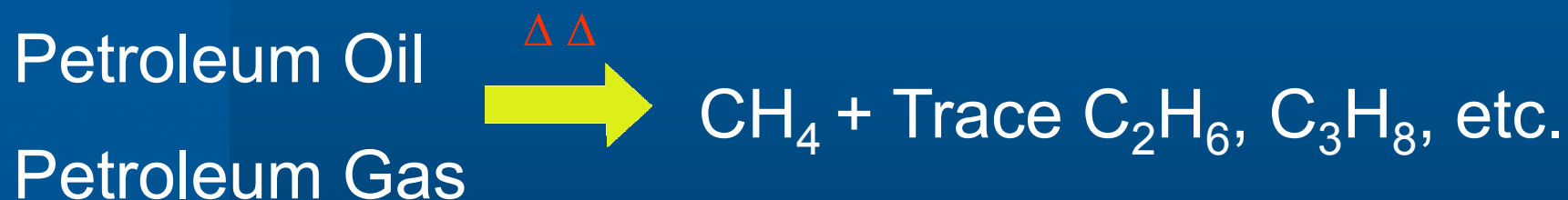


# Thermogenic Methane Formation

## Mature Source Rock

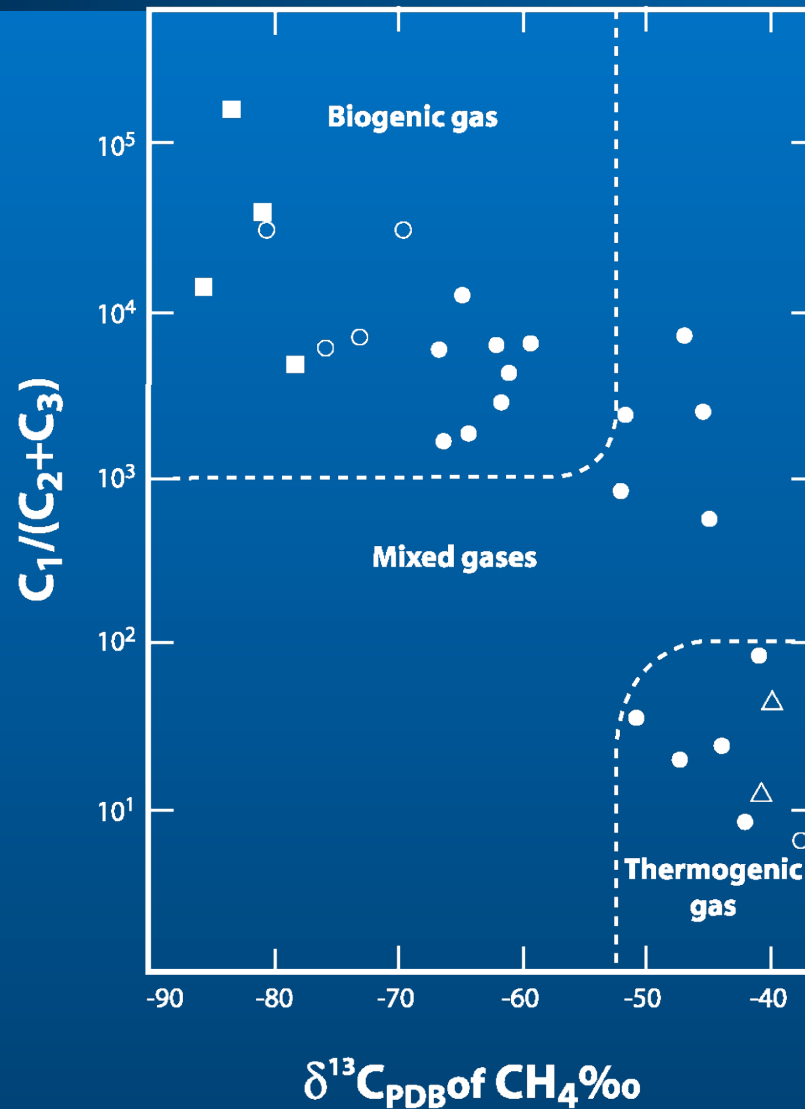


## Overmature Source Rock

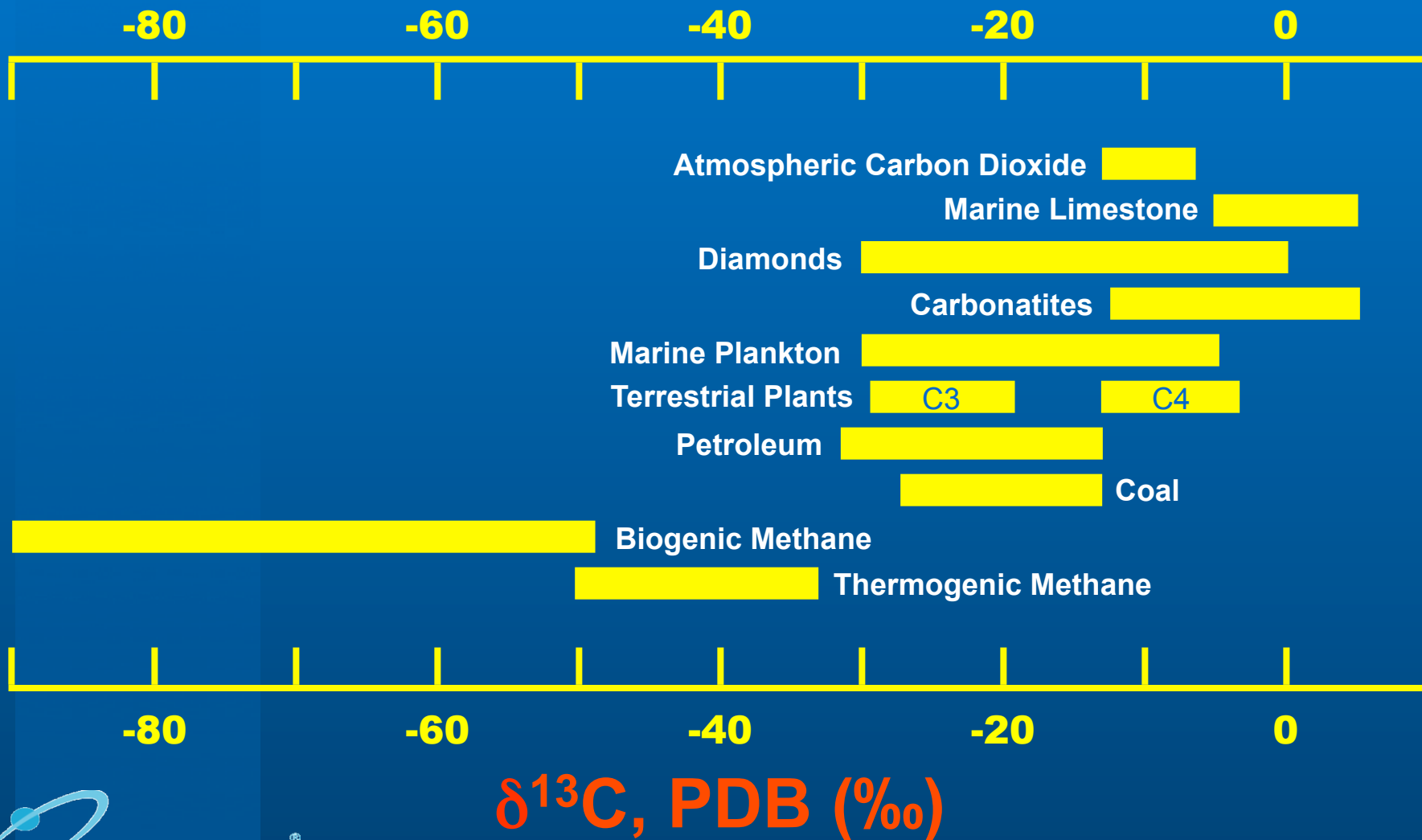




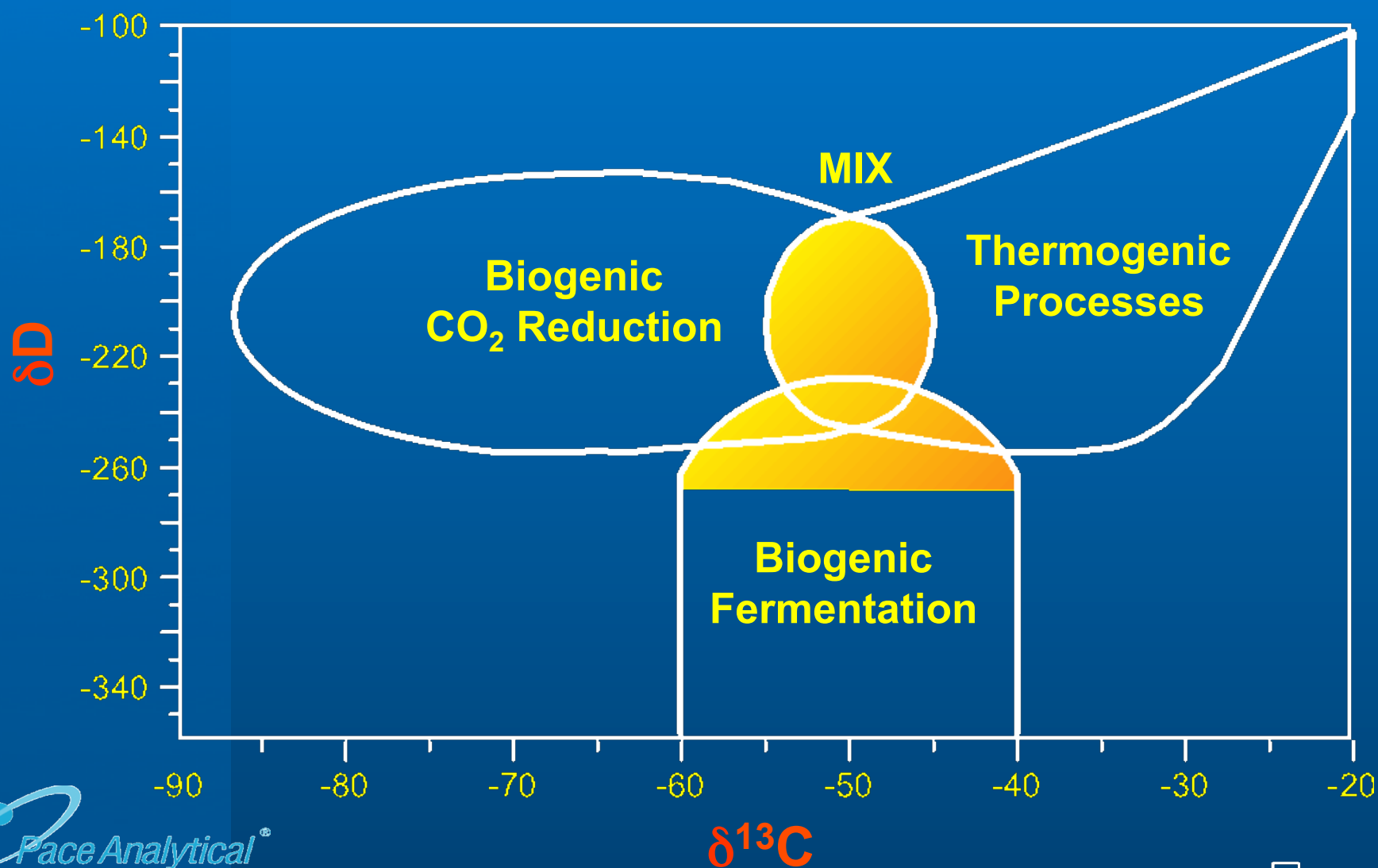
# Gas Composition and Isotope Ratio



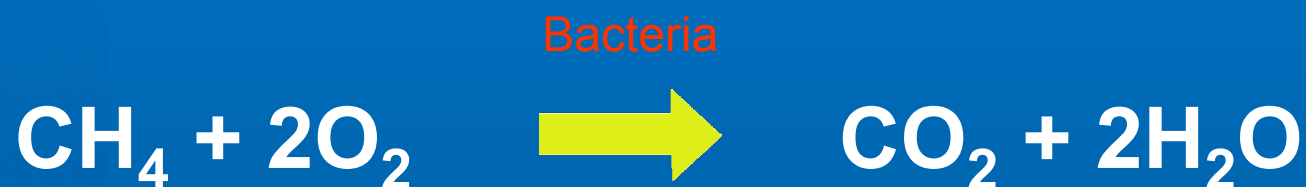
# $\delta^{13}\text{C}$ Values of Geochemical Materials



# Methane Isotope Ratios



# Complications: Methane Oxidation



- OFTEN OCCURS IN THE NEAR SURFACE
- CAN ALTER ISOTOPIC SIGNATURE



# Methane Oxidation

**$^{12}\text{C} - \text{X}$  Bonds are weaker than  $^{13}\text{C} - \text{X}$  Bonds**

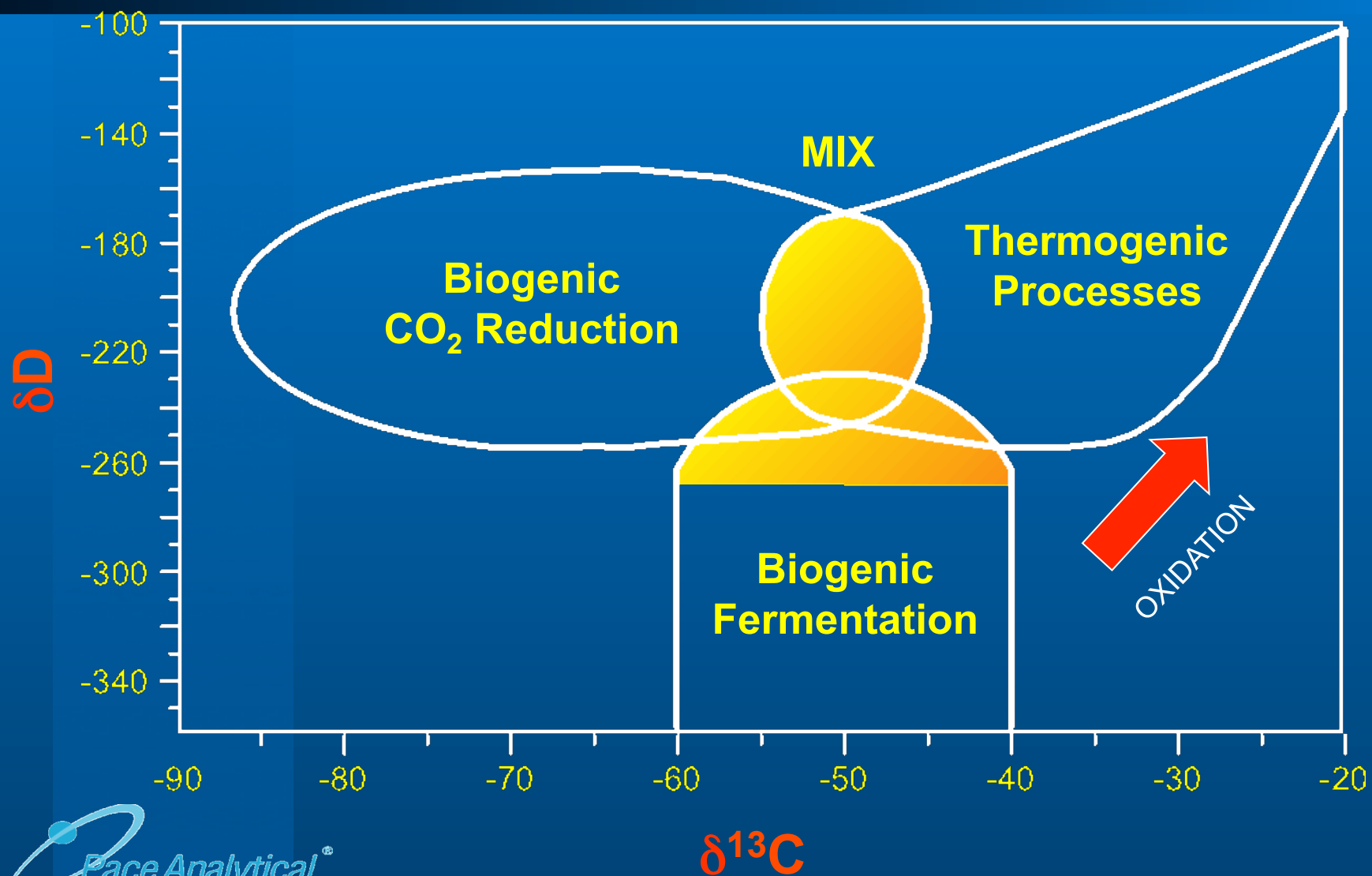
**In a chemical reaction,  $^{12}\text{C} - \text{X}$  Bonds break faster than  $^{13}\text{C} - \text{X}$  Bonds**

**If reaction proceeds to completion – all  $\text{CH}_4$  goes to  $\text{CO}_2$  - isotope ratio in product is the same as in starting material**

**If reaction is partially completed,  $^{12}\text{C}$  is concentrated in product, and  $^{13}\text{C}$  is concentrated in starting material**

**Starting material ( $\text{CH}_4$ ) changes to lower  $\delta^{13}\text{C}$  values**

# Alteration of Methane Isotope Ratios



# Case Study: Origin of Gas Seeps



The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

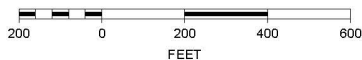
- Red Lines
- OIL AND GAS WELLS
  - Oil and Gas Wells
  - API Number
- HISTORIC WELLS
- AERIALS2009

Historic wells are approximate locations of oil wells from 1904 map of the field, 1908/1909 USGS reports and 1954 map of the field. Red dot is location of well plugged in 2009, which did not vent combustible gases at time of plugging.

The arrows point to two existing wells that we will sample at some point. Landowner denies their existence at present, but we have seen the casings and one is still supplying gas to the house.



SCALE 1 : 3,605



# Gas Seeps



IMAGE COURTESY OF GOOGLE EARTH, 2009

## LEGEND

- CONFIRMED PRODUCTION WELLHEAD
- POSSIBLE PRODUCTION WELLHEAD
- POSSIBLE ABANDONED GAS LINE (POTENTIAL SOURCE)
- POSSIBLE ABANDONED GAS LINE

## SUBSURFACE METHANE MEASUREMENTS

- 0 PARTS PER MILLION (PPM)
- 1 PPM - 500 PPM
- 501 PPM - 1,000 PPM
- 1,001 PPM - 10,000 PPM
- 10,001 PPM - 50,000 PPM
- > 50,000 PPM (EQUIPMENT MAXIMUM)

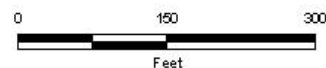


FIGURE 1  
SUBSURFACE METHANE MEASUREMENTS  
ORPHANED PRODUCTION WELL SITE



SOIL GAS SURVEY PERFORMED ON MAY 5, 2009

P:\COGCC\GIS\WIX\DFLORENCE2.mxd




# Seep Sample locations

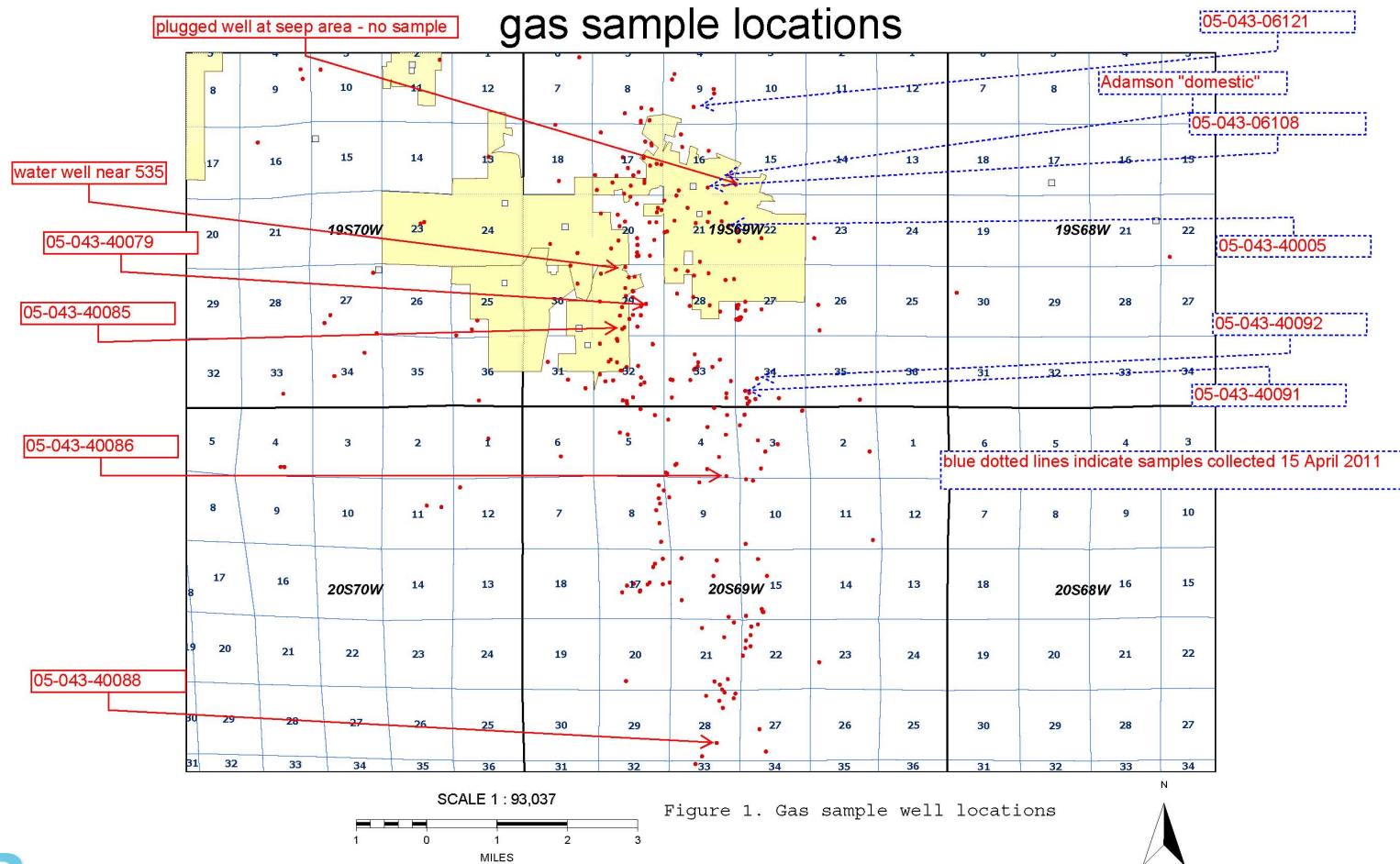


The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

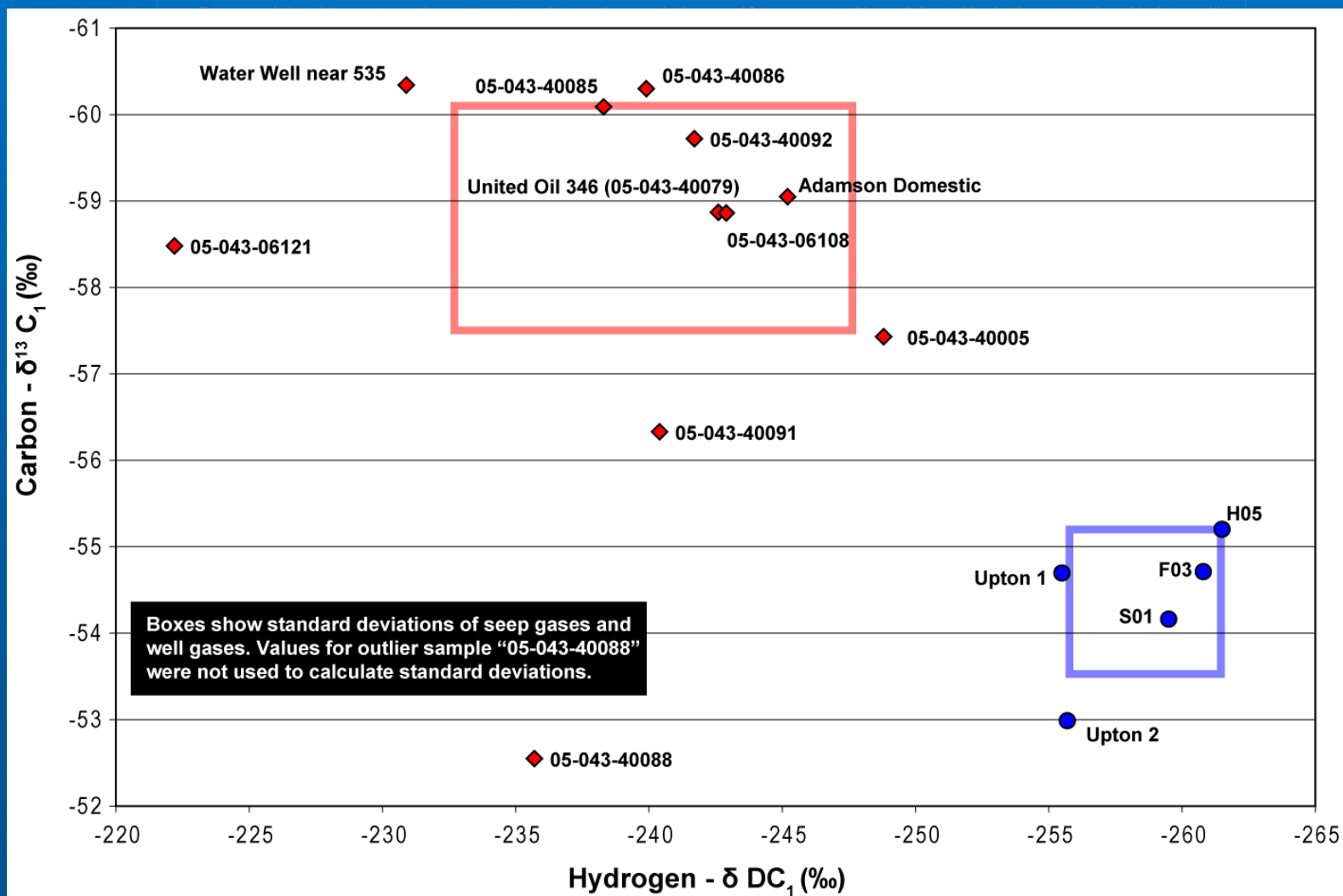


# Oil and Gas Production Wells

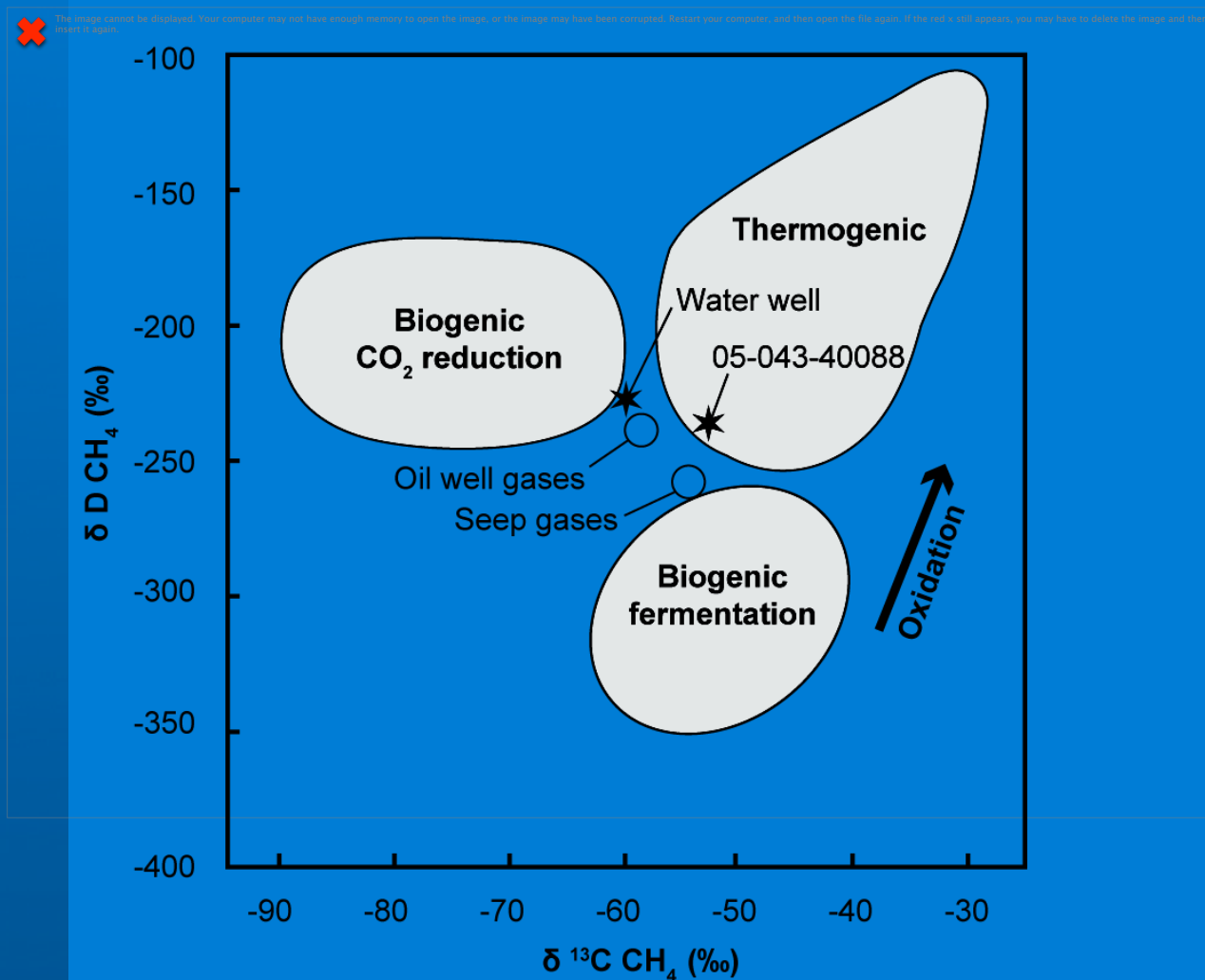
 The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.



# Methane Isotope Ratios



# Methane Genetic Fields





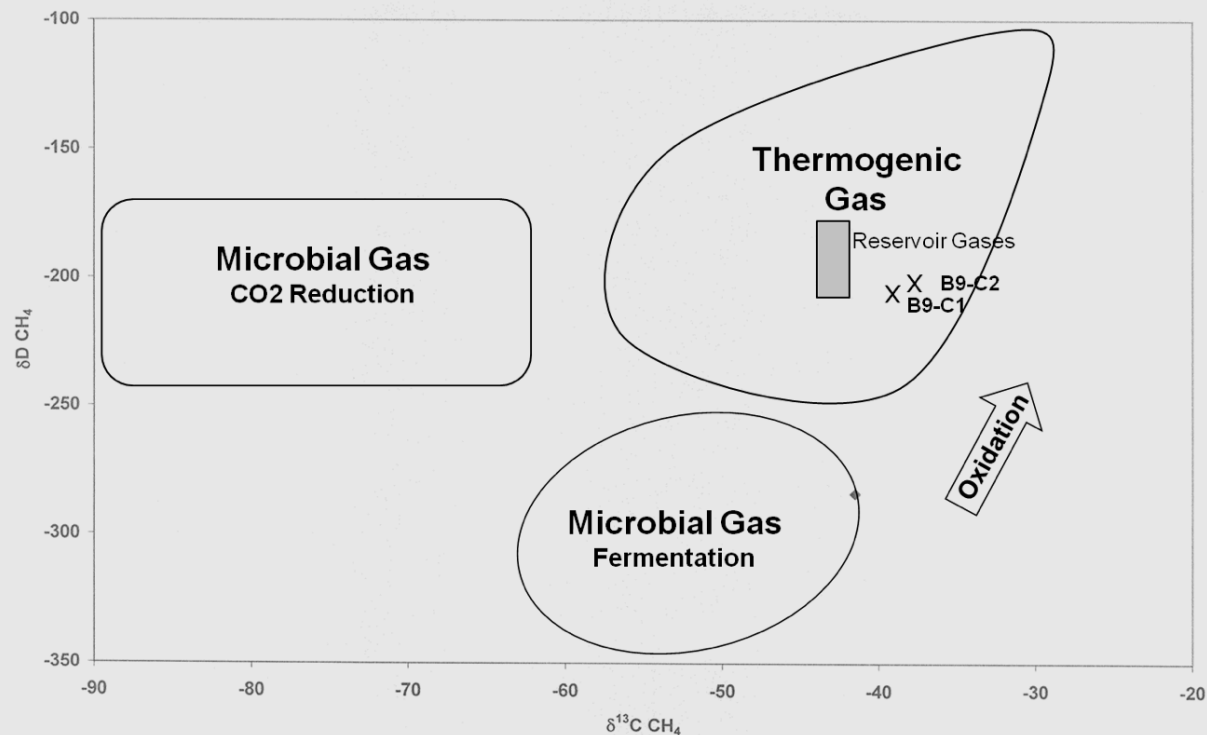
# Gas Explosion Los Angeles

- Explosion in an apartment underground parking
- Residual gas was collected

ZymaX ID	Sample ID	$\delta^{13}\text{C}$	$\delta\text{D}$	ppm	ppm
		$\text{CH}_4$	$\text{CH}_4$	$\text{CH}_4$	C2-C5
42122-2	#369 from B9-C2	-38.2	-199.1	8105	5.1
42122-3	#339 from B9-C1	-39.4	-203.3	2095	15.9

# Gas Explosion Los Angeles

Figure 1



After Coleman et al (1995)

# Marsh Gas



# Soil Methane, California

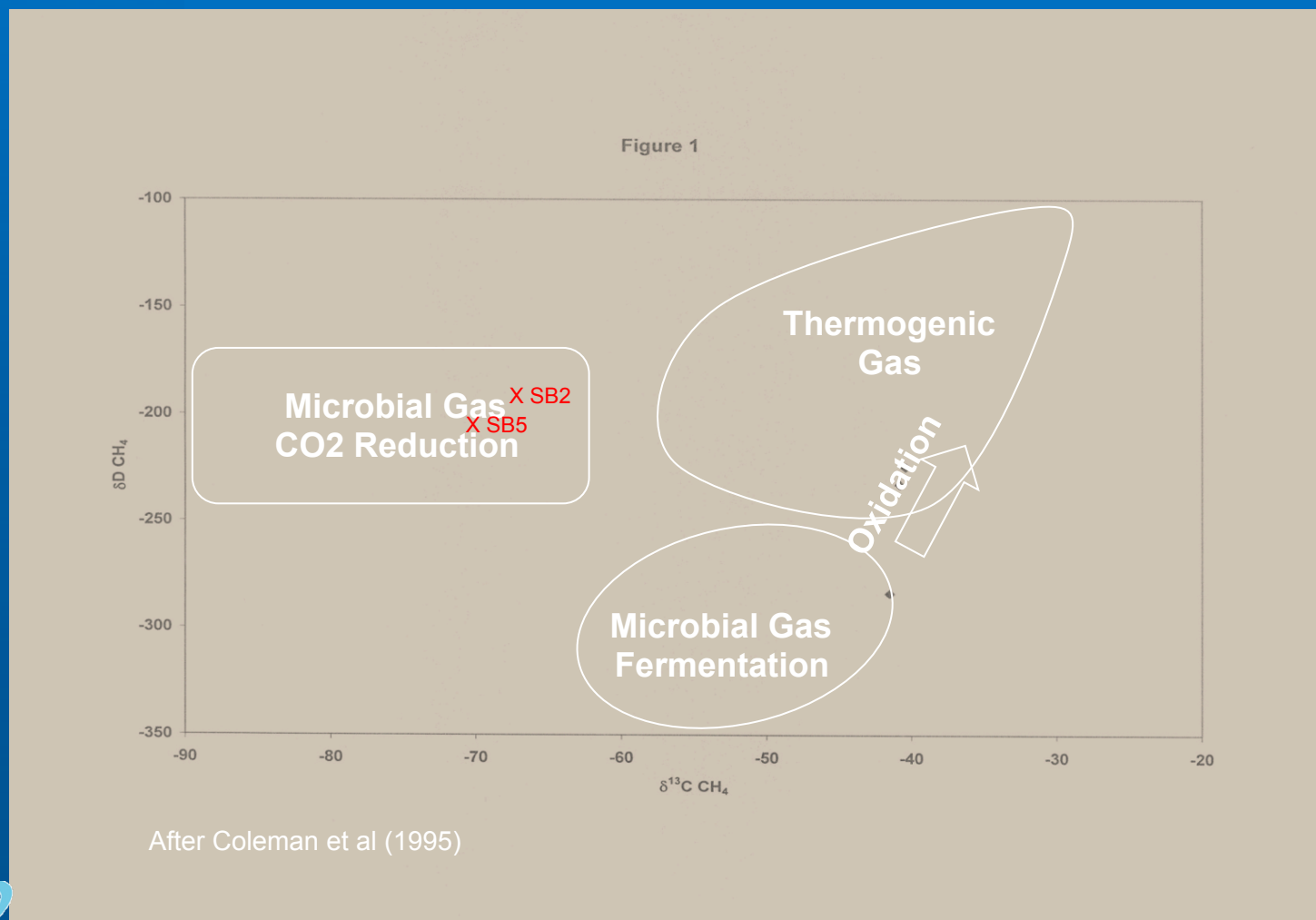


- Methane in soil at recreational ground
- North is service station with gasoline release

# Soil Methane, California

Sample ID	$\frac{\text{CH}_4}{\delta^{13}\text{C}}$	$\frac{\text{CO}_2}{\delta^{13}\text{C}}$	$\frac{\text{CH}_4}{\delta\text{D}}$
SB-6V-5 (8/24/11)		-25.2	
SB-5V-5 (8/24/11)		-23.9	
SB-2V-5 (8/24/11)	-66.9	-14.8	-189.9
SB-10V-5 (8/26/11)		-21.1	
SB-2V-5 (8/26/11)	-67.2	-15.2	-191.5
SB-8V-5 (8/26/11)	-70.1	-22.5	-202.3

# Soil Methane, California



# Soil Methane, California

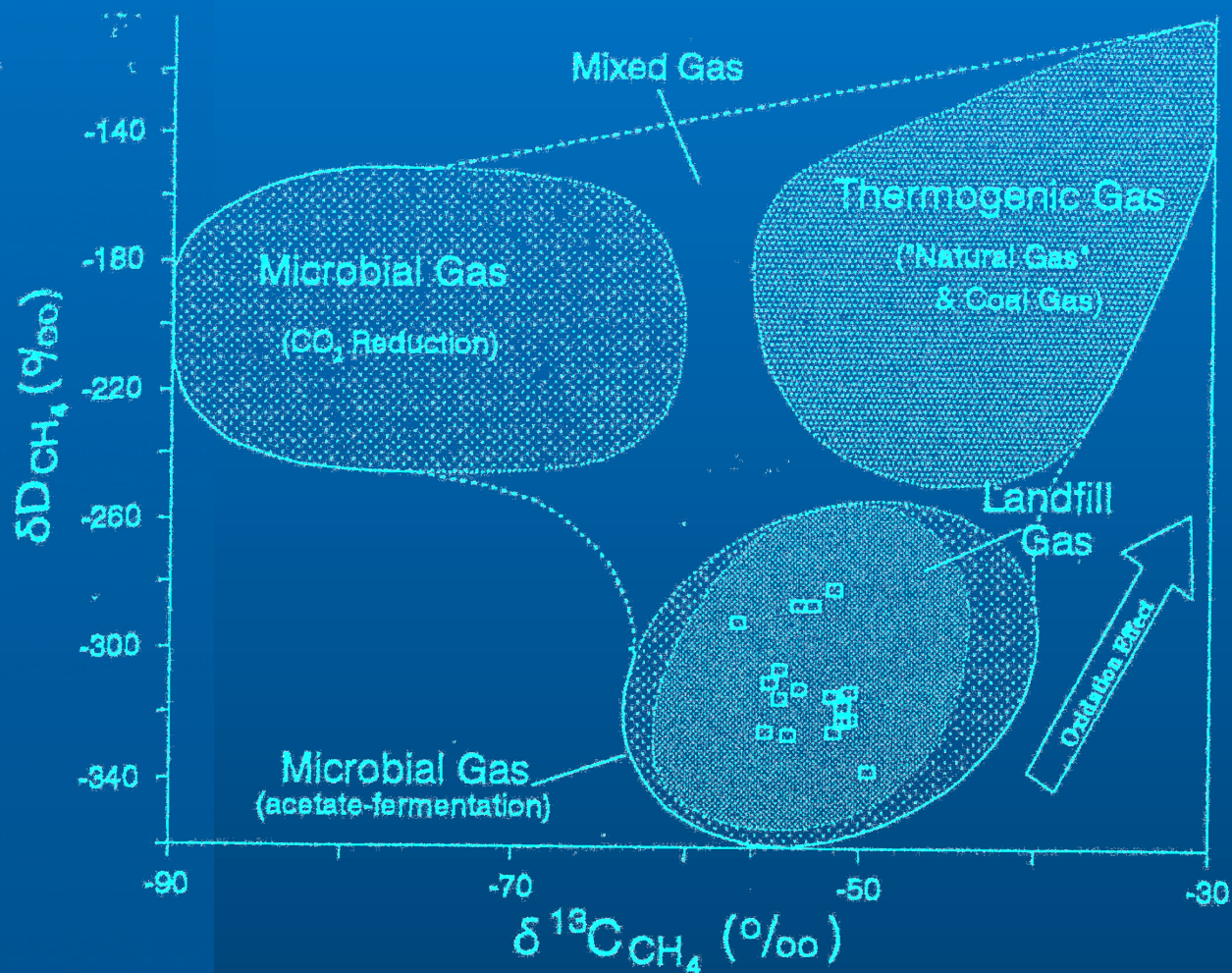


Sample ID	$\overline{\text{CH}_4}$ $\overline{\delta^{13}\text{C}}$	$\overline{\text{CO}_2}$ $\overline{\delta^{13}\text{C}}$	$\overline{\text{CH}_4}$ $\overline{\delta\text{D}}$
SB-6V-5 (8/24/11)		-25.2	
SB-5V-5 (8/24/11)		-23.9	
SB-2V-5 (8/24/11)	-66.9	-14.8	-189.9
SB-10V-5 (8/26/11)		-21.1	
SB-2V-5 (8/26/11)	-67.2	-15.2	-191.5
SB-8V-5 (8/26/11)	-70.1	-22.5	-202.3

- Samples with the highest  $\text{CH}_4$  concentrations (SB2V) contain the heaviest  $\text{CO}_2$
- Consistent with  $\text{CO}_2$  reduction to  $\text{CH}_4$



# Landfill Gas



Hackley et al (1996)

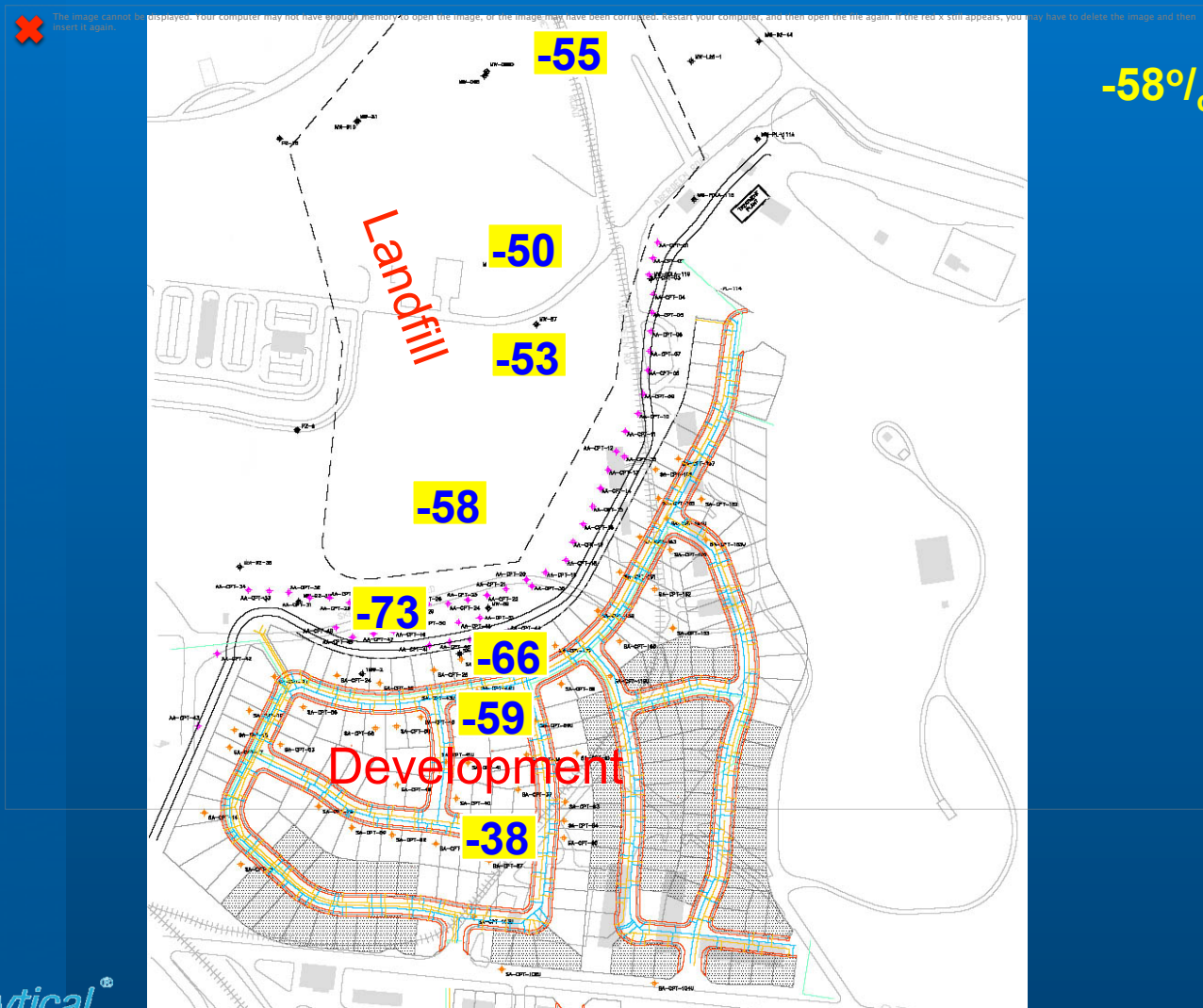
# Landfill Gas Characteristics

## Fermentation



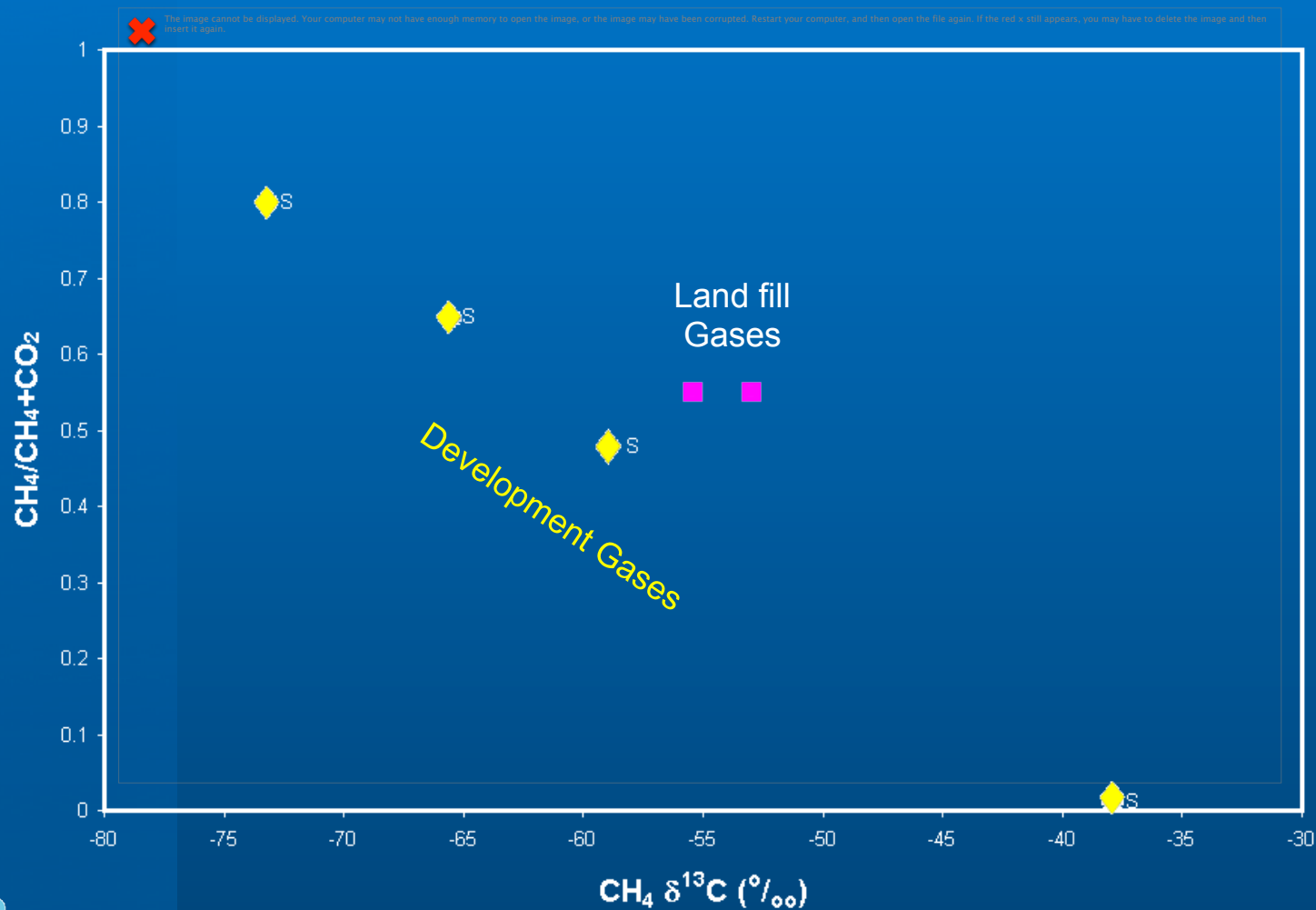
- ABUNDANT CO<sub>2</sub>
- OFTEN HIGH TRITIUM CONTENT IN METHANE

# Landfill Site

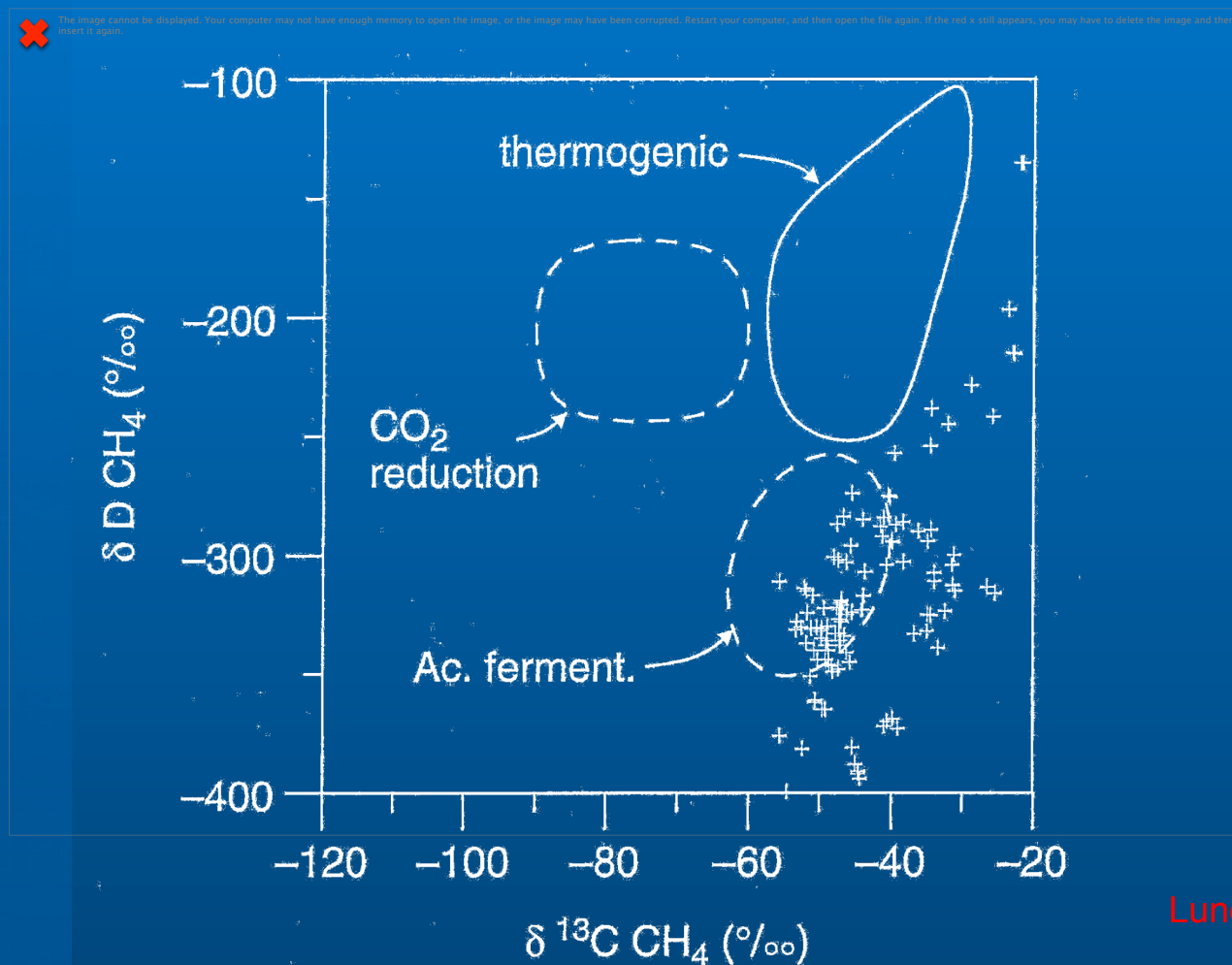


**-58‰** Methane  $\delta^{13}$

# Soil Gas Composition



# Methane from Hydrocarbon Degradation

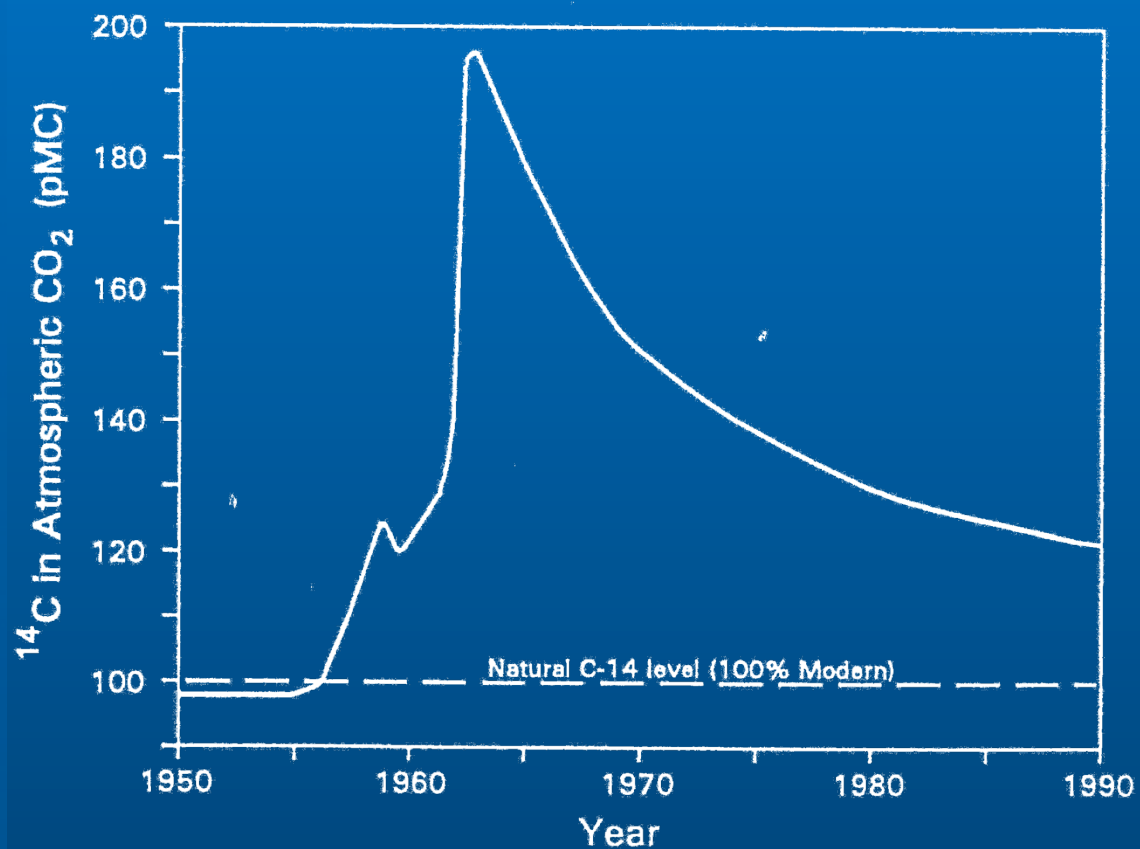


Lundegard, P.D. (2006)

# $^{14}\text{C}$ Analysis

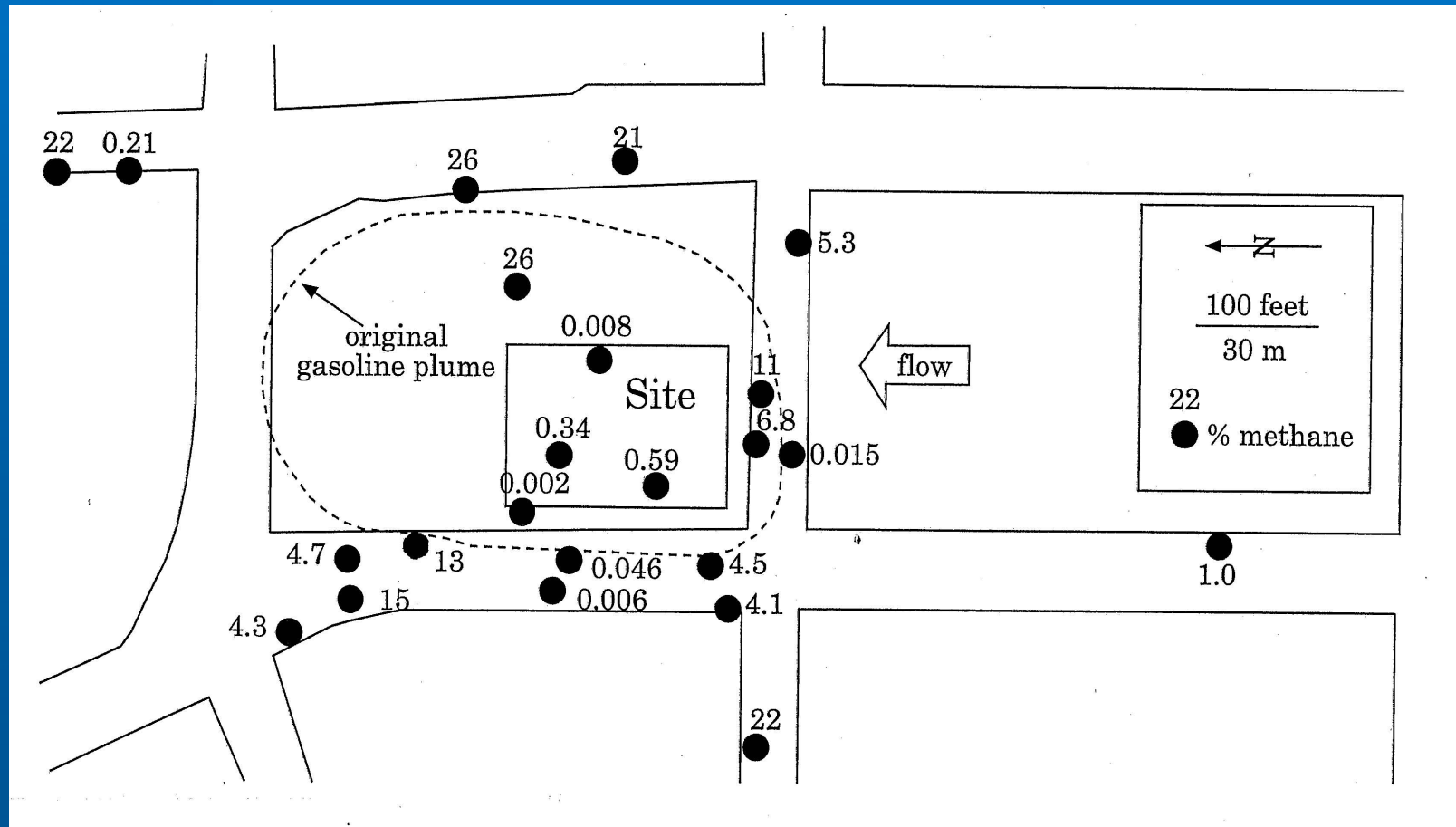
- $^{14}\text{C}$  Activity
- Percent Modern Carbon
- THERMOGENIC METHANE: 0 pMC
- BIOGENIC METHANE
  - Marsh gas: ~30 - ~120 pMC
  - Landfill gas: ~120 - ~150 pMC
  - Degradation of petroleum products: 0 pMC

# $^{14}\text{C}$ Analysis



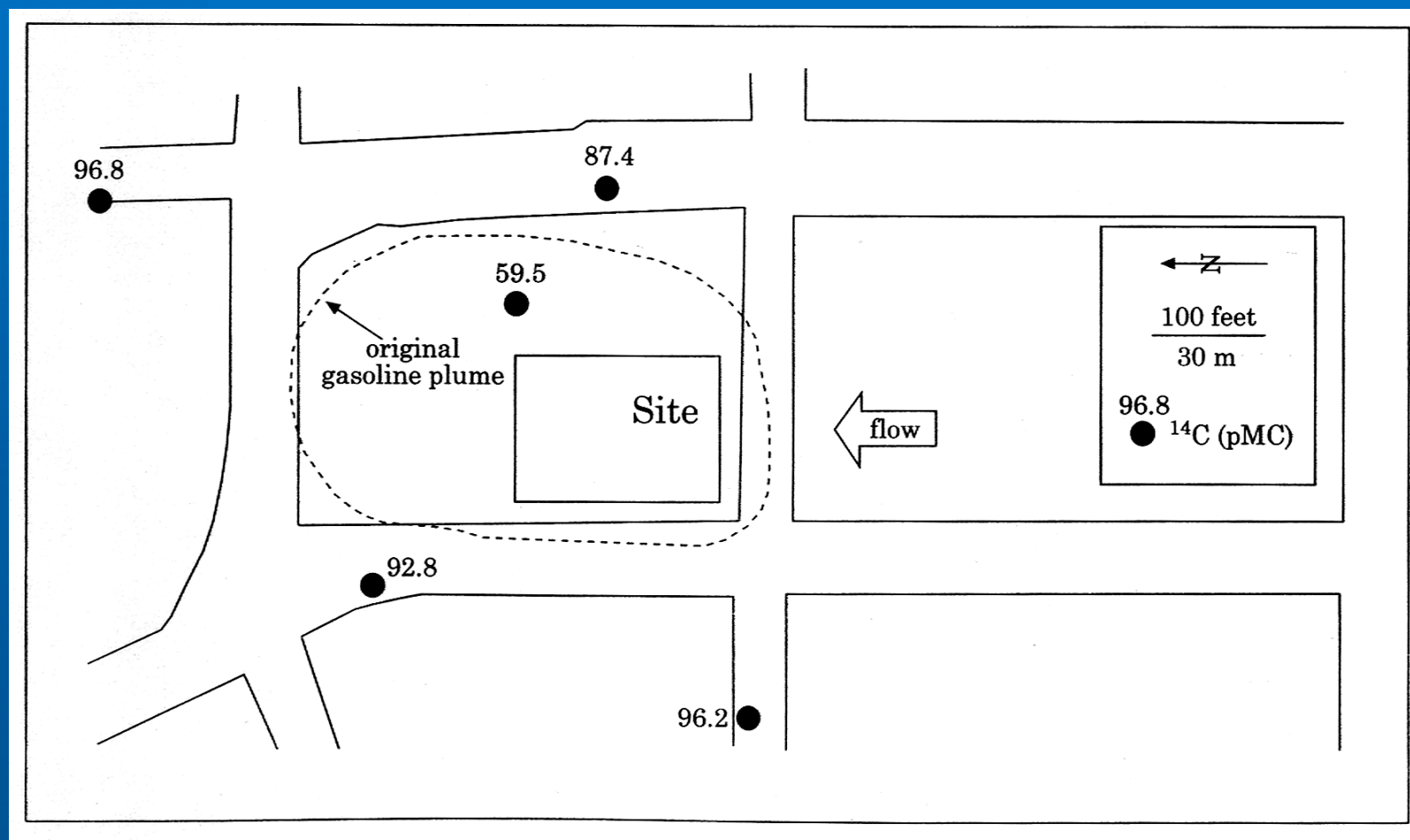


# Methane at Service Station Site

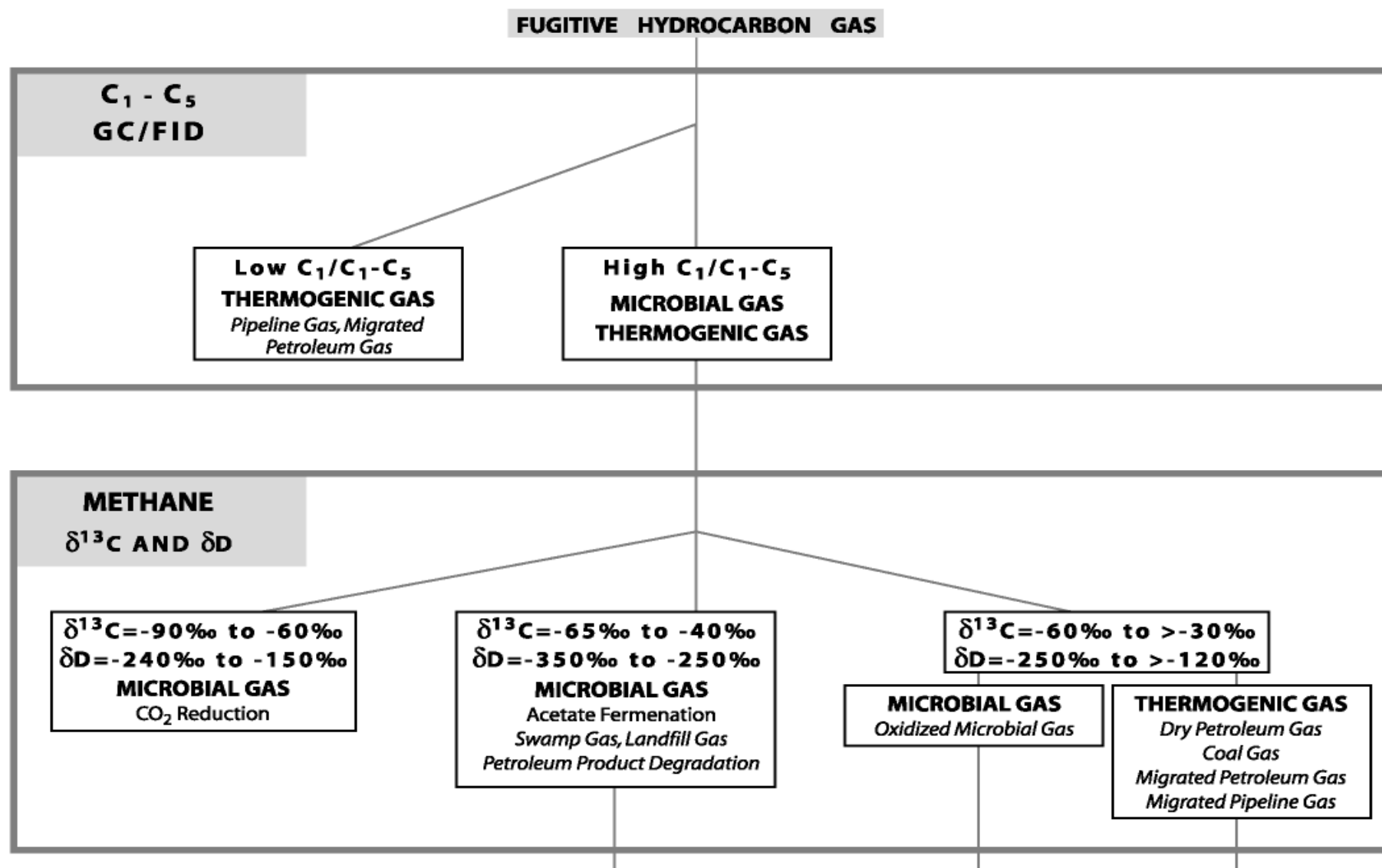


Lundegard et al, (2000)

# $^{14}\text{C}$ in Methane at Service Station Site



# Source Characterization Flow Chart



## METHANE

$\delta^{13}\text{C}$  AND  $\delta\text{D}$

$\delta^{13}\text{C} = -90\text{‰}$  to  $-60\text{‰}$   
 $\delta\text{D} = -240\text{‰}$  to  $-150\text{‰}$   
**MICROBIAL GAS**  
CO<sub>2</sub> Reduction

$\delta^{13}\text{C} = -65\text{‰}$  to  $-40\text{‰}$   
 $\delta\text{D} = -350\text{‰}$  to  $-250\text{‰}$   
**MICROBIAL GAS**  
Acetate Fermentation  
Swamp Gas, Landfill Gas  
Petroleum Product Degradation

$\delta^{13}\text{C} = -60\text{‰}$  to  $> -30\text{‰}$   
 $\delta\text{D} = -250\text{‰}$  to  $> -120\text{‰}$

**MICROBIAL GAS**  
Oxidized Microbial Gas

**THERMOGENIC GAS**  
Dry Petroleum Gas  
Coal Gas  
Migrated Petroleum Gas  
Migrated Pipeline Gas

## $^{14}\text{C}$ Analysis

**0pMC**

Petroleum Product  
Degradation

**> 120pMC**

Landfill Gas

**30-120pMC**

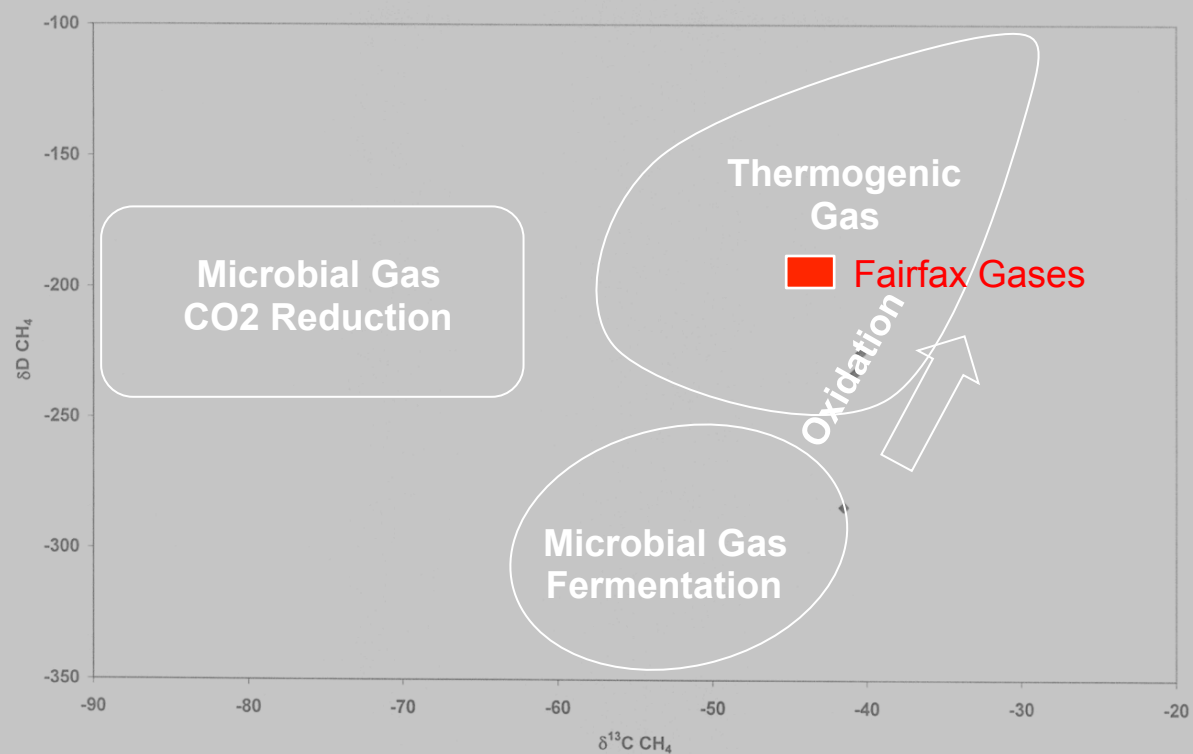
Swamp Gas

**0pMC**

Dry Petroleum Gas  
Coal Gas  
Migrated Petroleum Gas  
Migrated Pipeline Gas

# Ross Store, Fairfax District

Figure 1



After Coleman et al (1995)