

Near-Surface Hydrocarbon Seeps as Indicators of Petroleum Charge: The Evolution of Site Selection, Sample Collection, Laboratory Analysis, and Interpretation*

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Abstract

Oil and gas seeps gave the first clues to many of the well-known onshore and offshore petroleum bearing basins historically found. Seep hunting surveys have been based on the observation that migrated petroleum from deep source rocks and reservoirs can be analytically detected or otherwise proxied as thermogenic seepage in near-surface soils and sediments, such that results can be used to help evaluate a prospective petroleum system. The value of survey results has been aided by the evolution of tools and techniques for site selection, sample collection, lab analysis, and interpretation, resulting in our growing ability to determine charge, age, maturity, depositional environment, and even oil quality from the detected seepage. As a part of seep hunting, surface geochemical surveys search for chemically identifiable oil and gas compounds as well as seep-induced physical/geological expressions and biological communities and related features. Petroleum traps are dynamic, theoretically exhibiting some level of leakage, often with a resulting near-surface expression. Seep hunting tools have developed from the early days of onshore geographic grid surveys looking for micro-seepage anomalies related to petroleum traps, to offshore deep-coring, targeted, site-specific micro- and macro-seepage surveys. This talk will summarize the evolution and advancements in the tools and techniques used.

Site selection and sample collection: Onshore surveys differ from those offshore. Onshore surveys have tended to focus on specific prospects using a simple grid or transect approach with direct shallow-push-core-sampling above the prospect assuming vertical migration of seepage, whereas marine surveys have developed into more complex deep-core sampling of targeted features related to discrete migration conduits and pathways. Marine seismic and multibeam surveys are used to select coring locations based on various types of surface expression of faults, hardgrounds, mud volcanos, and other seabed features associated with upward migration of oil and gas. Vessels deployed to sample these targets often also collect additional acoustic data with a sub-bottom profiler, looking for subsurface features. Seeping oil and gas can be sampled from these surface expressions depending on the seepage rates and seabed conditions. The depth of sampling can have a significant impact on the results due to an array of near-surface processes (physical, geological, chemical, and biological) that can potentially alter, hinder,

or block petroleum seepage. For example, the utility and value of light hydrocarbon gas as a seepage indicator improves significantly with depth over the range retrievable by standard piston coring techniques.

Sample extraction and analysis: Direct geochemical measurements by analysis of soil/sediment samples include the determination of a range of low, medium, and high molecular weight hydrocarbon analytes. Measurement of low molecular weight compounds includes the light hydrocarbon gases from methane thru pentanes (C₁-C₅) and perhaps carbon dioxide and helium. The measurement of medium molecular weight HCs, includes the gasoline-plus range of petroleum hydrocarbons and comprises molecules with 5 to 12 carbons (C₅-C₁₂) arranged in linear, branched and cyclic aliphatic structures along with monoaromatic hydrocarbons such as benzene, toluene and xylenes. The high molecular weight hydrocarbon measurements typically include determination of the C₁₂-C₃₅ petroleum related compounds.

Light hydrocarbon gases can reside in near-surface sediments simultaneously in a number of different ways: (1) as free gas and gas hydrates in the effective porosity, (2) as interstitial gas which is dissolved and occluded in pore water between grains, and (3) as gas adsorbed onto the sedimentary particles or within carbonate cements. The relative fractions of gas existing in each of these three matrices are different in terrestrial soils from marine sediments. On land, gas may exist in significant proportions in each of these forms in the complicated soil matrix. In the simpler soil matrix of near-surface marine sediments, interstitial gas dominates and may turn into free gas in a retrieved (hydrostatic pressure-released) core. The determination of light hydrocarbons in sediments is useful because gases are the most mobile phase of reservoir hydrocarbons, vary over several orders of magnitude, and can be detected, quantified, and distinguished from local background and biogenic/diagenetic contributions. The bound light hydrocarbon gases are extracted using an acid extraction method pioneered by Horvitz Research Laboratories in the 1970s. The bound gases, also known as adsorbed gas, are believed to be attached to organic and/or mineral surfaces, entrapped in structured water, or entrapped in authigenic carbonate inclusions thus require a more rigorous analytical procedure to extract. The free and interstitial light hydrocarbon gases are extracted by equilibrium partitioning into a clean headspace. The extracted C₁-C₅ hydrocarbons by either type of extraction are then analyzed by gas chromatography (GC) and their stable carbon isotopes by isotope-ratio mass spectrometry (IRMS).

The gasoline-plus range hydrocarbons require a more specialized protocol to collect, analyze, and interpret. The methods currently active include vapor phase extraction by passive samplers such as the *Gore Sorber* or solid phase micro-extraction (SPME). The extracted C₅ to C₁₂ hydrocarbons are then analyzed by GC or GC/MS. For onshore sorber surveys, a pilot hole is developed in the soil to an average depth of perhaps 60-80 cm below grade. A sorber is then tied to a section of cord and inserted into the hole with a rod. The cord is secured at the ground surface by collapsing the hole, and the sorber is left for exposure to volatiles for 15-30 days. Exposed sorbers are then retrieved and analyzed by thermal desorption followed by GC/MS. Marine procedures are the same except that the sorbers are put into selected sections from recovered cores for exposure.

After solvent extraction of dried samples, the high molecular weight hydrocarbons are determined using total scanning fluorescence (TSF) and GC. TSF provides information about aromatic hydrocarbons contained in extracts. C₁₅⁺GC analysis quantifies petroleum-related normal alkanes, isoprenoids, and the unique unresolved complex mixture (UCM) generally found to be associated with extracts that contain at least traces of oil. Selected samples that show promise of seepage from TSF and C₁₅⁺GC results are further analyzed for saturate and aromatic biological markers by GC/MS or GC/MS/MS. These more detailed and expensive analyses can confirm the presence of migrated petroleum and

are also often used to match hydrocarbons in the sediment extract with a specific produced oil and/or source rock, yielding information about age, maturity, depositional environment, and quality.

Biological proxies: As seeping hydrocarbons approach the surface (land or marine), they encounter microbial communities that have adapted to make a living in the reduced-carbon-rich (and reduced-sulfur-rich) substrates. The composition of microbial communities associated with petroleum seeps include organisms that can metabolize the leaking oil, gas, and H₂S along with other organisms up that food chain. The proxy methods include culture-based analysis and DNA-based procedures such as serial analysis of ribosomal DNA 16S rRNA (SARD). In addition, chemosynthetic communities that have established a food chain starting with microbes, are proxies for present or past seepage of oil and gas. Indeed, living or long dead communities produce the substrate from which authigenic carbonate hardgrounds are formed, and these features are used to find seep target locations with multibeam backscatter techniques as a part of the seep hunting survey.

Interpretation: The end-product of a seep hunting survey is a listing with locations of the acquired cores that display clear evidence of migrated thermogenic hydrocarbons. Such conclusions and interpretive opinions are typically presented as a series of figures and a defining table. Challenges to accurate interpretation of seepage anomalies include (1) distinguishing thermogenic anomalies from background, including a correct understanding of analyte recoveries from the sample matrix, (2) correctly discerning any altered chemistry of the detected compounds, (3) correctly discerning the true proportions of thermogenic, biogenic, and diagenetic hydrocarbons, and (4) correctly discerning whether the tools and techniques used are the right ones for the particular survey. All onshore and offshore sediments contain low-level background concentrations of hydrocarbons related to local microbial generation, diagenesis, and/or reworked petroleum. Properly identifying what is real thermogenic seepage relative to these background signatures is critical. For example, 2-10% mole fractions of the C₂⁺ alkane gases from a producing well are clearly indicative of thermogenic gas, but in marine sediments the background levels of biogenic/diagenetic C₂⁺ gases are often high enough to be misinterpreted as thermogenic. Moreover, microbial activity and hydrate formation can alter the compositions of the hydrocarbon mix. Unlike the simple gases, gasoline-plus range hydrocarbons must be discerned by sophisticated statistical pattern recognition techniques due to the sheer number of individual compounds existing in natural sediments. Likewise, the high molecular weight hydrocarbons are best discerned and screened by plotting the detector response to the bulk aromatics (TSF) against the detector response to the bulk saturates (the UCM), simply because of the overwhelming number of existent compounds. Background issues, mixing with local production, diagenesis, and alterations affect the detected gasoline-plus range and high molecular weight hydrocarbons such that their thermogenic signal is often quite difficult to discern from the background morass. Examples of each of these interpretive challenges are presented.

Near-surface hydrocarbon seeps as indicators of petroleum charge:

The evolution of site selection, sample collection, laboratory analysis, and interpretation

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Methods of:

- **Site selection**
- **Sample collection**
- **Lab analysis**
- **Interpretation**

**Seeps -
the early
days**

**Seeps -
the early
days**



Oracle of Delphi (8th–4th centuries BC)



Seeps in the Bible

Genesis 11:3

They said to each other, "Come, let's make bricks and bake them thoroughly." They used brick instead of stone, and **tar** for mortar.

Genesis 14:10

Now the Valley of Siddim was full of **tar** pits, and when the kings of Sodom and Gomorrah fled, some of the men fell into them and the rest fled to the hills.

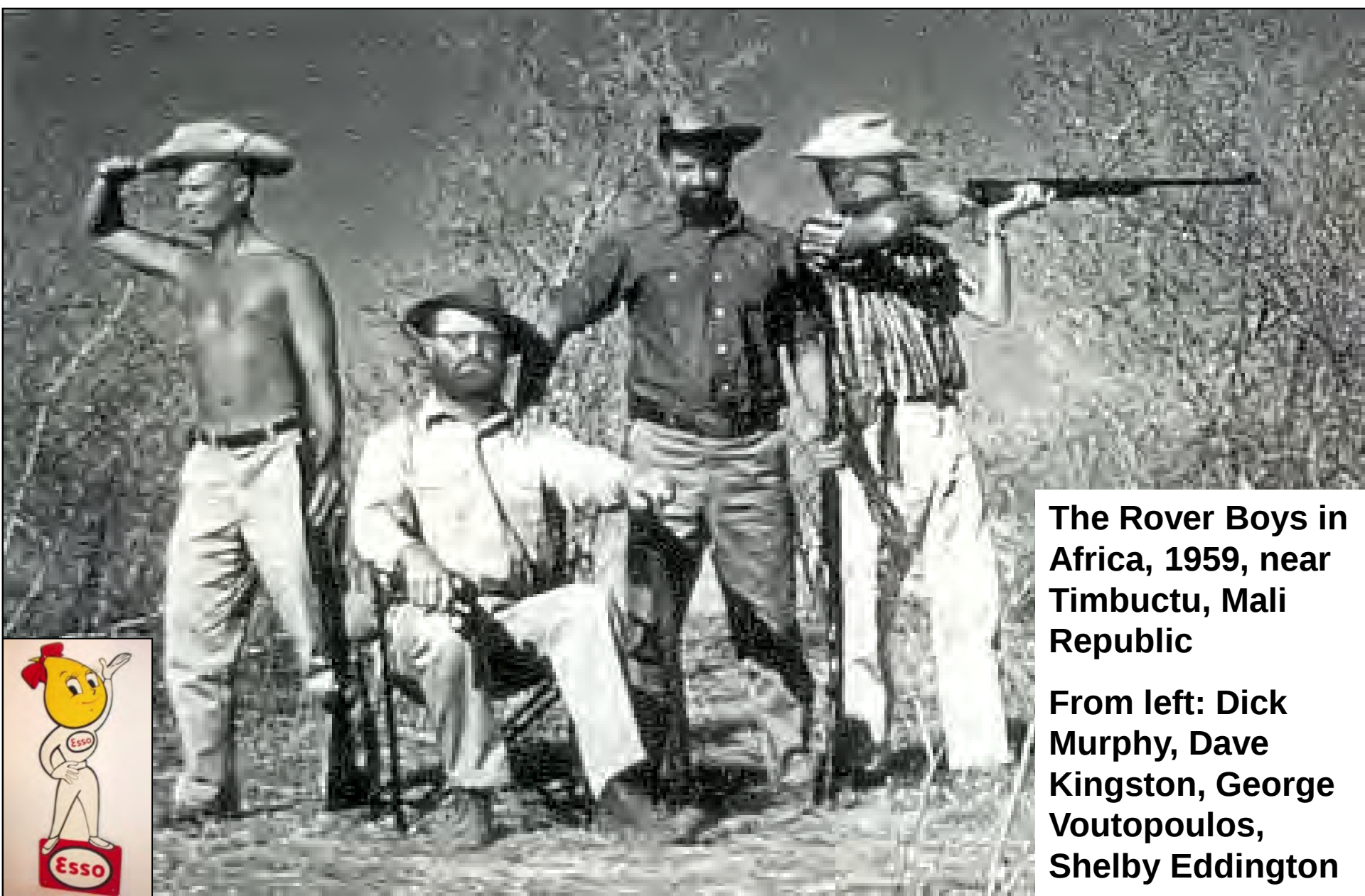
Exodus 2:3

But when she could hide him no longer, she got a papyrus basket for him and coated it with **tar** and pitch. Then she placed the child in it and put it among the reeds along the bank of the Nile.

Ancient uses of seeps

- **as mortar in Ziggurats, city walls, and gutters**
- **to caulk boats**
- **to manufacture water-proof containers**
- **in fireworks**
- **in lamps**
- **to lubricate wheels**
- **to glue gemstones into artefacts**
- **to remove dirty stains from clothes**
- **to heat and cook**
- **for mummification**
- **for medicine, wound dressing, liniment, laxative**
- **for numerous incendiary and flaming weapons**
- **to boil & desalinate seawater**

Esso's Rover Boys – seep hunting (1950s)



**The Rover Boys in
Africa, 1959, near
Timbuctu, Mali
Republic**

**From left: Dick
Murphy, Dave
Kingston, George
Voutopoulos,
Shelby Eddington**



Link (1952) - ties seepage to geological features

Volume 36

Number 8

BULLETIN
of the
AMERICAN ASSOCIATION OF
PETROLEUM GEOLOGISTS

AUGUST, 1952

SIGNIFICANCE OF OIL AND GAS SEEPS
IN WORLD OIL EXPLORATION¹

WALTER K. LINK¹

New York, N. Y.

SEEP ON HOMOCLINE
WHERE OIL-BEARING BEDS COME TO SURFACE

cal features

SEEP CAUSED BY CRUSHING

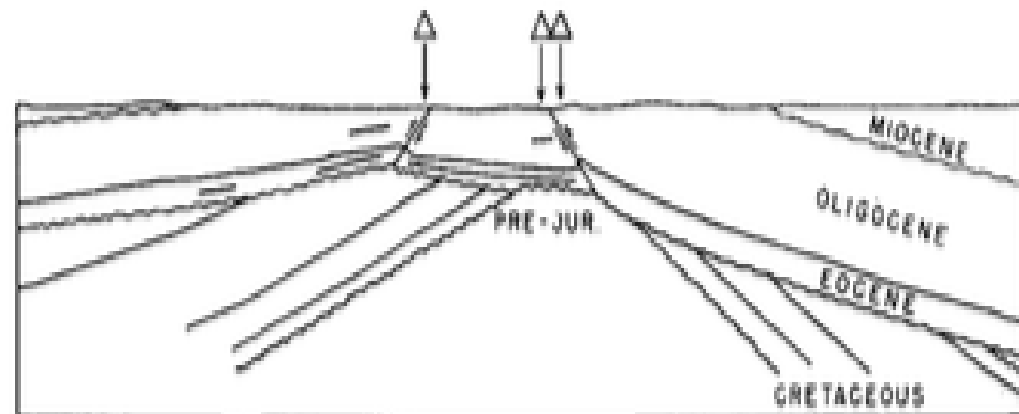
Number 8

SEEP OVER A LEAKING REEF RESERVOIR

NORMAL FAULT SEEP

SEEPS ON ERODED ANTICLINE
WITH OIL SANDS EXPOSED

OIL COMING UP THROUGH MINOR FAULTS
ON A PRODUCING STRUCTURE



LA CIRA FIELD, COLOMBIA

— OIL PRODUCTION

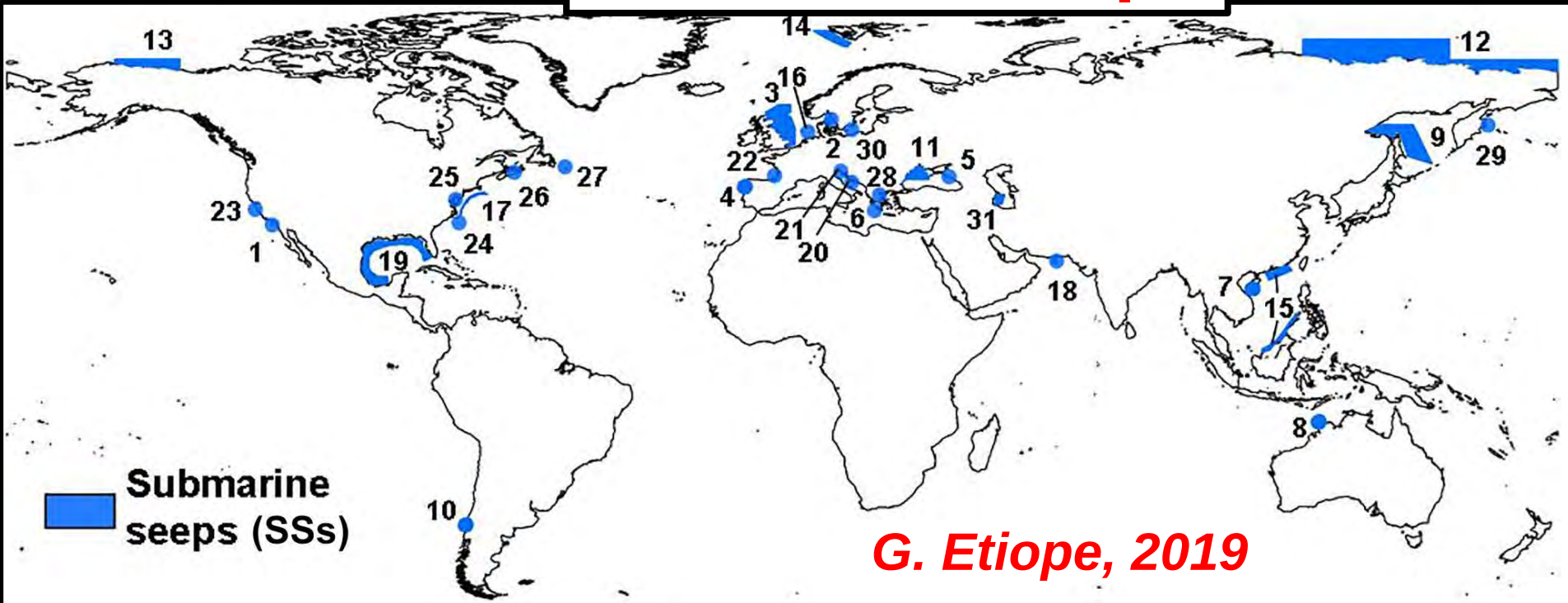
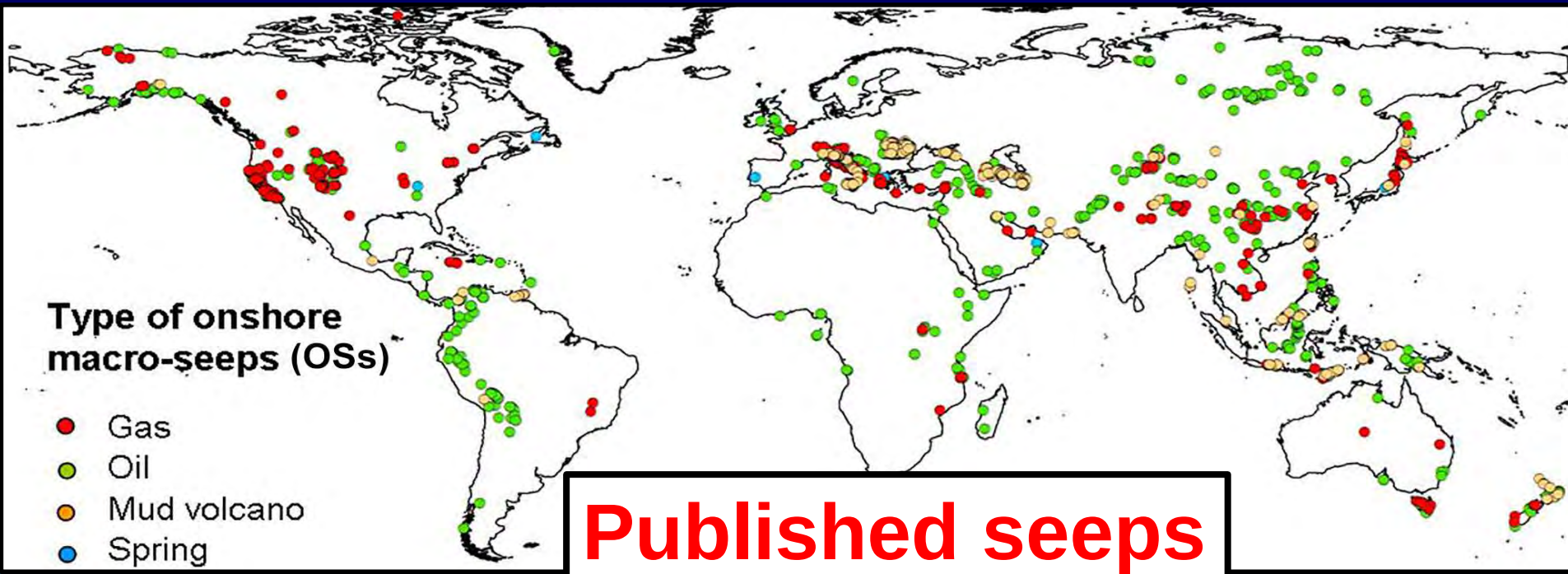
COURTESY OF
INTERNATIONAL PETROLEUM COMPANY, LTD

FIG. 8 (Seep type 3).—La Cira is a wide domal fold with considerable faulting on its crest. Production starts at 1,000 feet or less. On the top of the structure are numerous oil seeps. As none of the producing formations is exposed the seepage oil had to migrate from the producing zone upward along the faults.

Clampett et al. (1962)



- **“Come listen to a story about a man named Jed, a poor mountaineer, barely kept his family fed.**
- **Then one day he was shootin at some food, and up through the ground came a bubblin crude.**
- **Oil that is, black gold, Texas tea.”**

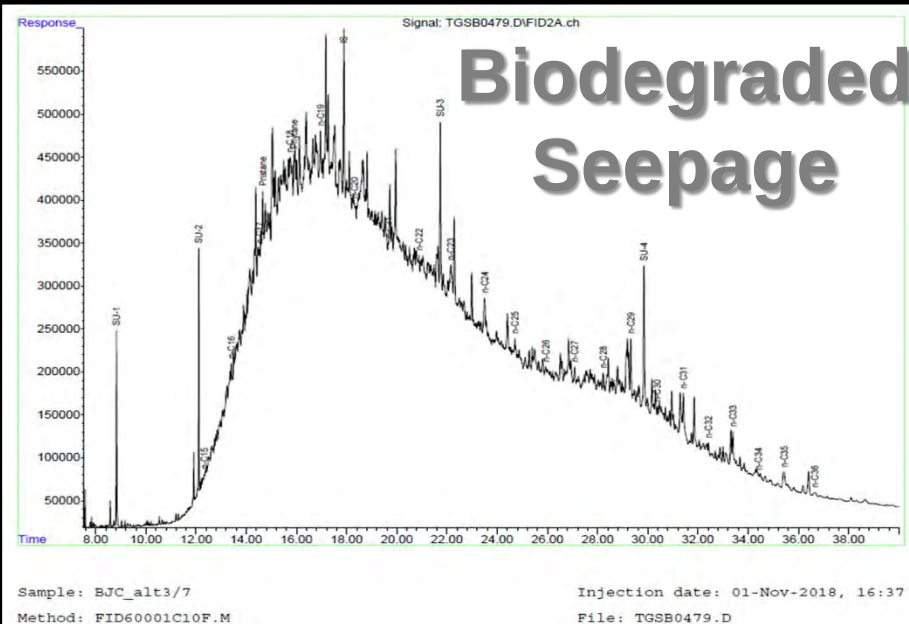


Oil seepage vs. natural background

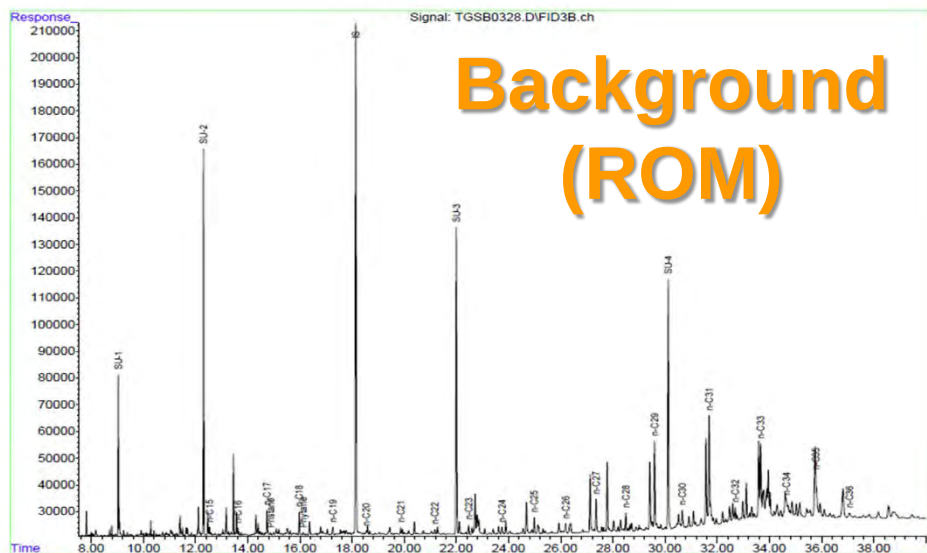
**“Live”
Seepage**



**Biodegraded
Seepage**

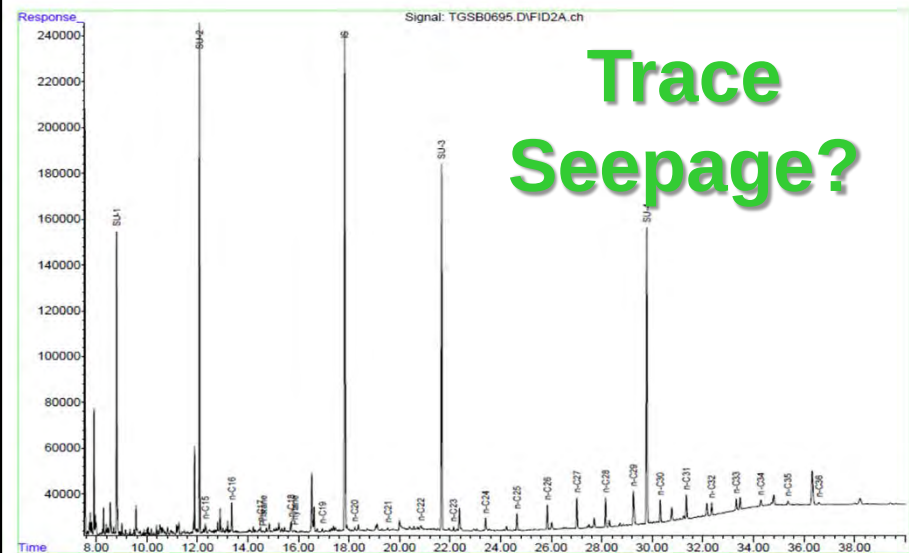


**Background
(ROM)**



Sample: TBZ105/16
Injection date: 08-Sep-2018, 08:36
Method: FID60002C10B.M
File: TGSB0328.D

**Trace
Seepage?**

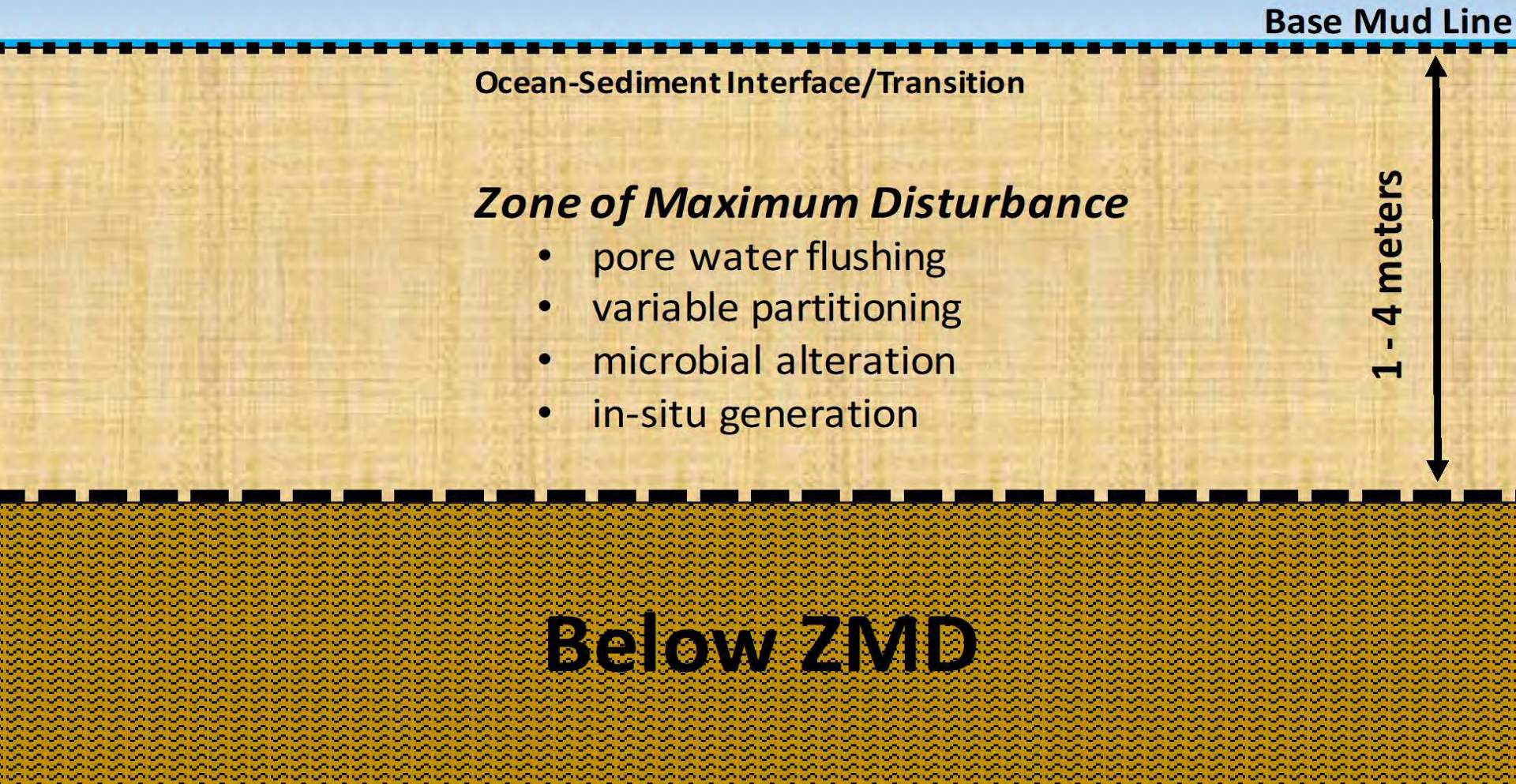


Sample: TBZ183/17
Injection date: 12-Nov-2018, 08:51
Method: FID60001C10F.M
File: TGSB0695.D

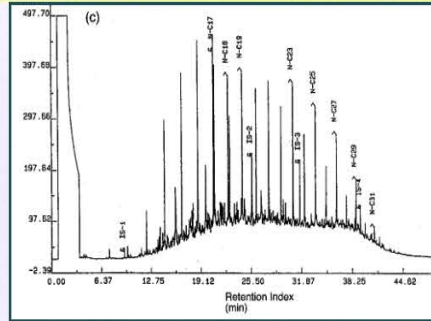
Abrams (1992) - understanding background

Zone of Maximum Disturbance (ZMD)

Ocean Column

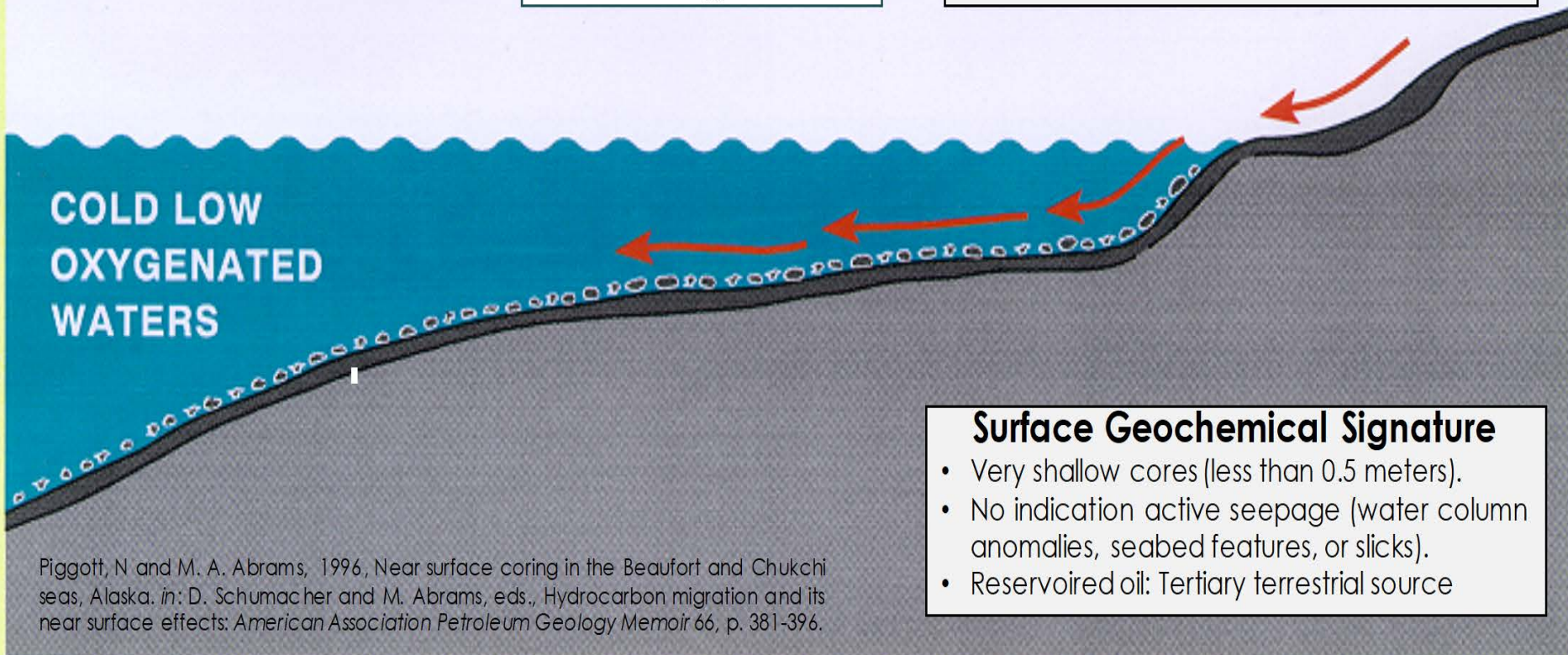


Abrams (1996) – source rock reworking delivered HC “bkgd” unrelated to seepage



Surface Geochemical Signature

- No anomalous interstitial sediment.
- Extract GC: n-alkanes present thermogenic.
- Extract TSF thermogenic signature
- Biomarkers marine Lower Cretaceous HRZ

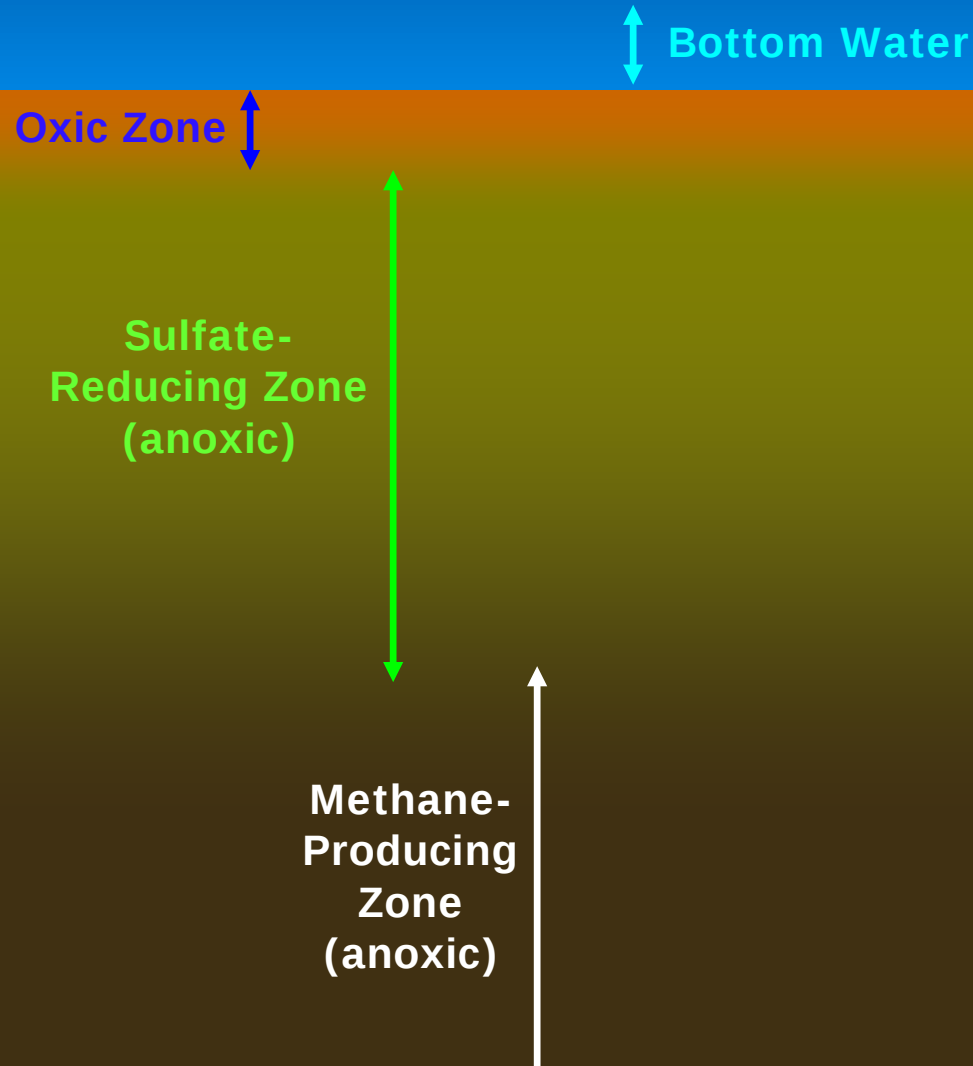


Piggott, N and M. A. Abrams, 1996, Near surface coring in the Beaufort and Chukchi seas, Alaska. in: D. Schumacher and M. Abrams, eds., Hydrocarbon migration and its near surface effects: American Association Petroleum Geology Memoir 66, p. 381-396.

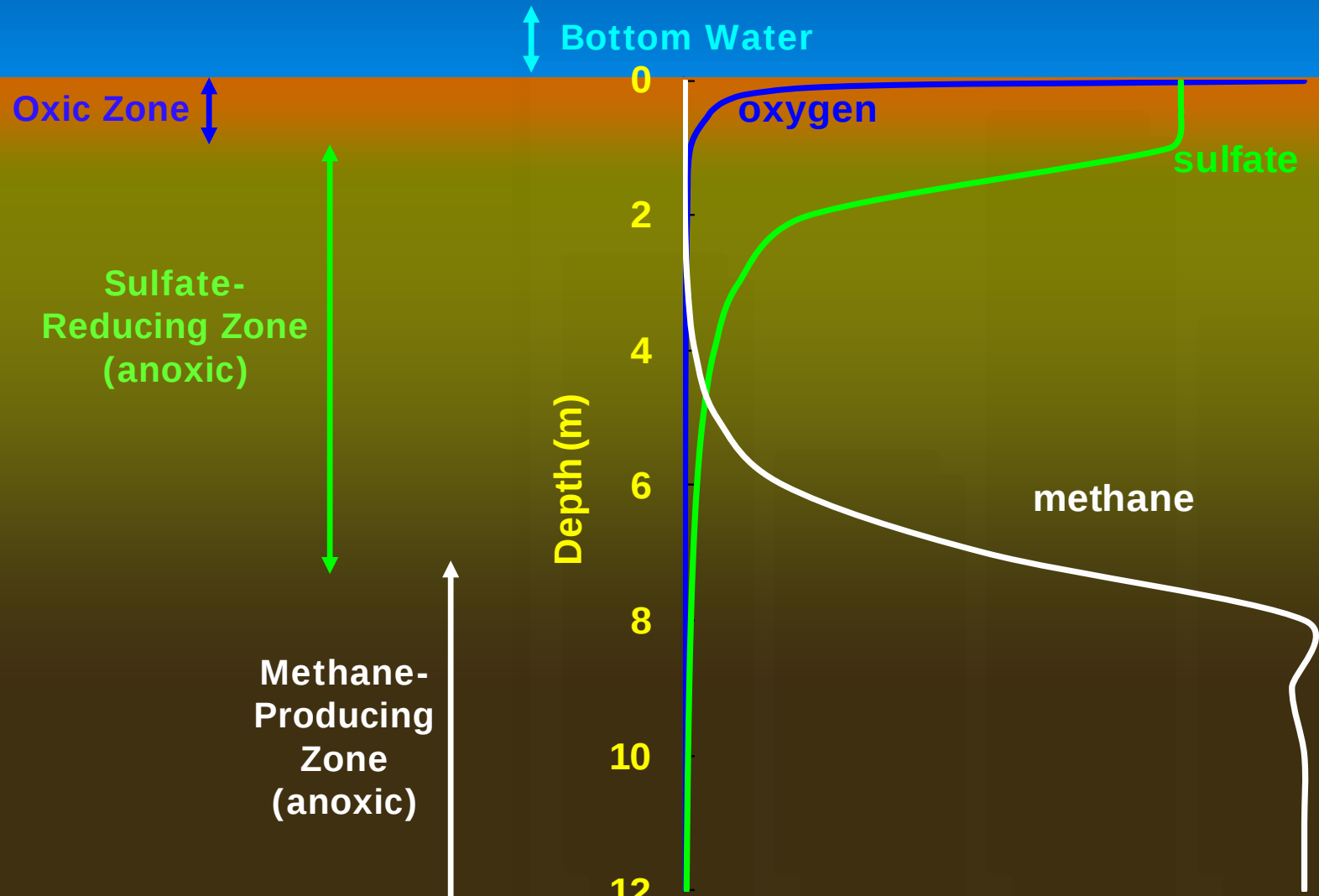
Surface Geochemical Signature

- Very shallow cores (less than 0.5 meters).
- No indication active seepage (water column anomalies, seabed features, or slicks).
- Reservoired oil: Tertiary terrestrial source

Seabed gas zones (world-wide background)



Seabed gas zones (world-wide background)



Objectives of Seep Hunting

Intent 1: To find and discern a seep **proxy**
anomaly from local ***background***
“contamination from biogeochem processes.”

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Intent 2: To use the proxy to understand regional & site-specific distribution of seepage to ***prove up charge***, and to help calibrate petroleum system model.

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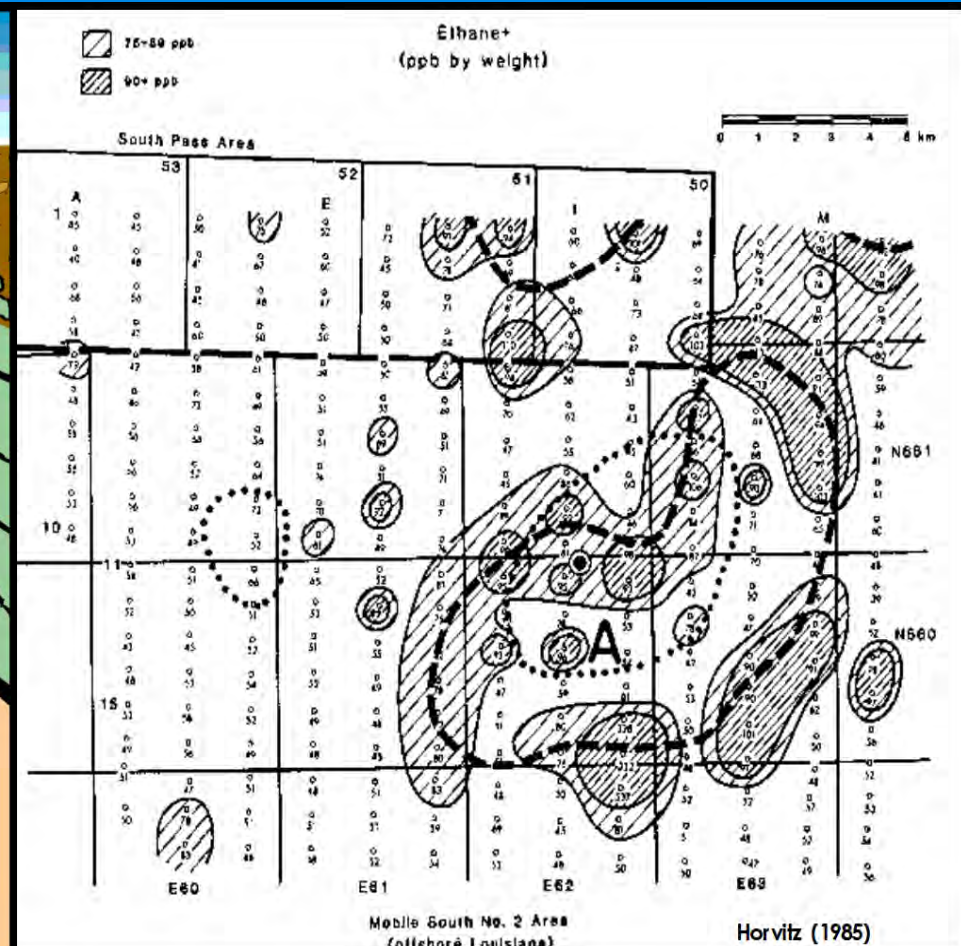
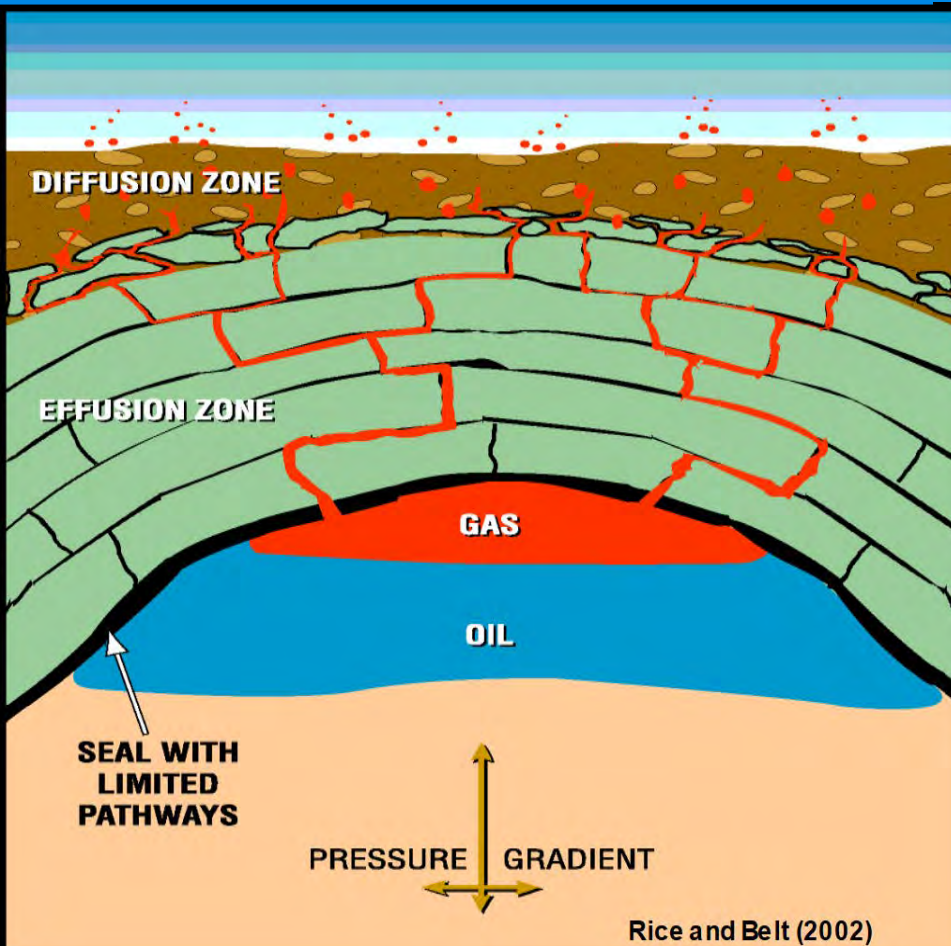
Intent 3: To compare seep biomarkers to regional oils for discerning ***age, maturity, depositional environment, quality.***

Site selection:

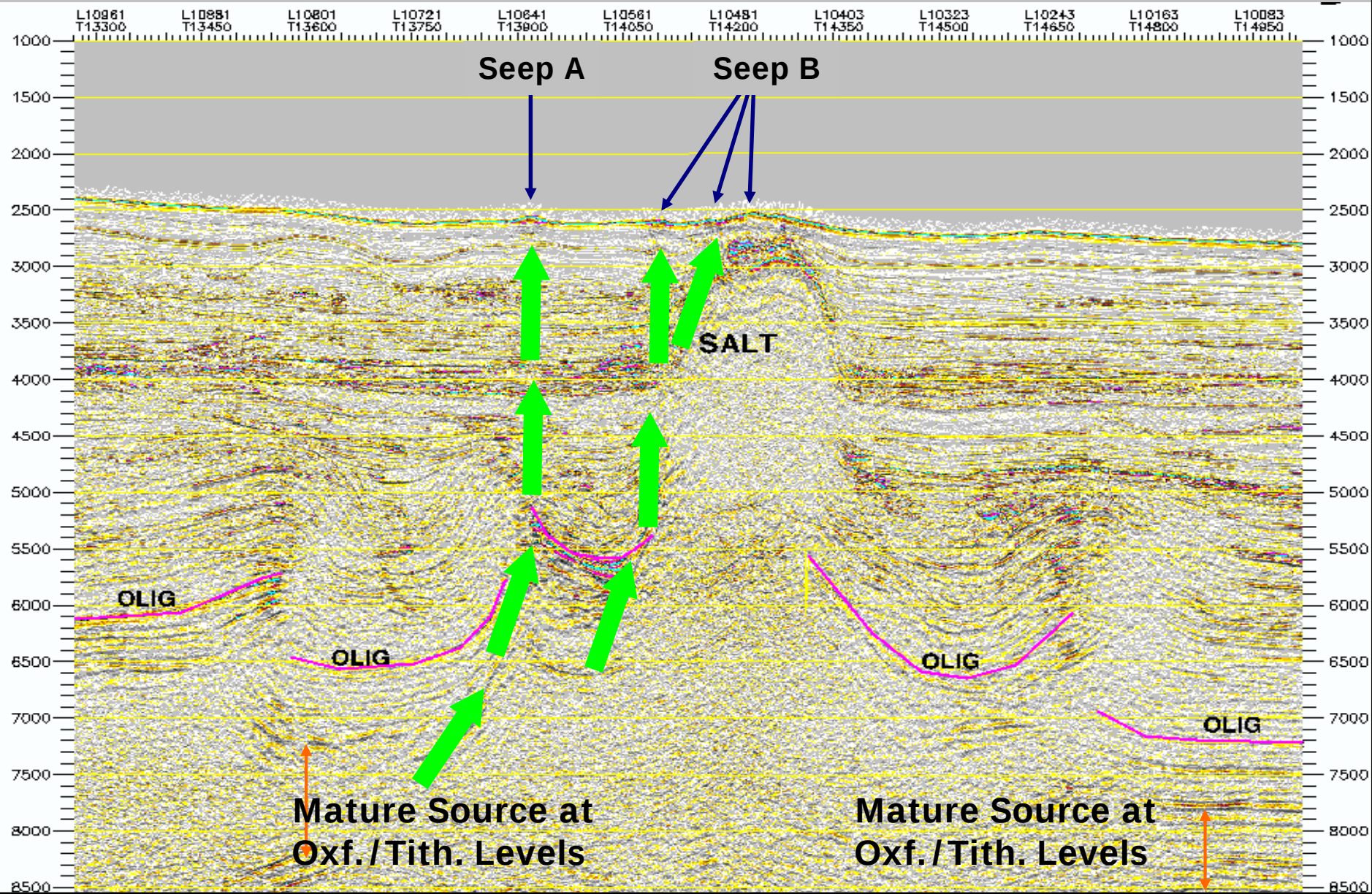
- types of seep proxies
- onshore vs. offshore
- grid-based vs. targeted

Soil-gas surveys based on vertical migration model, using grid approach

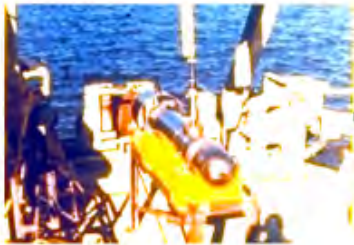
- Surface results are contoured in map-view to identify anomalies
- Any anomaly (halo) is used as evidence for charged trap



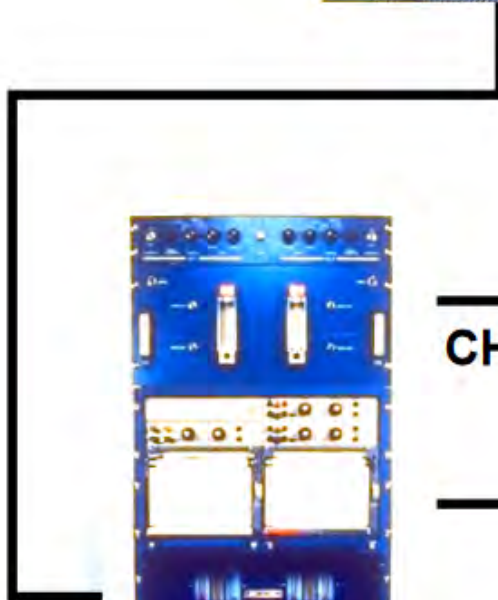
Targeted-site approach using seabed seismic expressions as seep proxies



SNIFFERS



**WATER
INTAKE
SYSTEM**

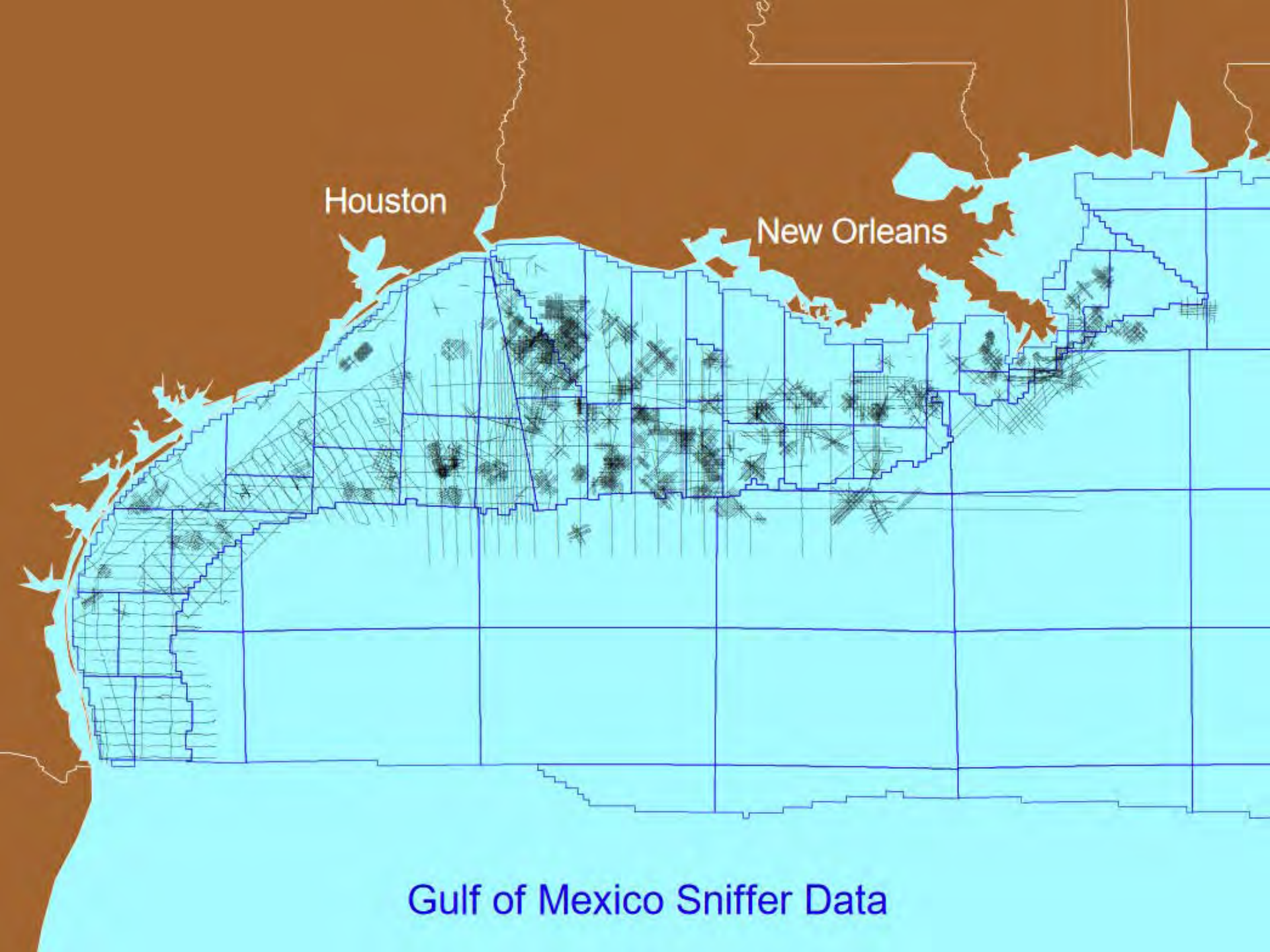


**GAS
CHROMATOGRAPH**

**GAS
STRIPPER**

**DATA
LOGGER**

**AUXILIARY
PARAMETERS
LOCATION
TEMPERATURE
WATER DEPTH
TOW DEPTH**

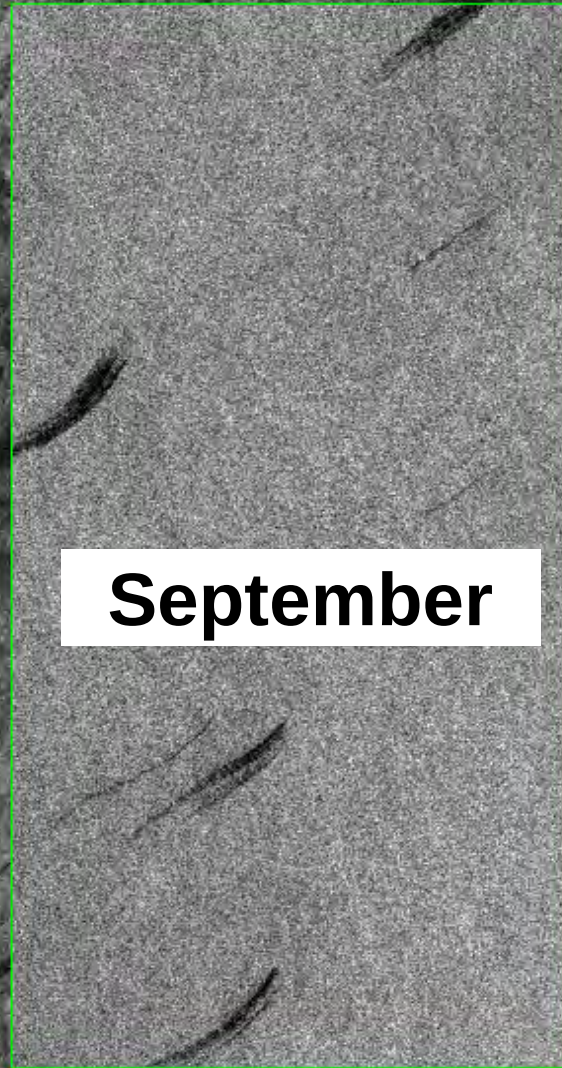


Gulf of Mexico Sniffer Data

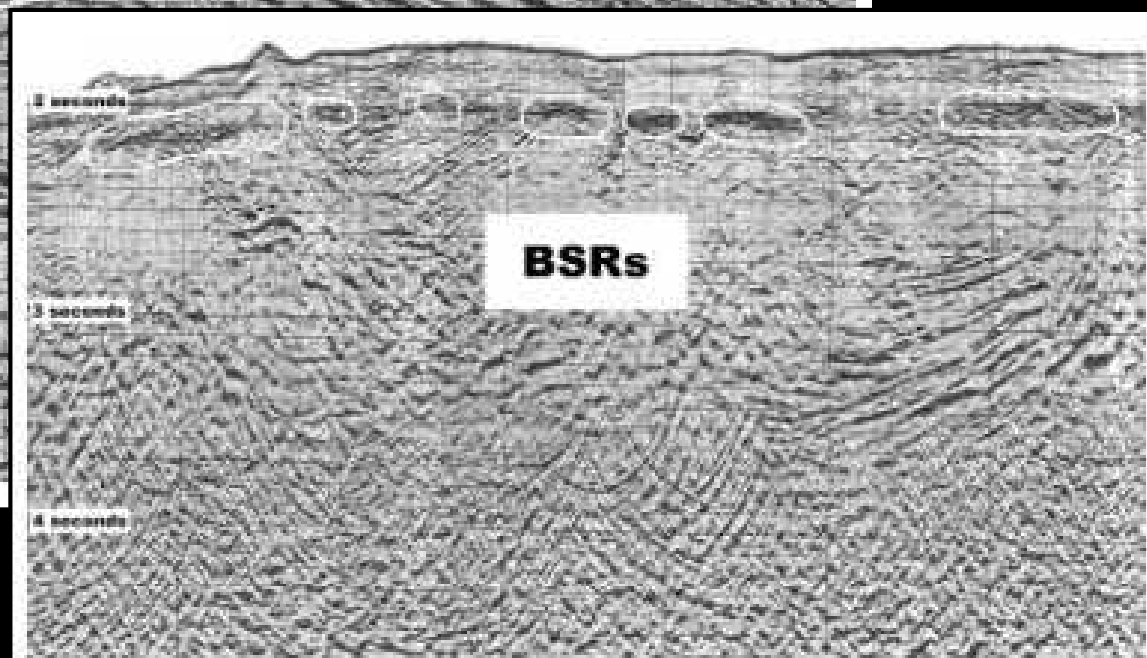
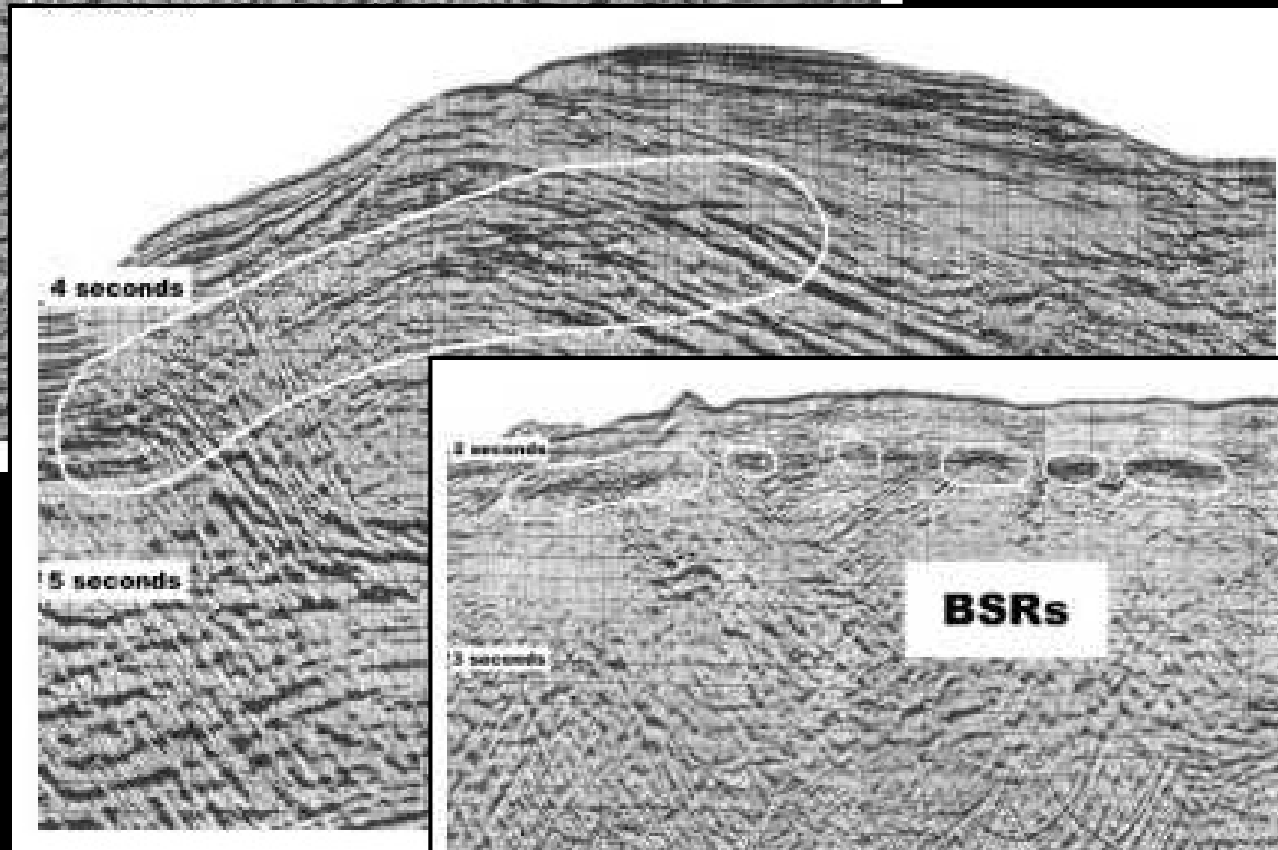
Seep Proxies: sea-surface slicks

February

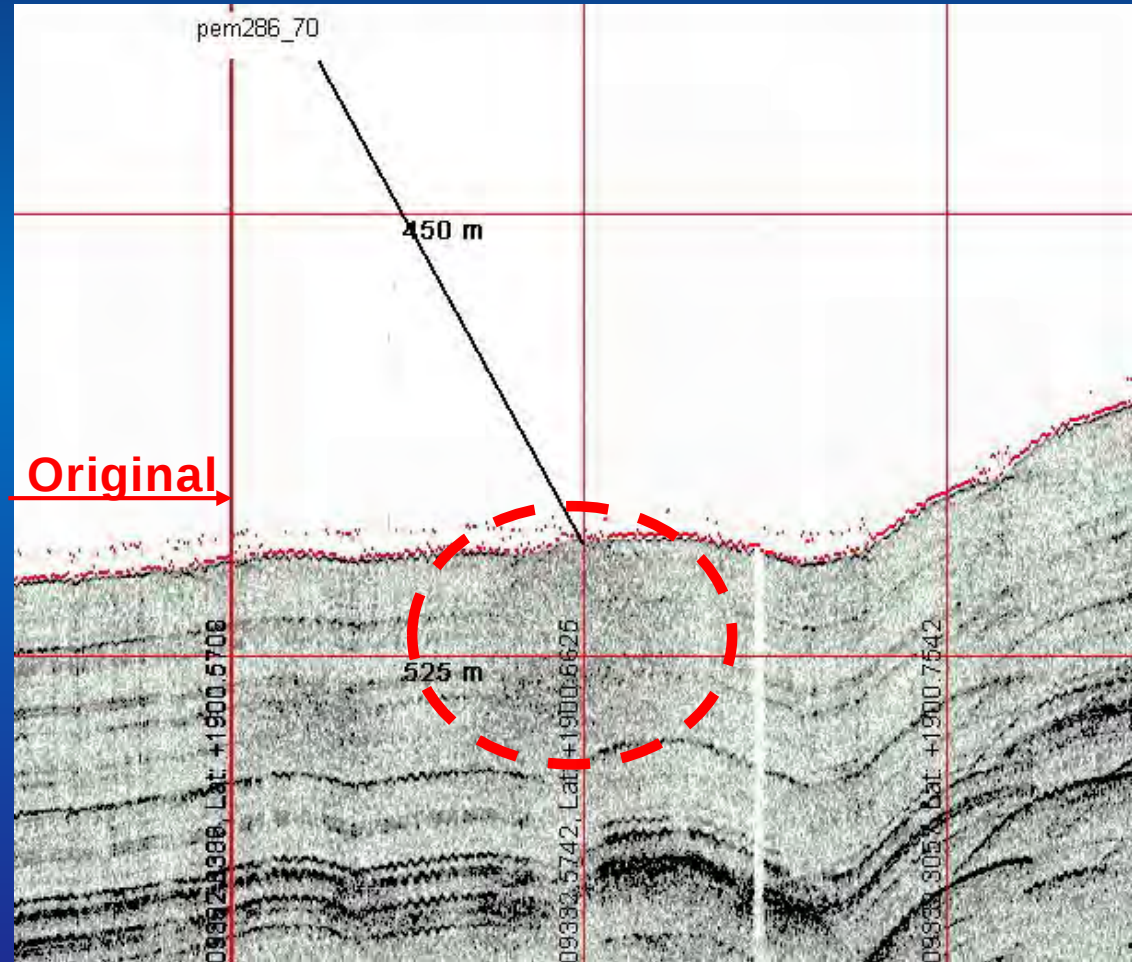
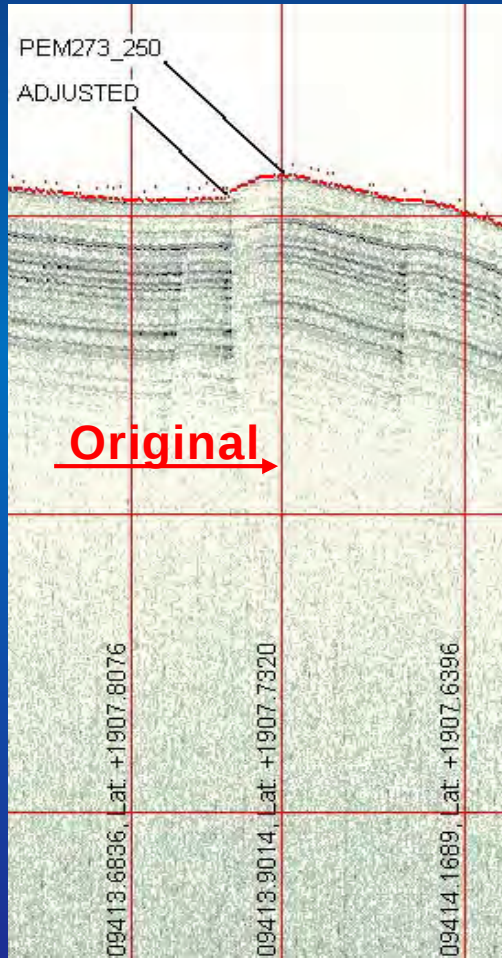
September



Bottom Simulating Reflectors (BSRs) as seep proxies



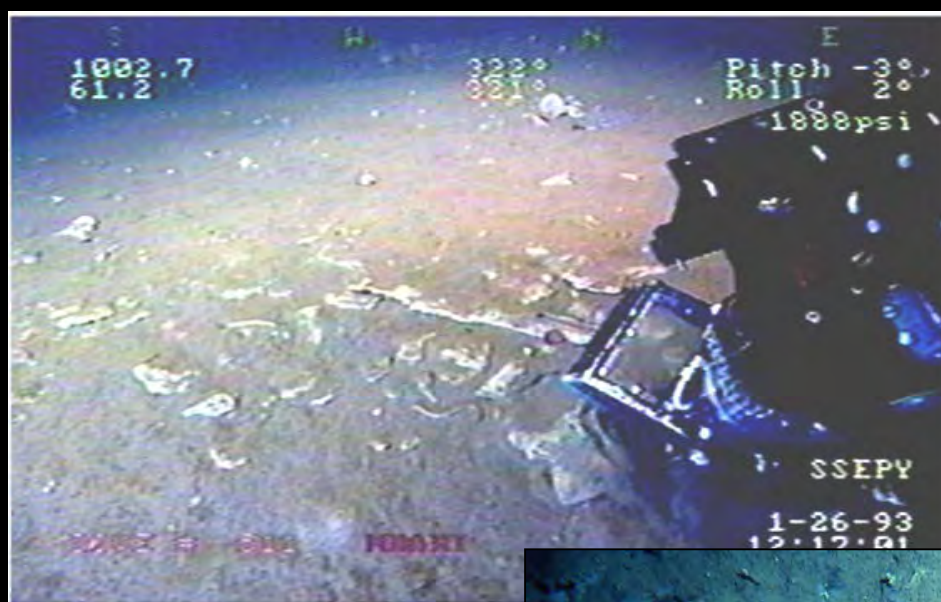
Sub-Bottom Profiler (SBP) images as seep proxies



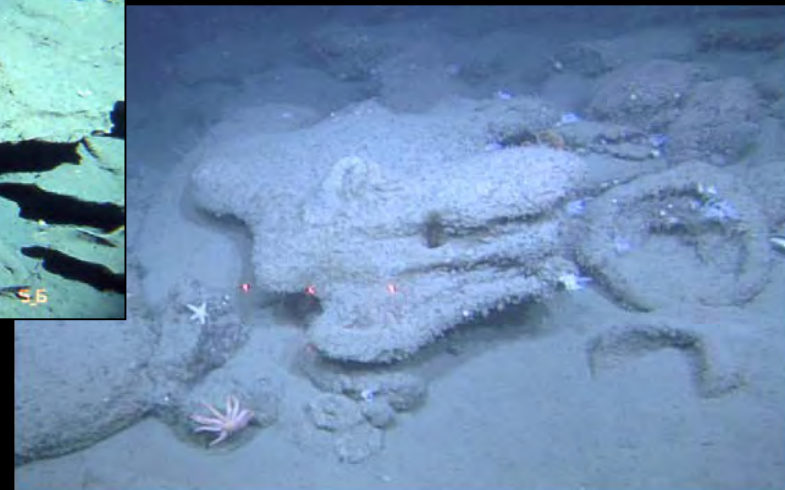
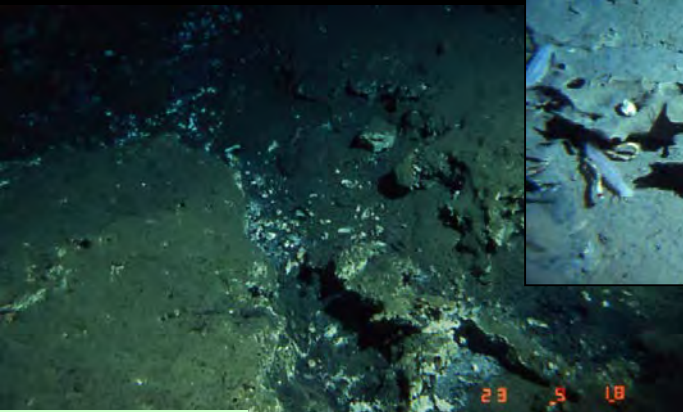
Chemosynthetic animal communities as seepage proxies



Authigenic carbonate hardgrounds as seep proxies (proxies for past chemos)

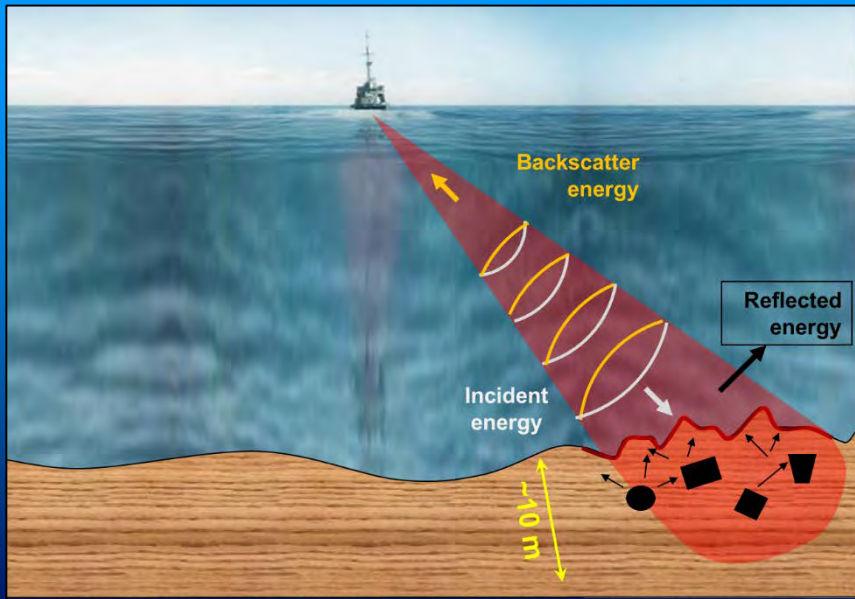
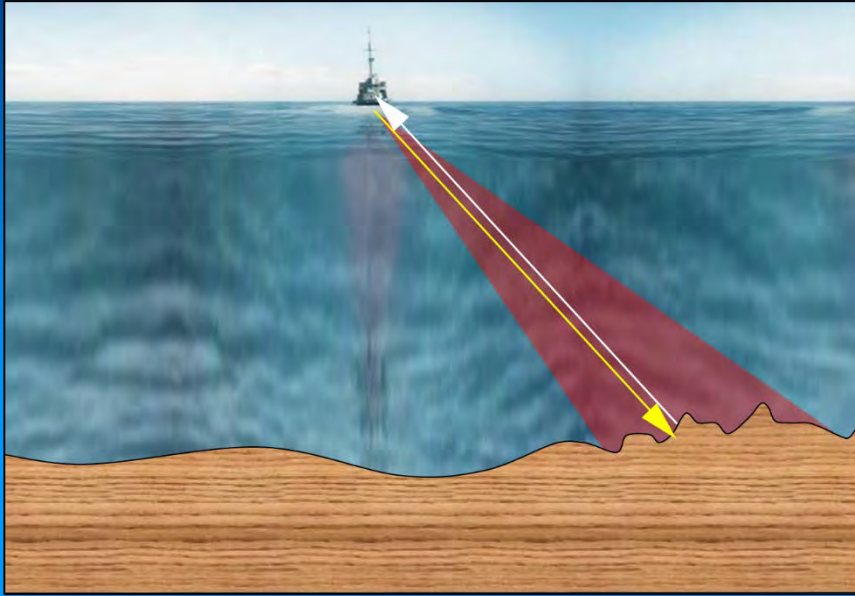


Ian MacDonald



Casey Moore

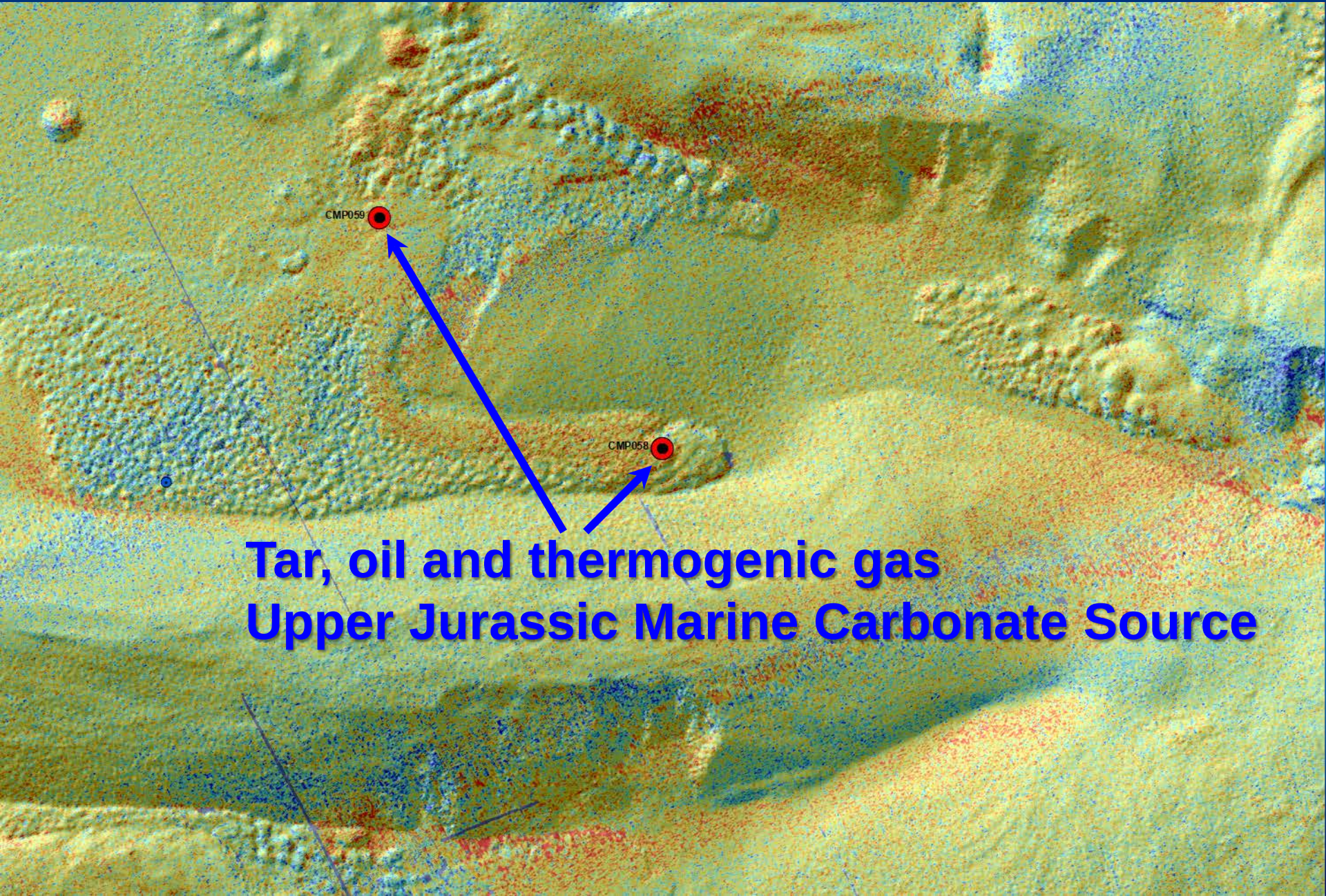
Multibeam *Backscatter* detecting and mapping hard-grounds as seep proxies



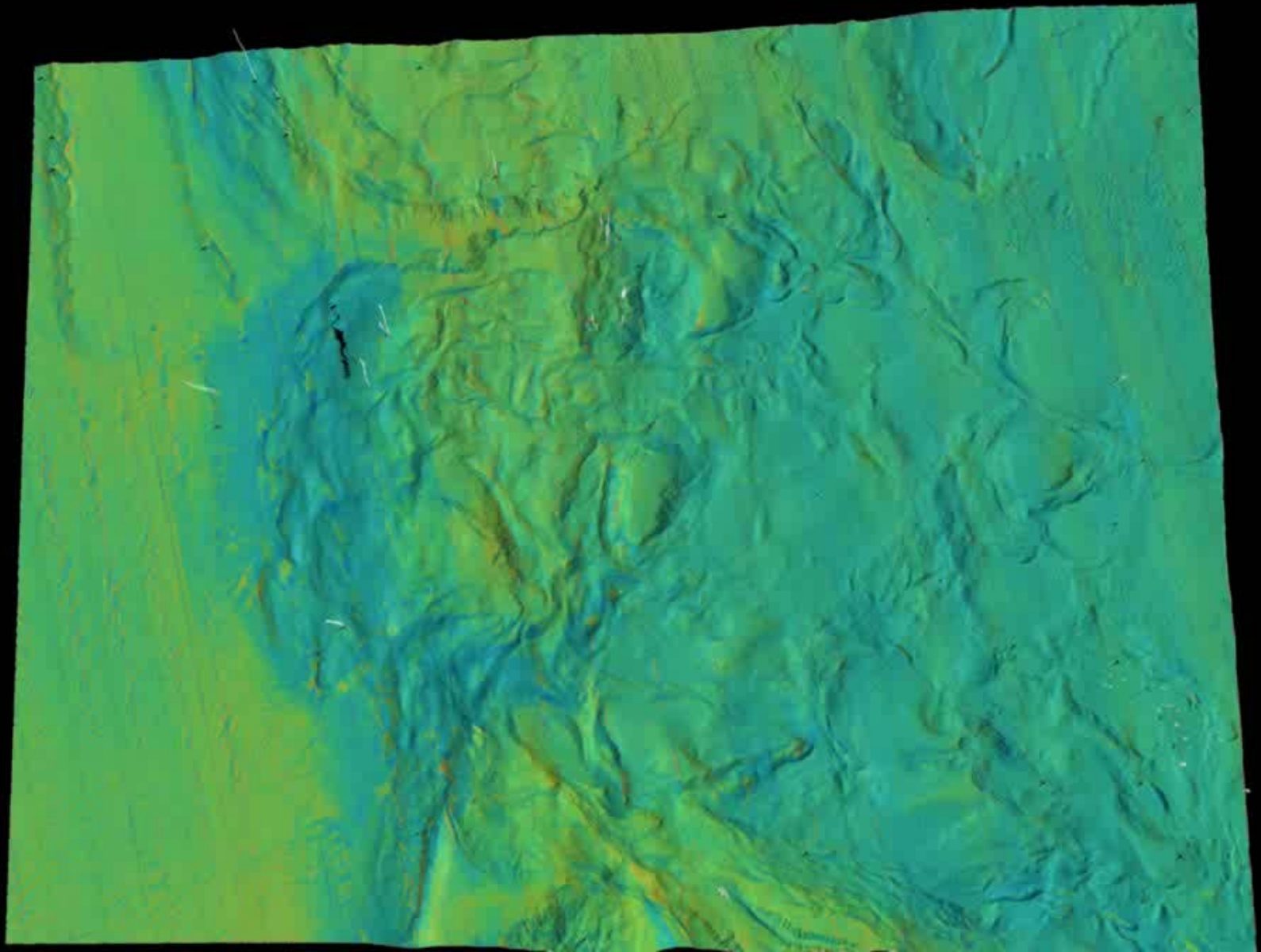
Backscatter is a function of

- 1) the hardness of the seafloor*
- 2) the roughness of the seafloor*
- 3) scattering immediately below the seabed*

Popcorn Field = Tar Mat



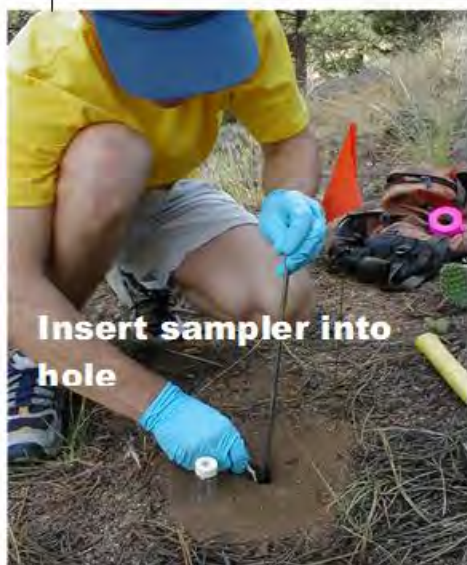
3D View of Multibeam Data



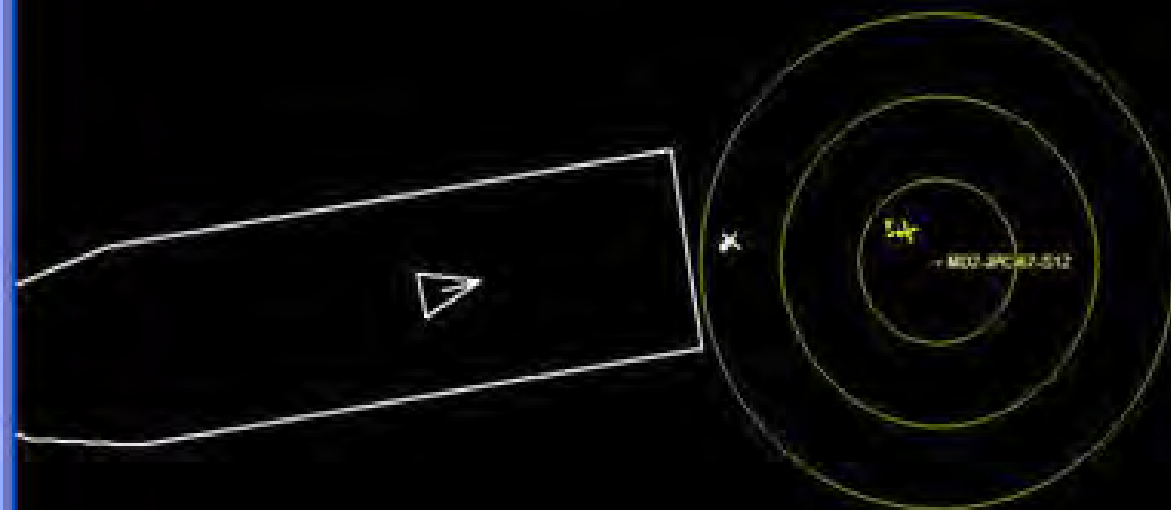
Seep-proxy sample collection:

- HCs from land surveys
- HCs from seabed surveys
- *(microbial)*

Sampling for Gases & Volatiles on Land



Seabed sampler (corer) positioning with USBL Navigation



COG 079.7
HDG 281.8
ETA 13:29

BRG 098.9T
SPD 0.1kts
WPT MD2-JPC-67-S12

N27 07.4763
PITCH 2.6
13:28:16.3

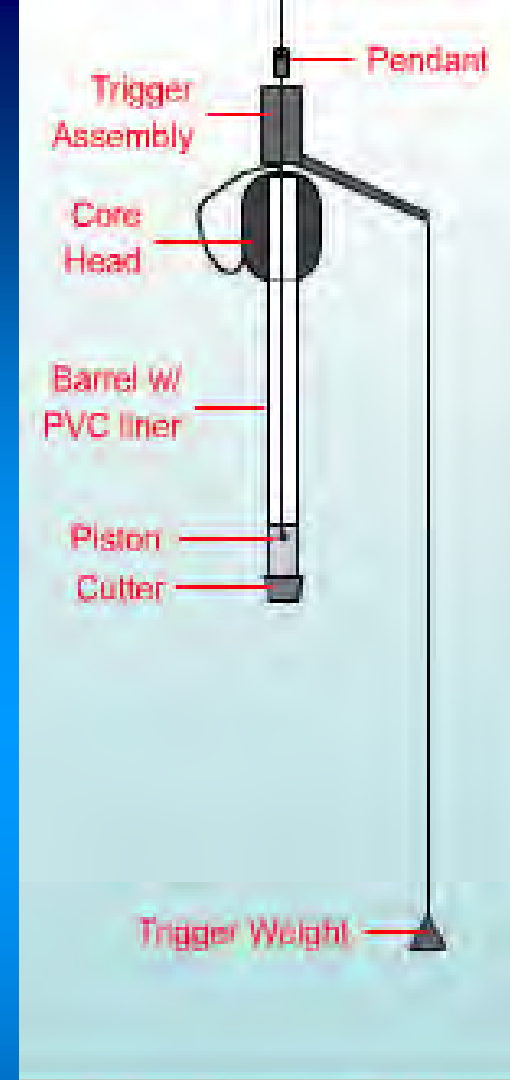
W090 16.4583
ROLL 0.3
RNG 13.2m

ROV D 2135.7m
WPT MD2-JPC-67-S12

Corer
RNG 2.7m

Collecting samples from seabed:

- Piston corer (6m)
- Gravity corer (6m)
- Vibrocorer (5m)



Core Sectioning for Geochem Analysis

*Upper Meter:
Unsampled due to
possible contamination*

Archive Sample



BOTTOM

TOP



0

1m

*The upper meter was capped and
saved for later biostratigraphic and
sedimentological analysis.*



Sample Processing for Geochem Analysis



MACRO-seepage of oil and gas in cores (the best proxies)

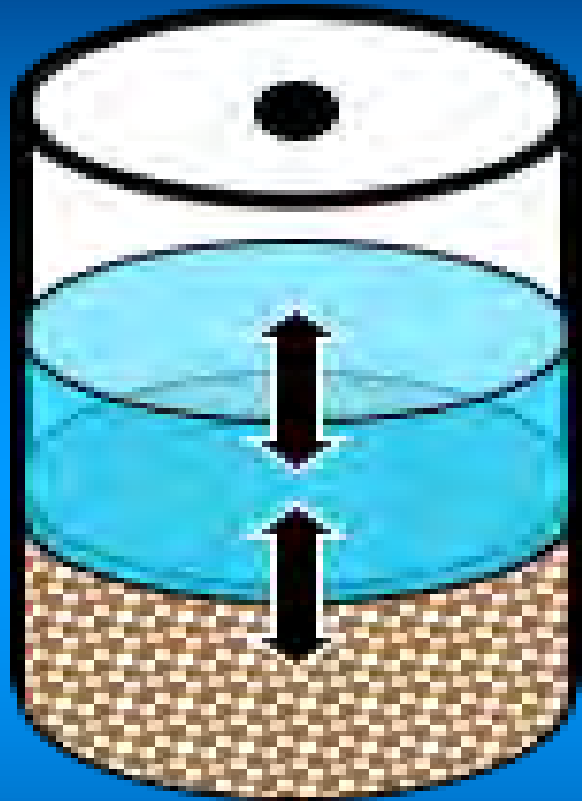


Geochem analysis for HCs:

(extraction → separation → detection)

- LMW (C_1 - C_5 gases)
- HMW (C_{15} - C_{35} liquids)
- mid-range (C_6 - C_{14} volatiles)

LMW HCs (gases): two types of extraction

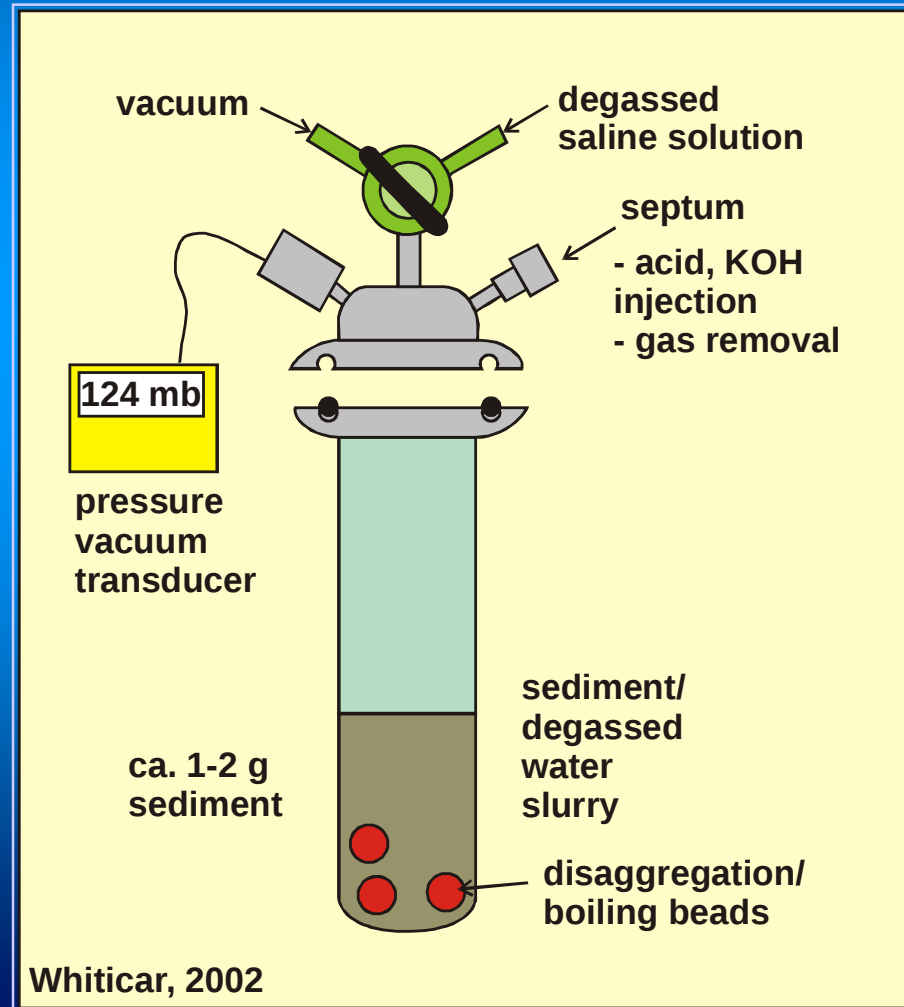


Interstitial (dissolved)

Gases contained within sediment pore space, dissolved in pore waters, or as free gas.

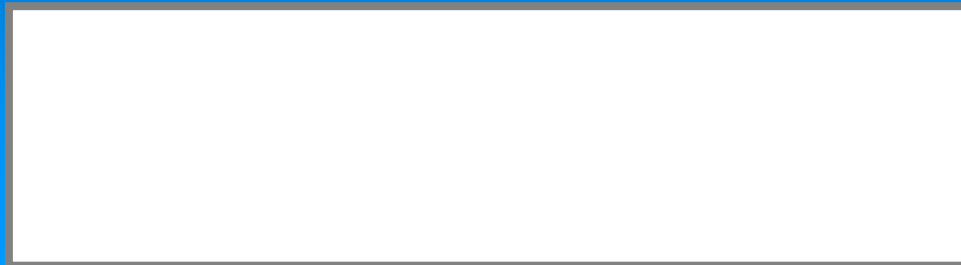
Bound (adsorbed)

Gases attached to mineral surfaces, entrapped in structured water, or authigenic carbonate inclusions.

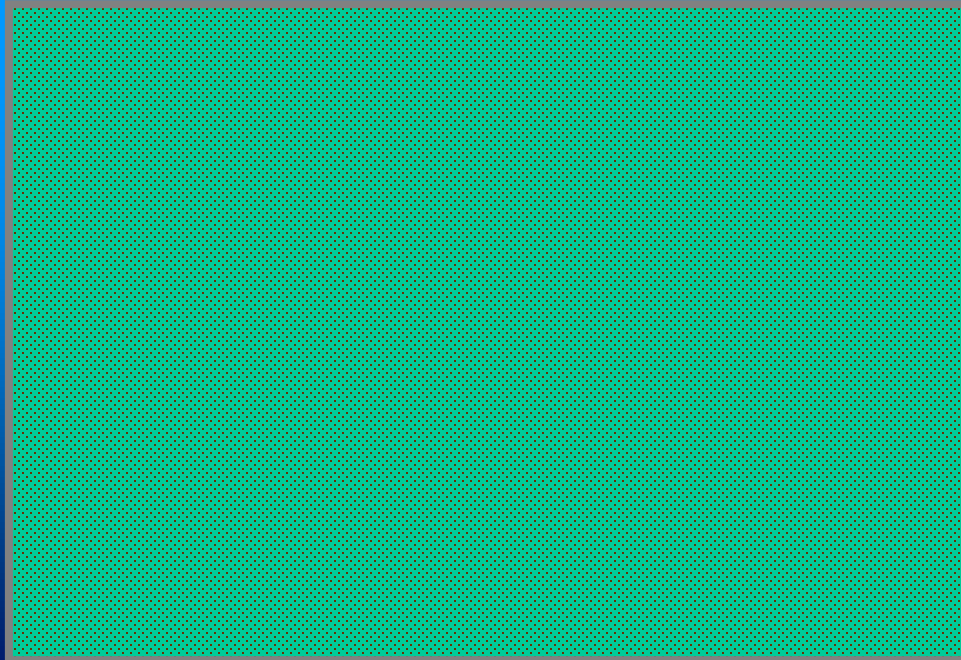


Interstitial gas extraction by partitioning

Inert Gas
headspace



Sediment
and
saltwater



Interstitial gas extraction by partitioning

Heated Agitation (40°C)

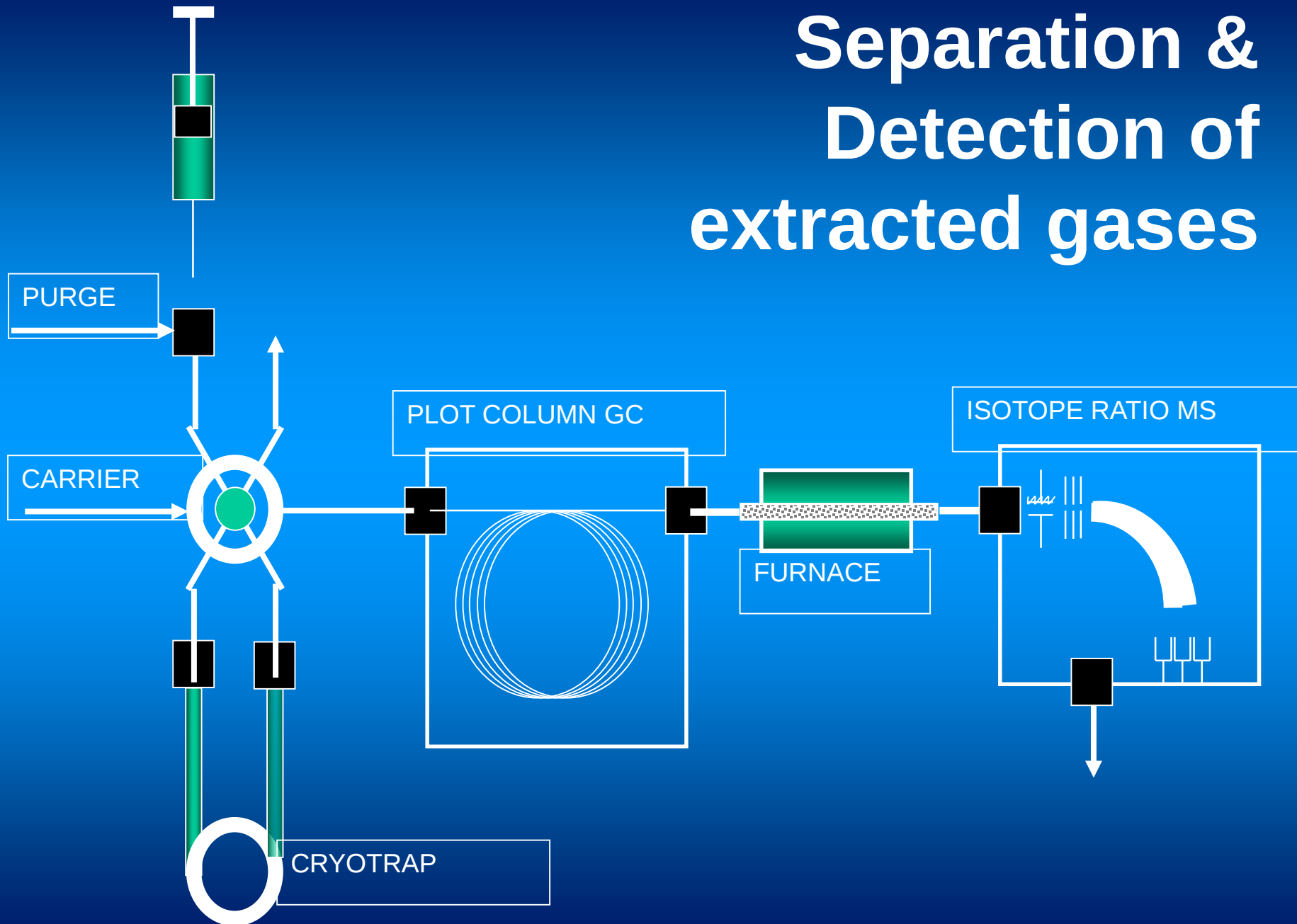
Inert Gas
headspace

Methane+ (95%)

Sediment
and
saltwater

Methane+ (5%)

Separation & Detection of extracted gases





**Hot
solvent
extraction
of dried
sediment
for HMW
HCs**

Separation & Detection of mid & HMW HCs

for Screening:

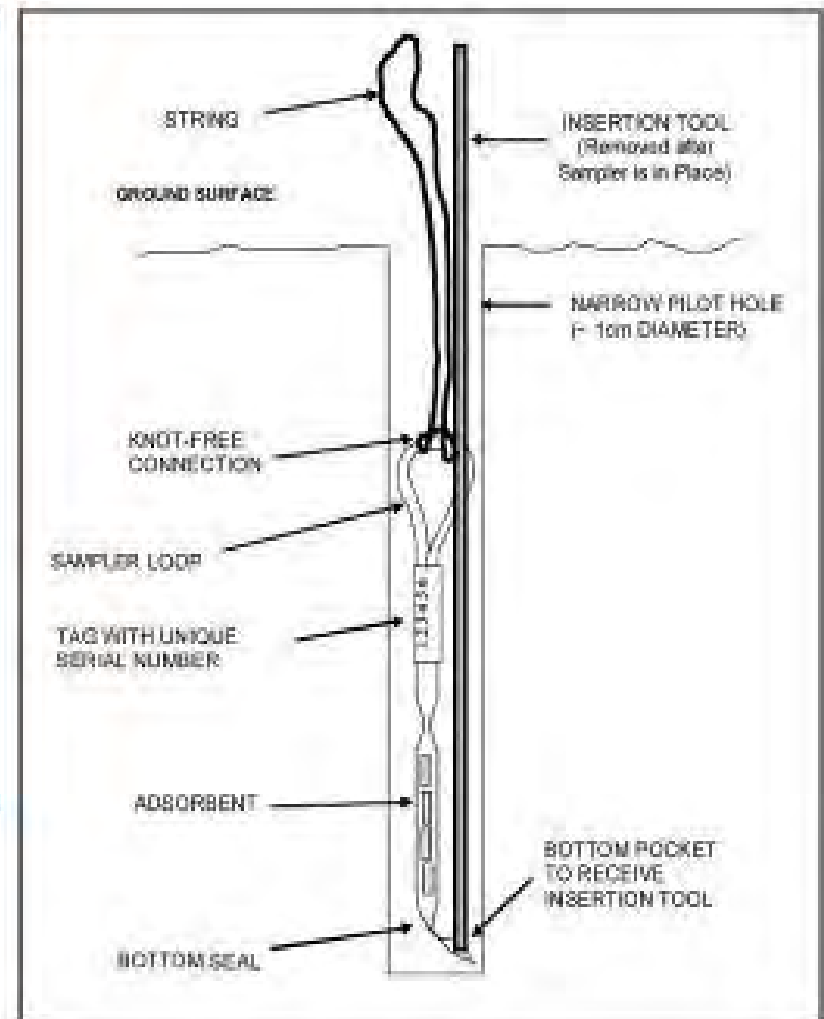
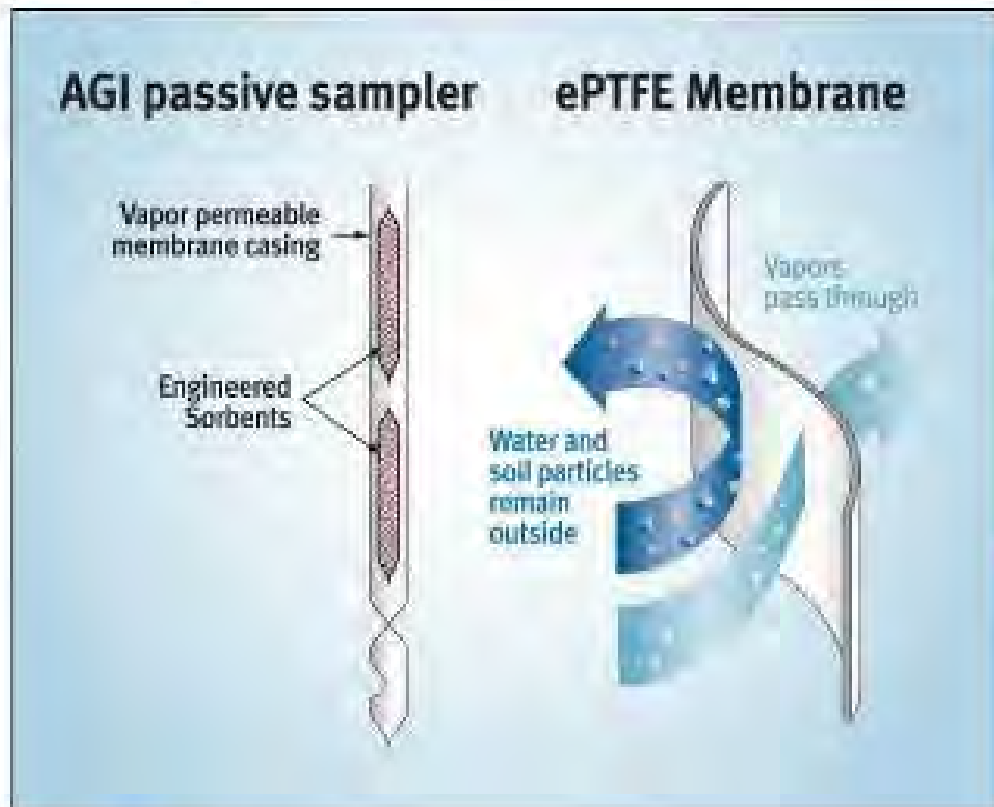
- Total Scanning Fluorescence for aromatics
- Gas Chromatography for saturates

for Advanced:

- GC/MS for Biomarkers



Mid-Range HCs: by passive-sorbent extraction



Passive sorbent used for sampling marine sediments

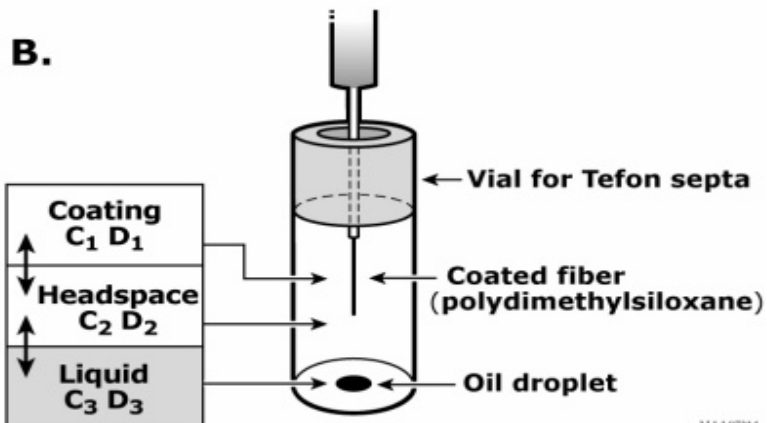
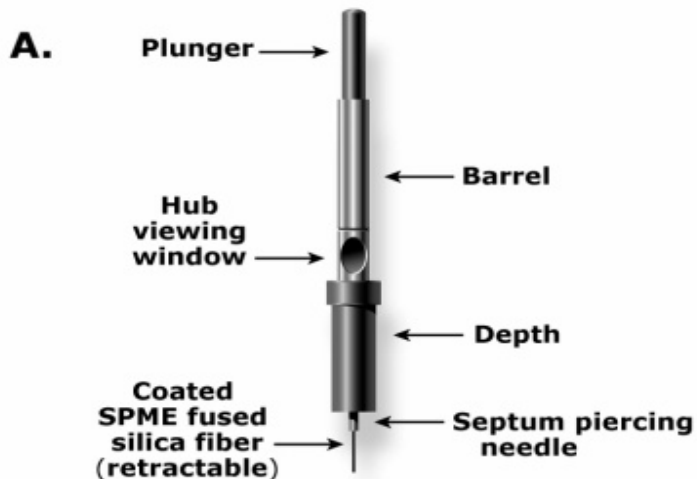


Volatile HCs
equilibrate in
closed system



Mid-range HCs: by Headspace Solid Phase Micro-extraction (SPME)

Solid Phase Micro Extraction (SPME)



MAA107214



Geochemical Interpretation of Proxies

- of mid range HCs
- of light HC gases
- of liquid HCs
- of some recent observations

Mid-range HC hotspots from seabed grid survey

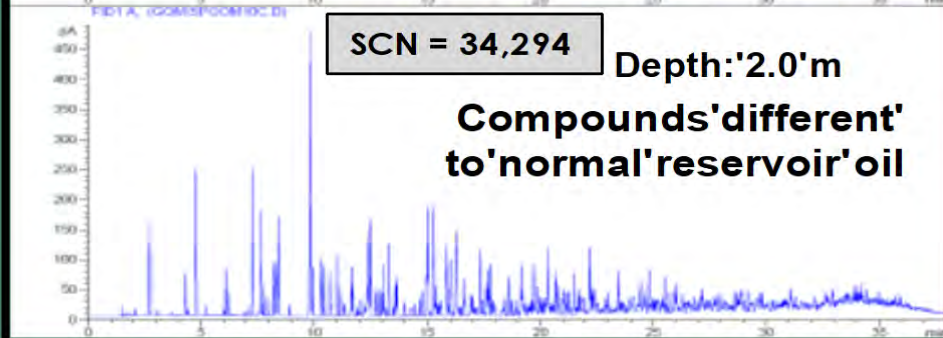
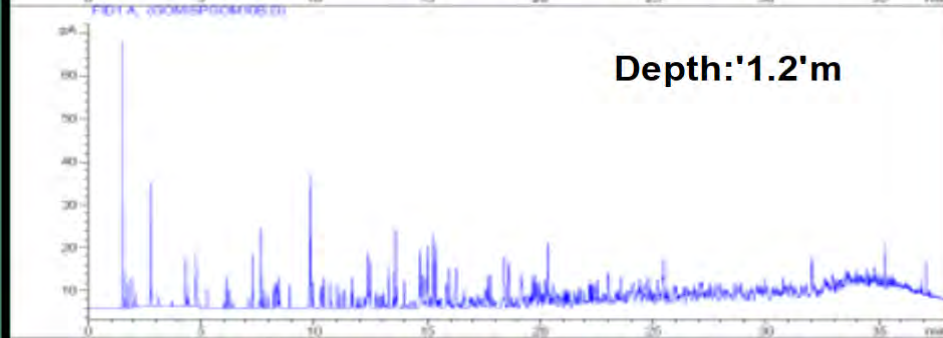
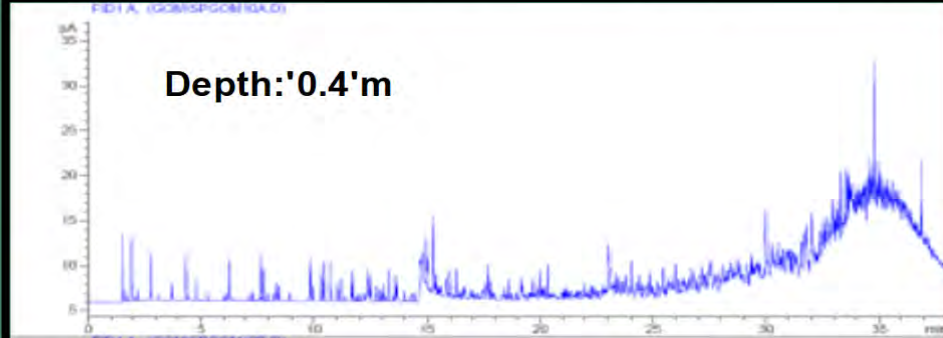
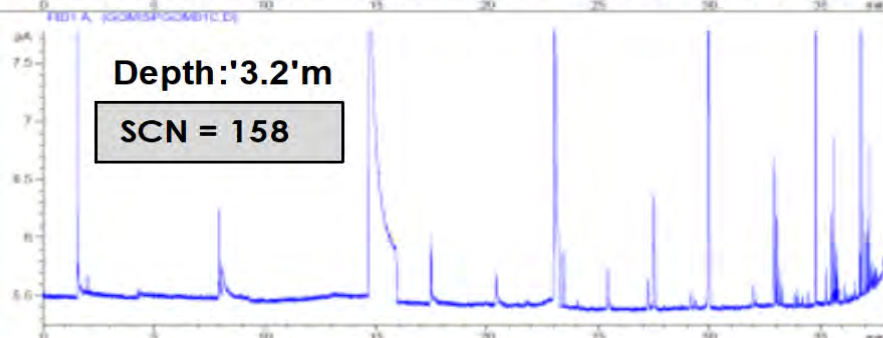
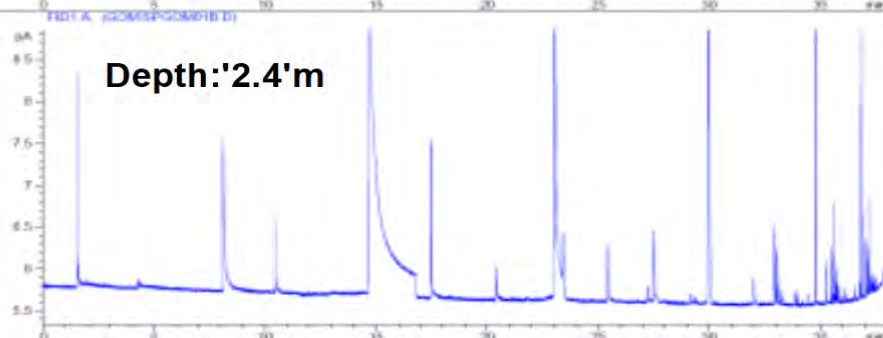
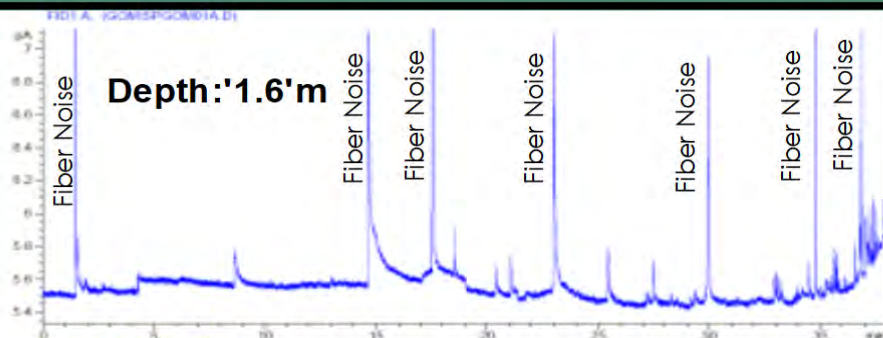
Example Results using SPME

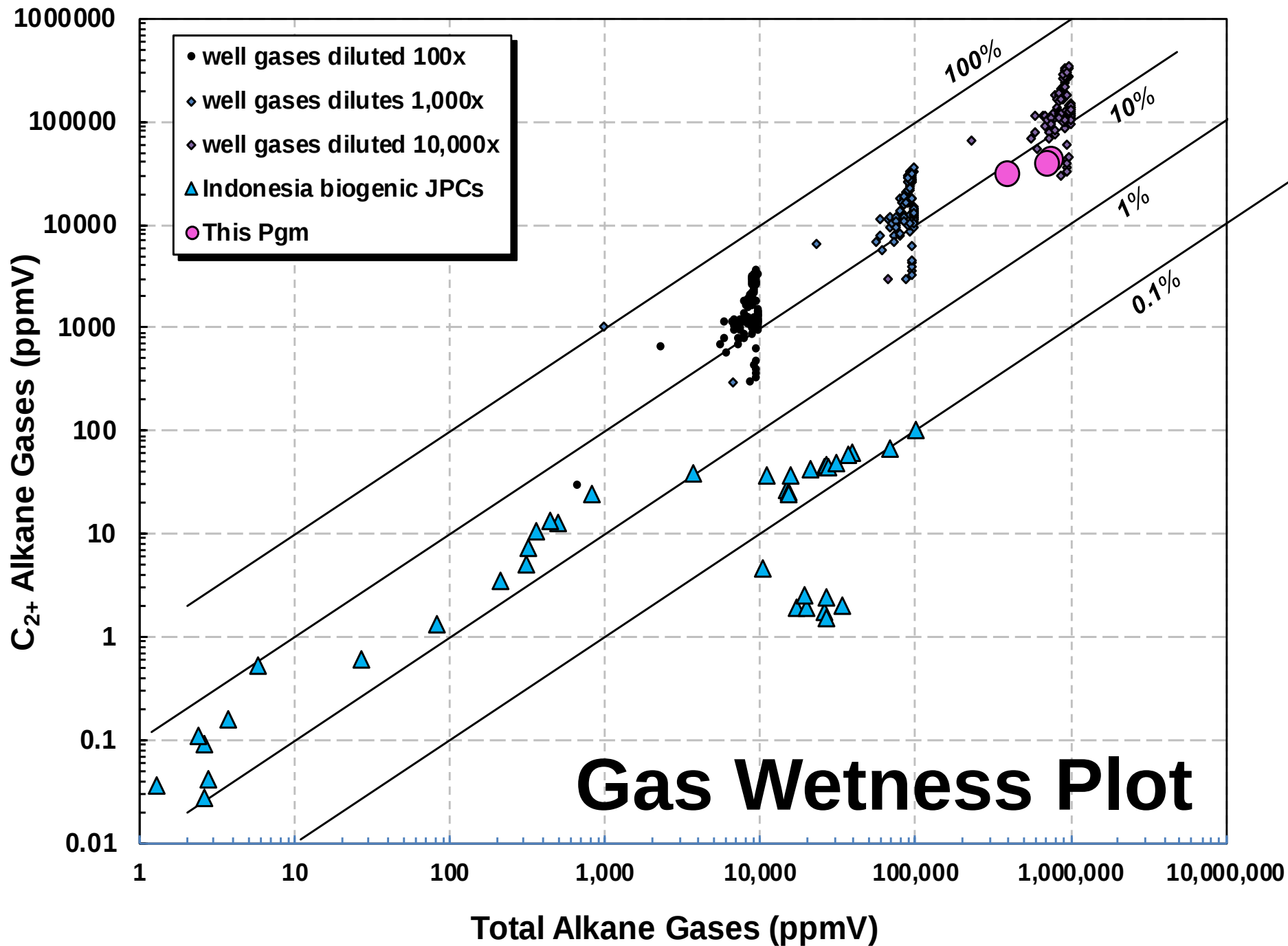
Background Sample

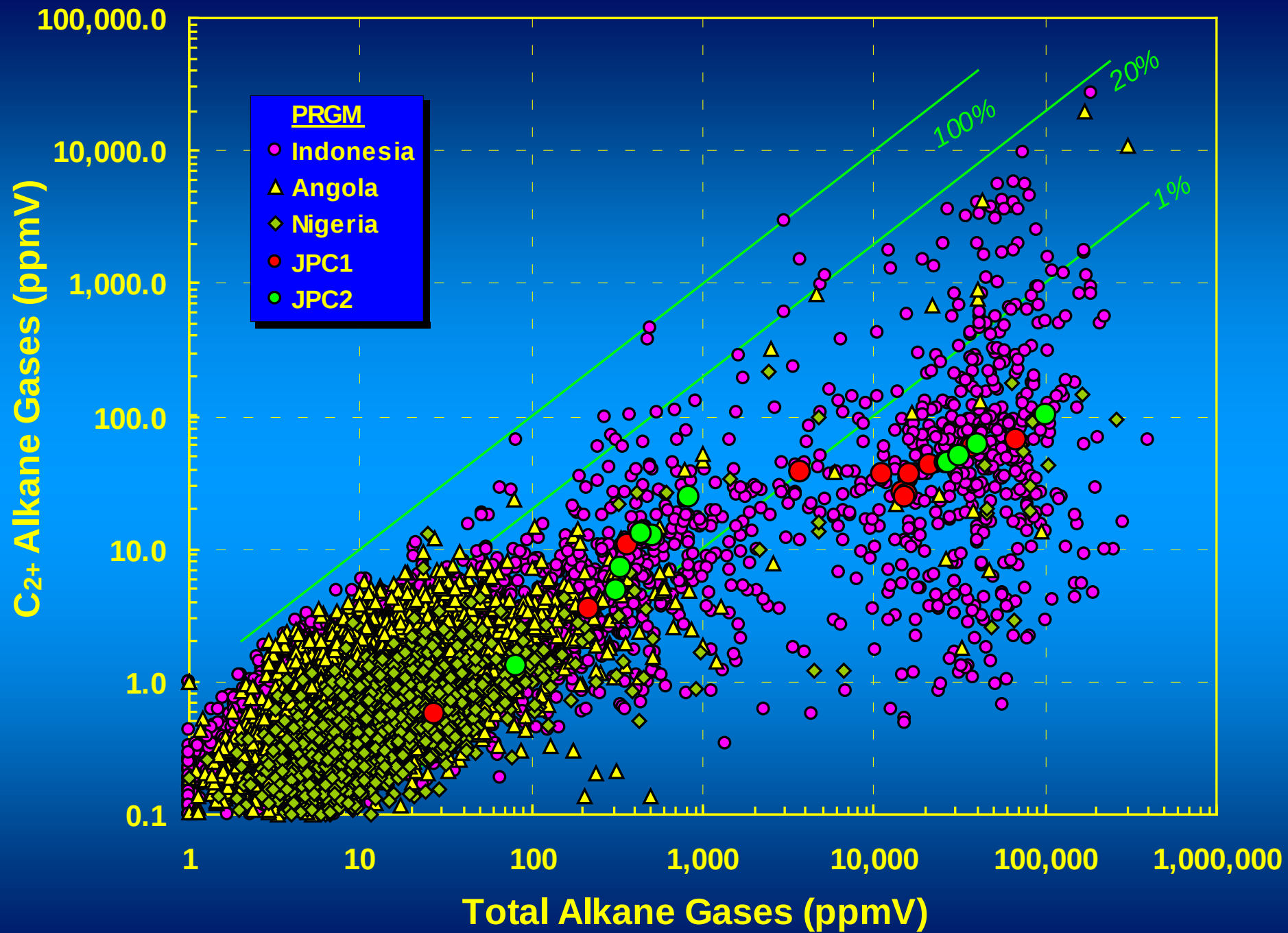
Core Number	Sum'SCN SPME	Methane ppm	Total'Disrupter C1@5	Wet'gas Fraction
1A	76	9	11	0.2
1B	181	16	21	0.2
1C	158	11	15	0.3

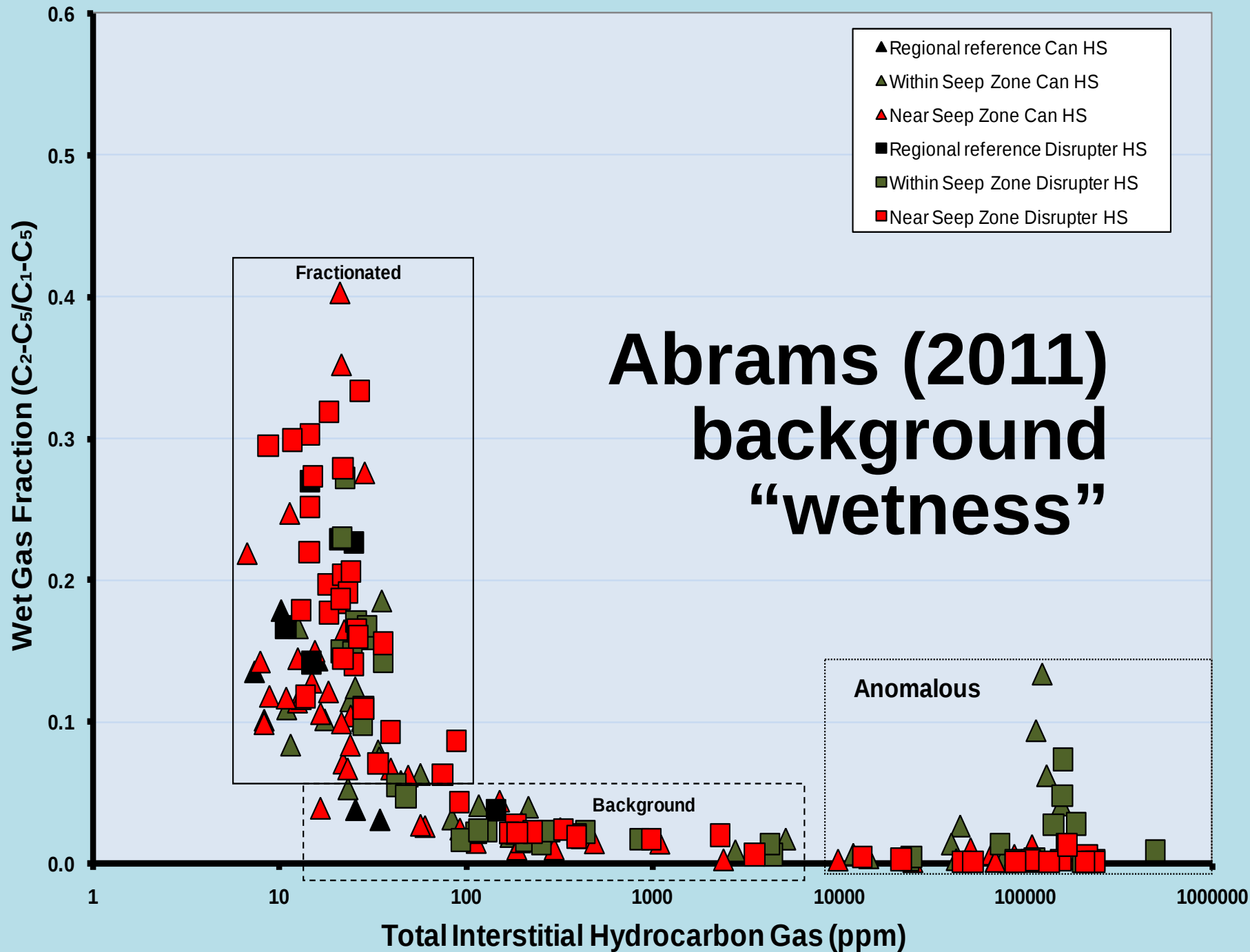
Within'Seep'Zone

Core Number	Sum'SCN SPME	Methane ppm	Total'Disrupter C1@5	Wet'gas Fraction
10A	4588	71454	72445	0.01
10B	4859	136500	140343	0.03
10C	34294	181780	186992	0.03

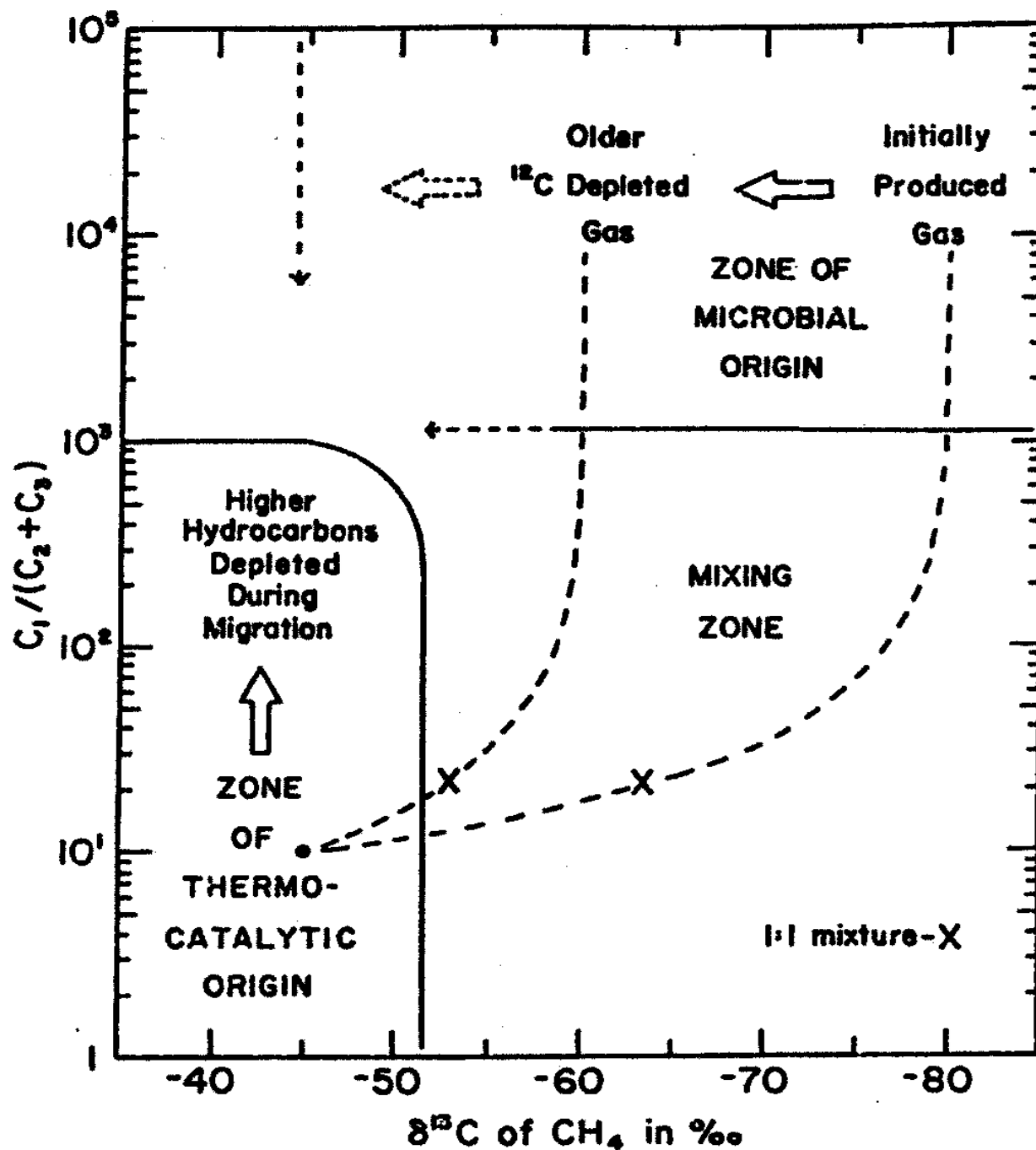


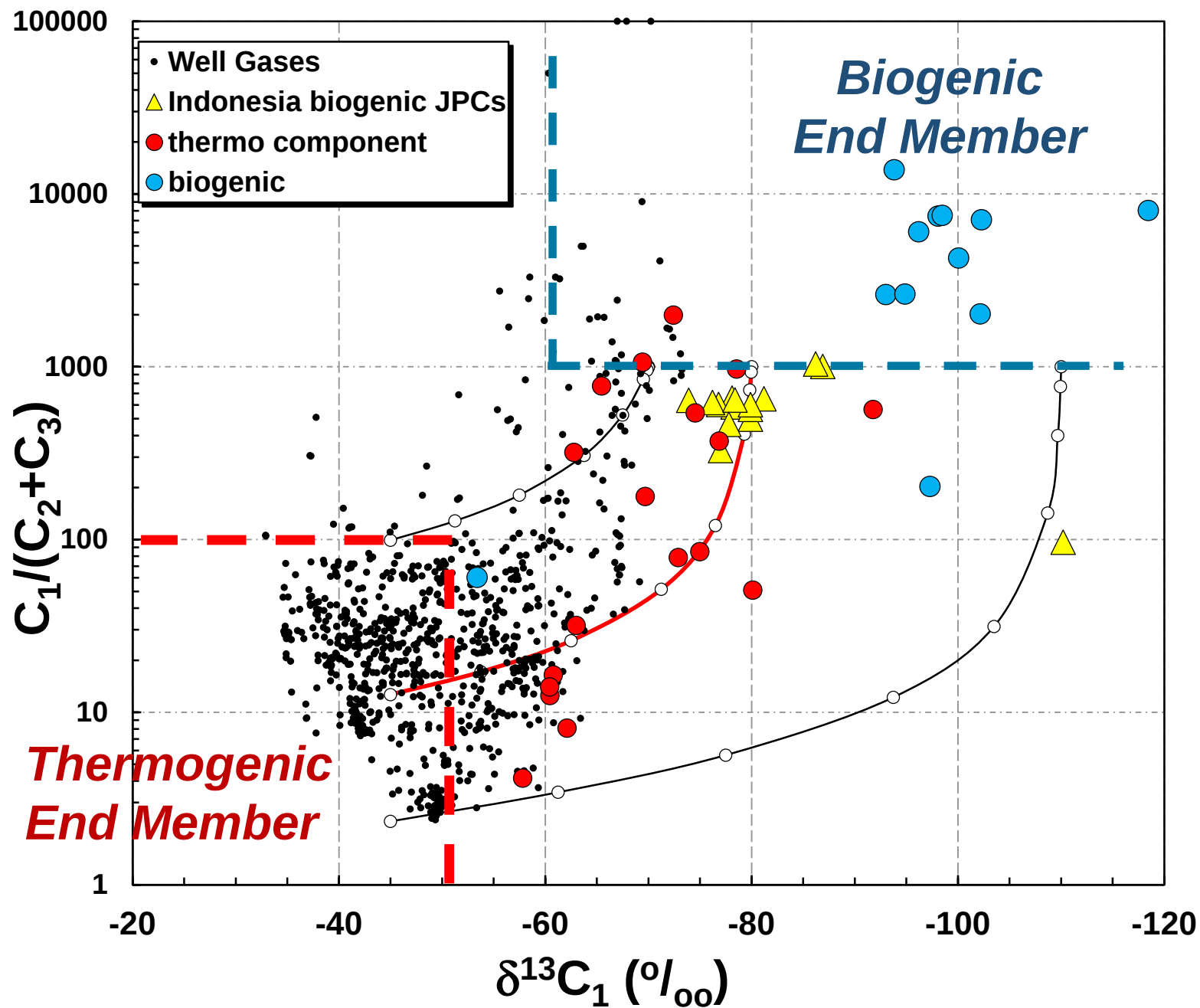




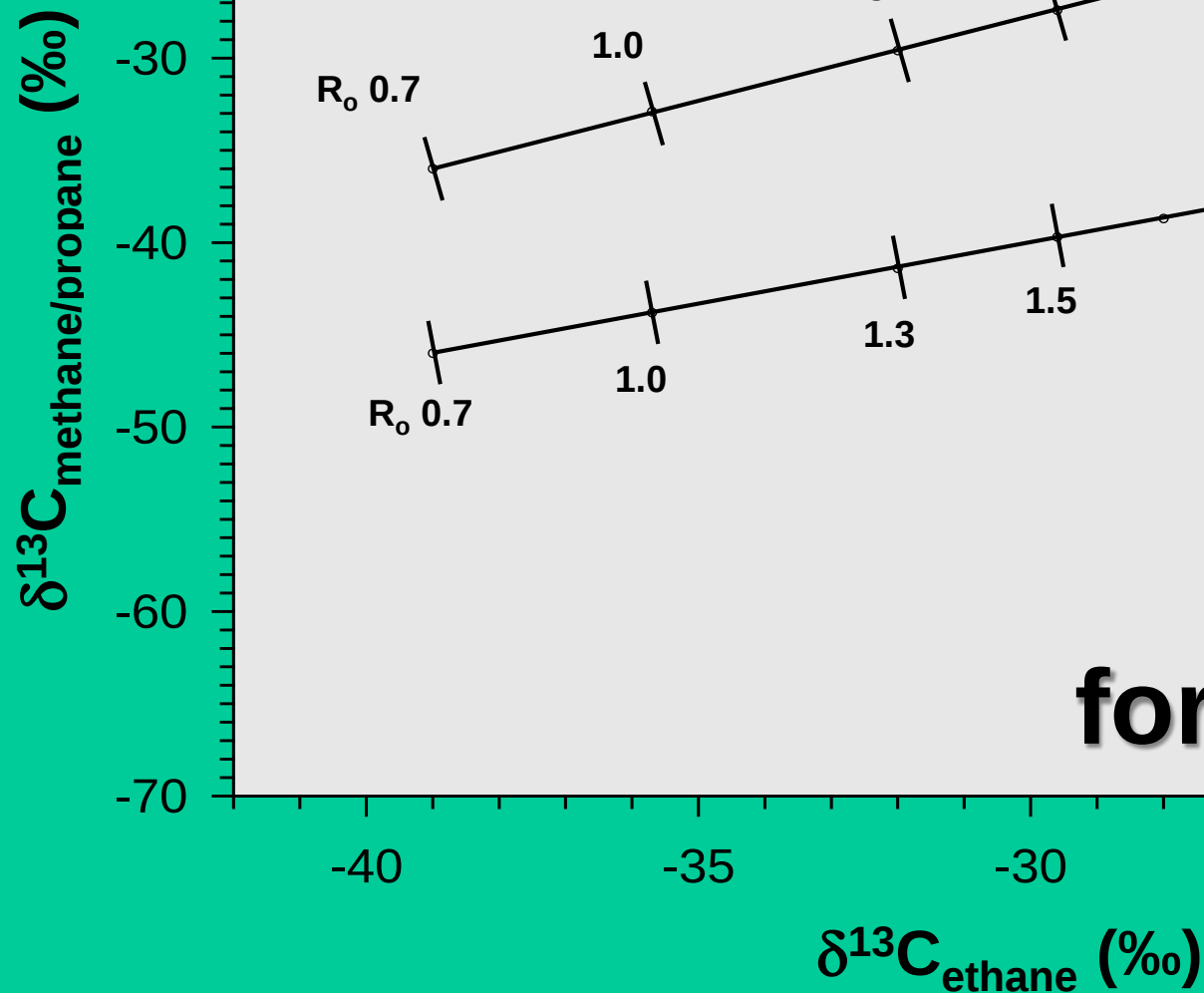


Bernard's plot (1978) of thermogenic, biogenic, mixed gases

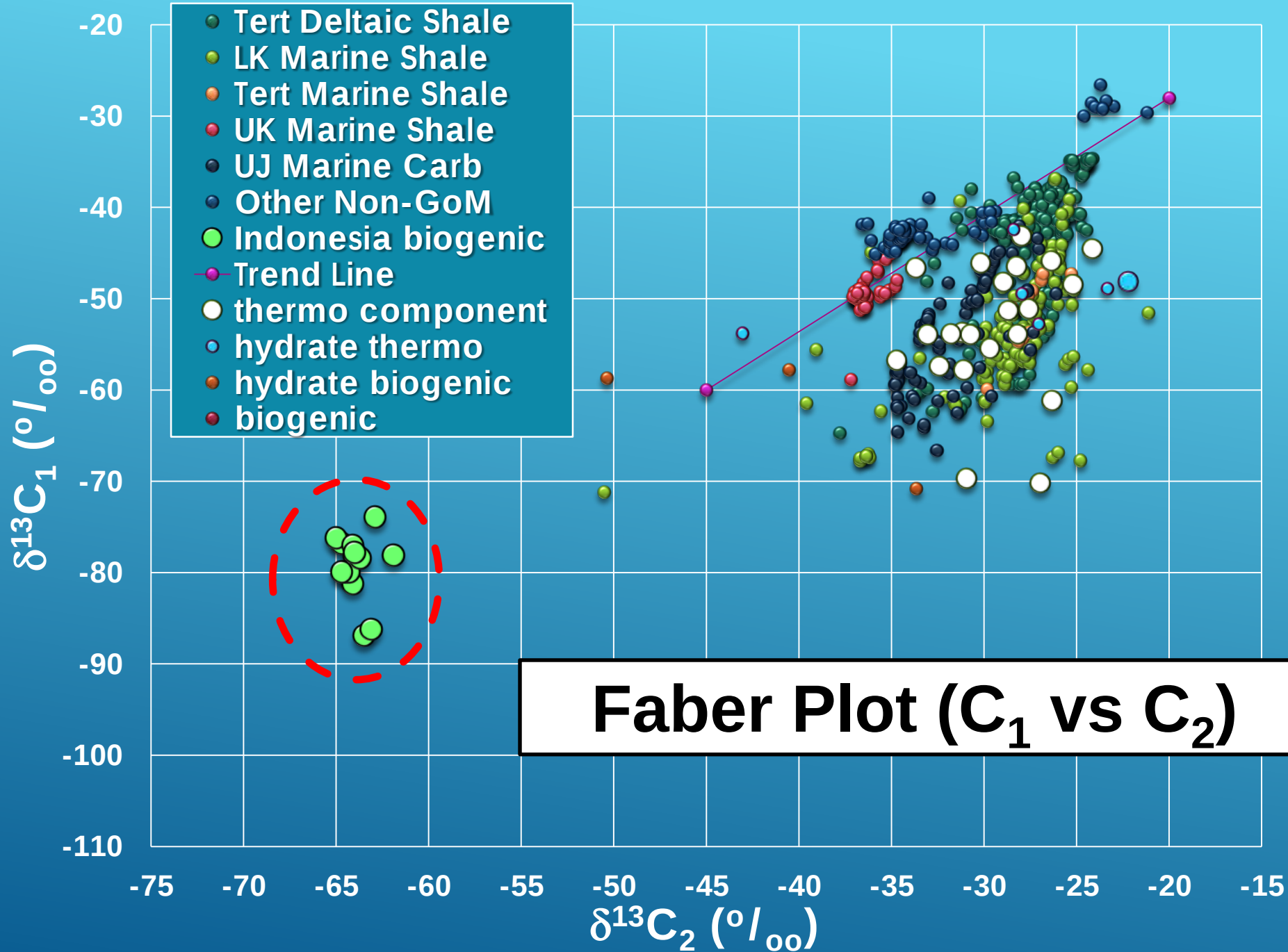


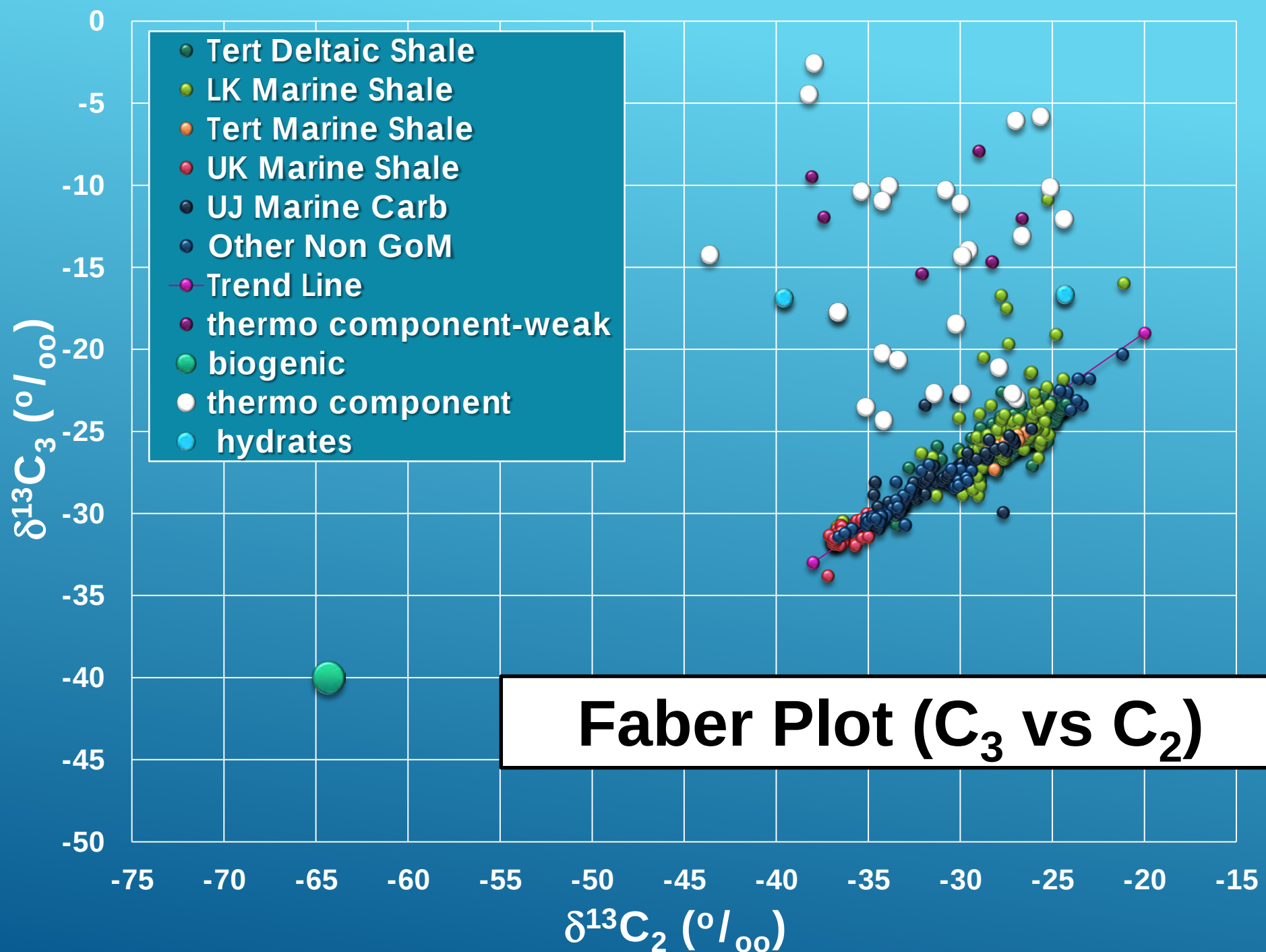


Faber's Plot (1987)

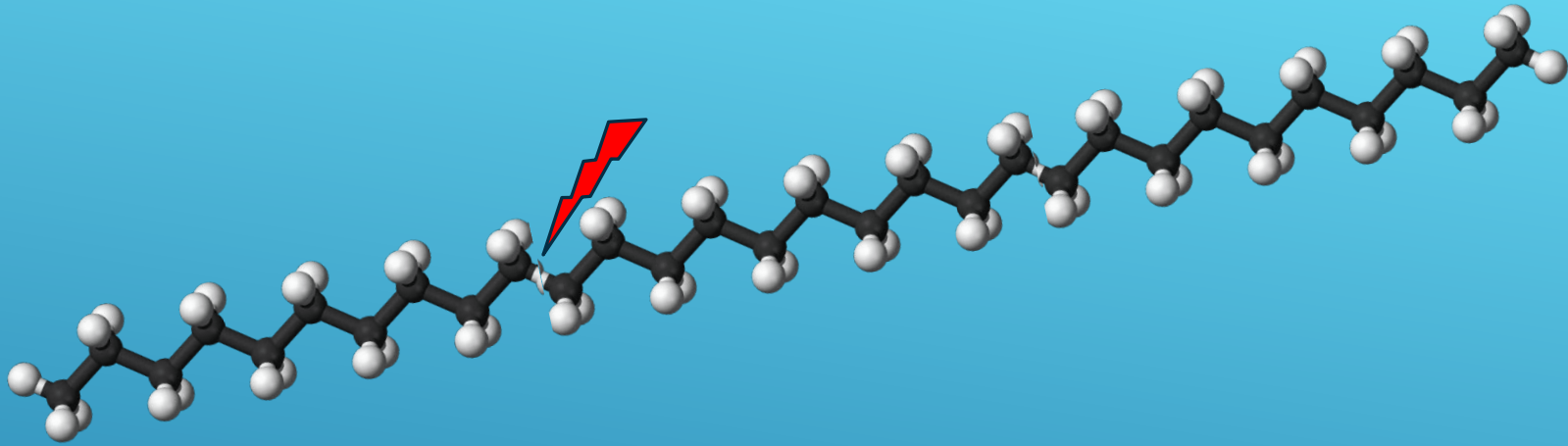


for well gases

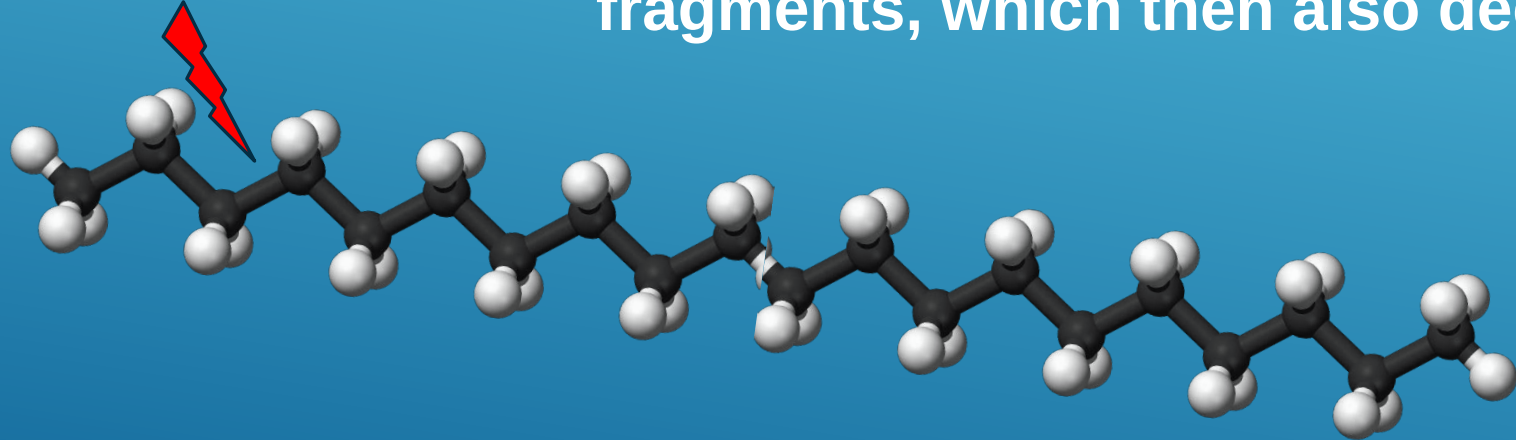




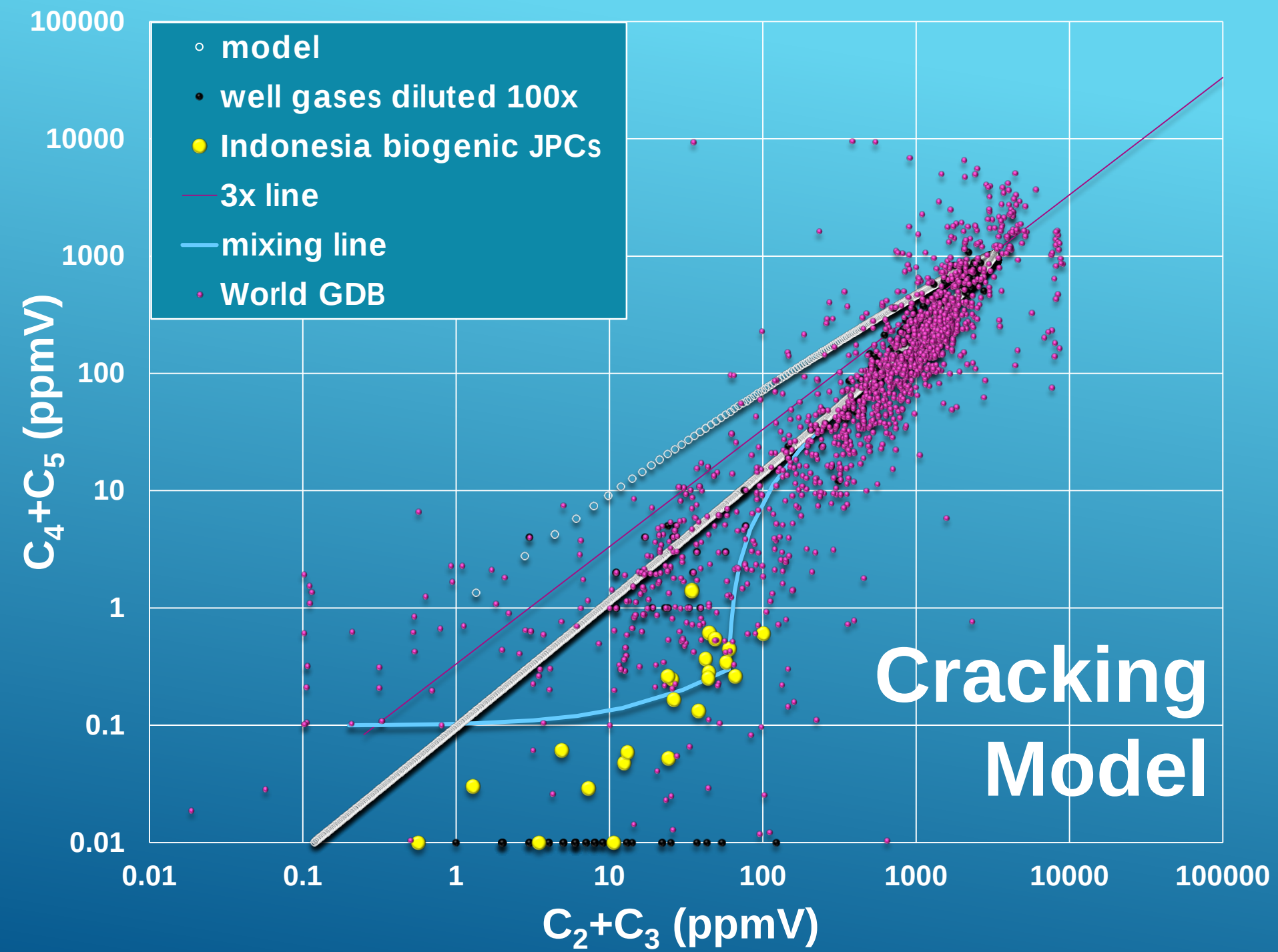
Thermocatalytic cracking to make wet gas

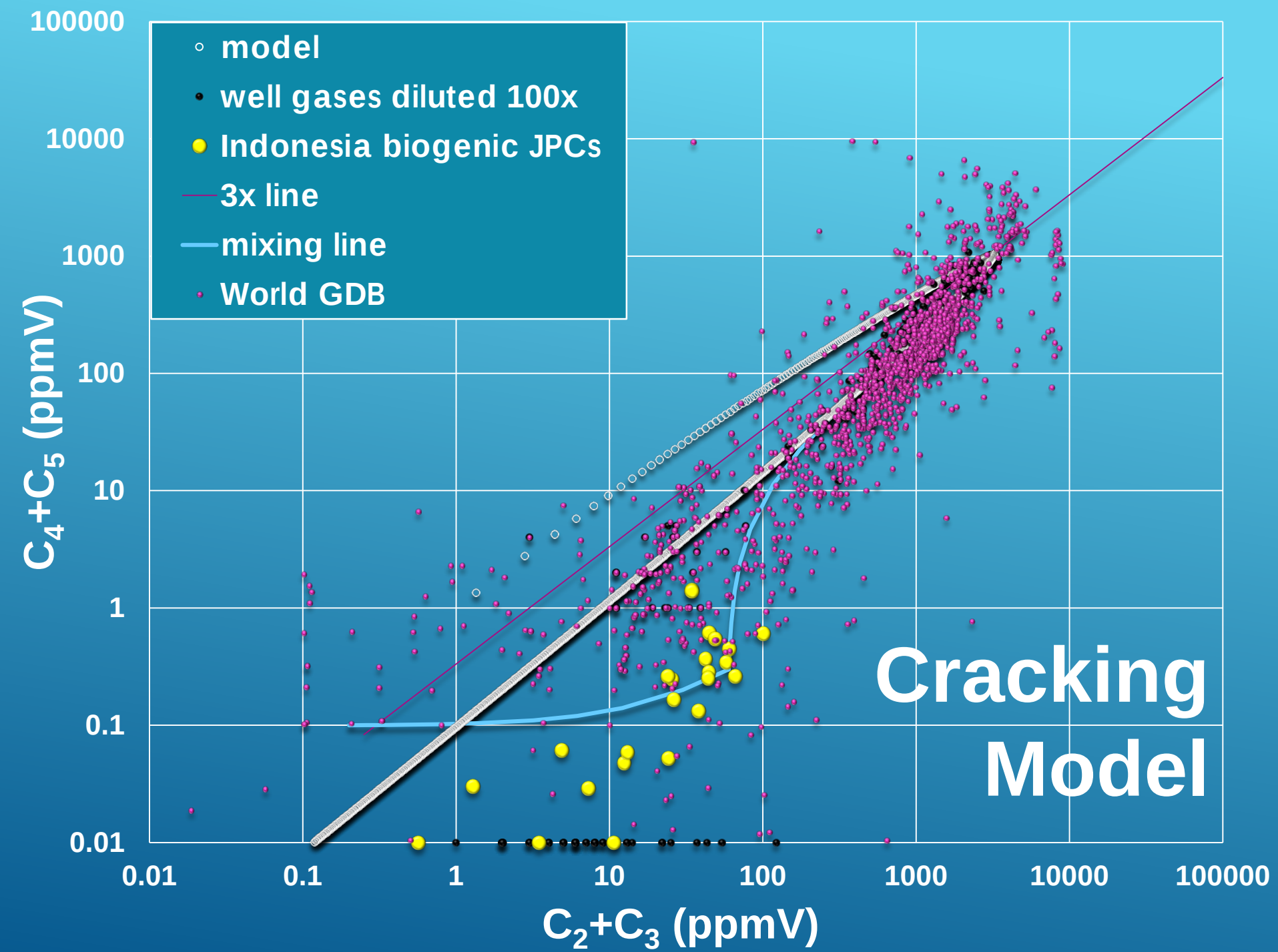


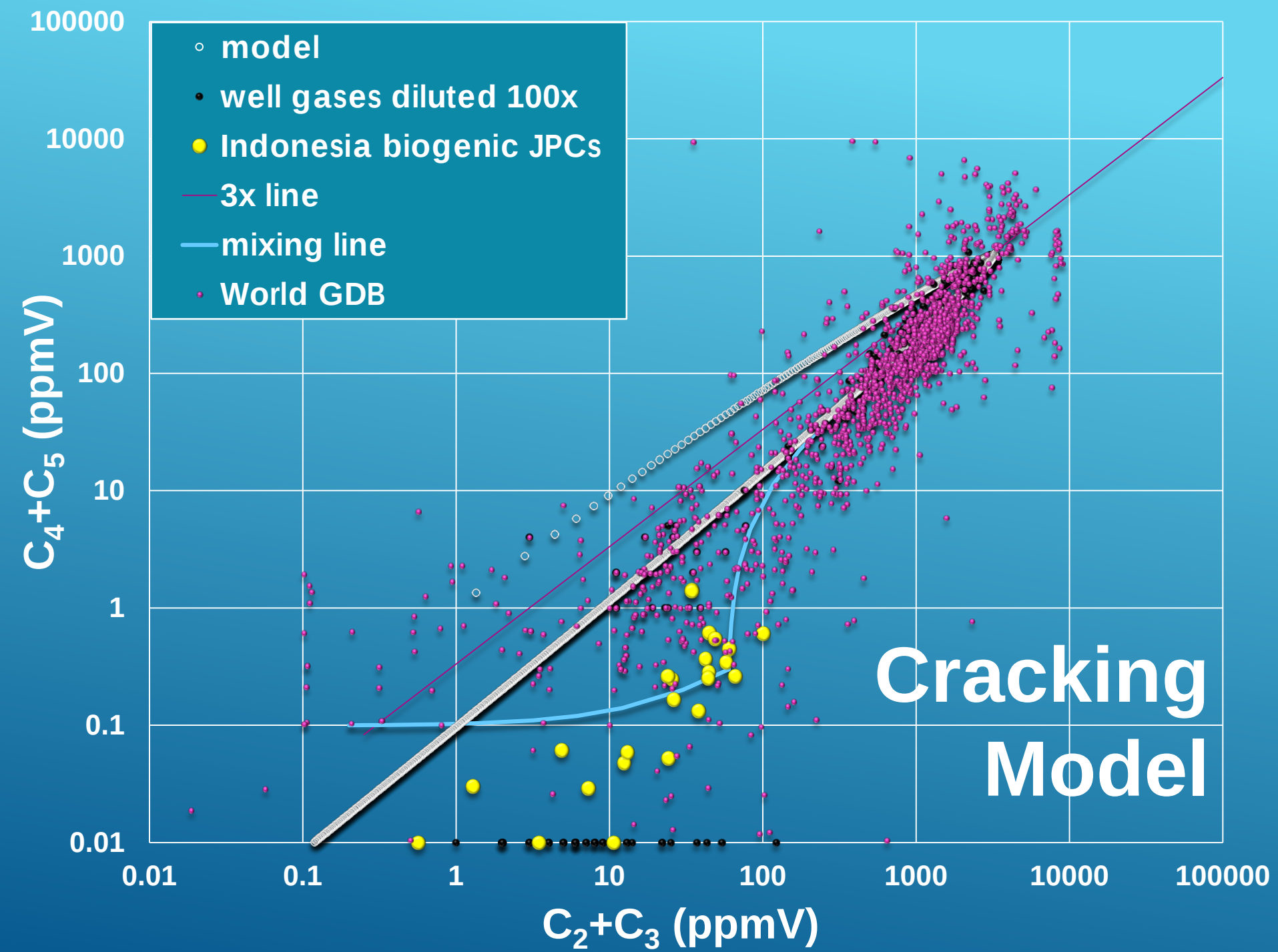
n-C₂₀ to n-C₃₀ cracking to cleave off daughter fragments, which then also decay

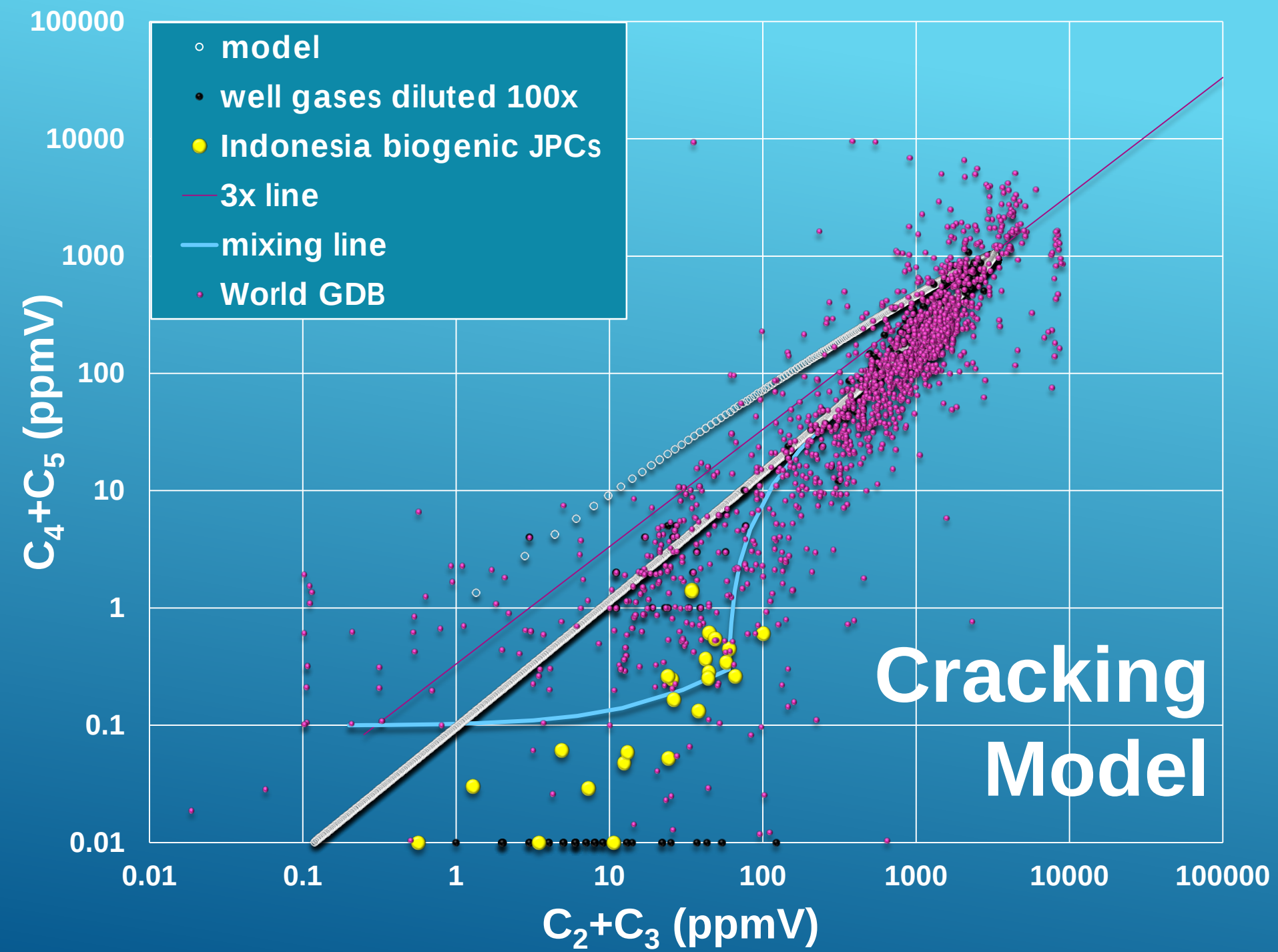


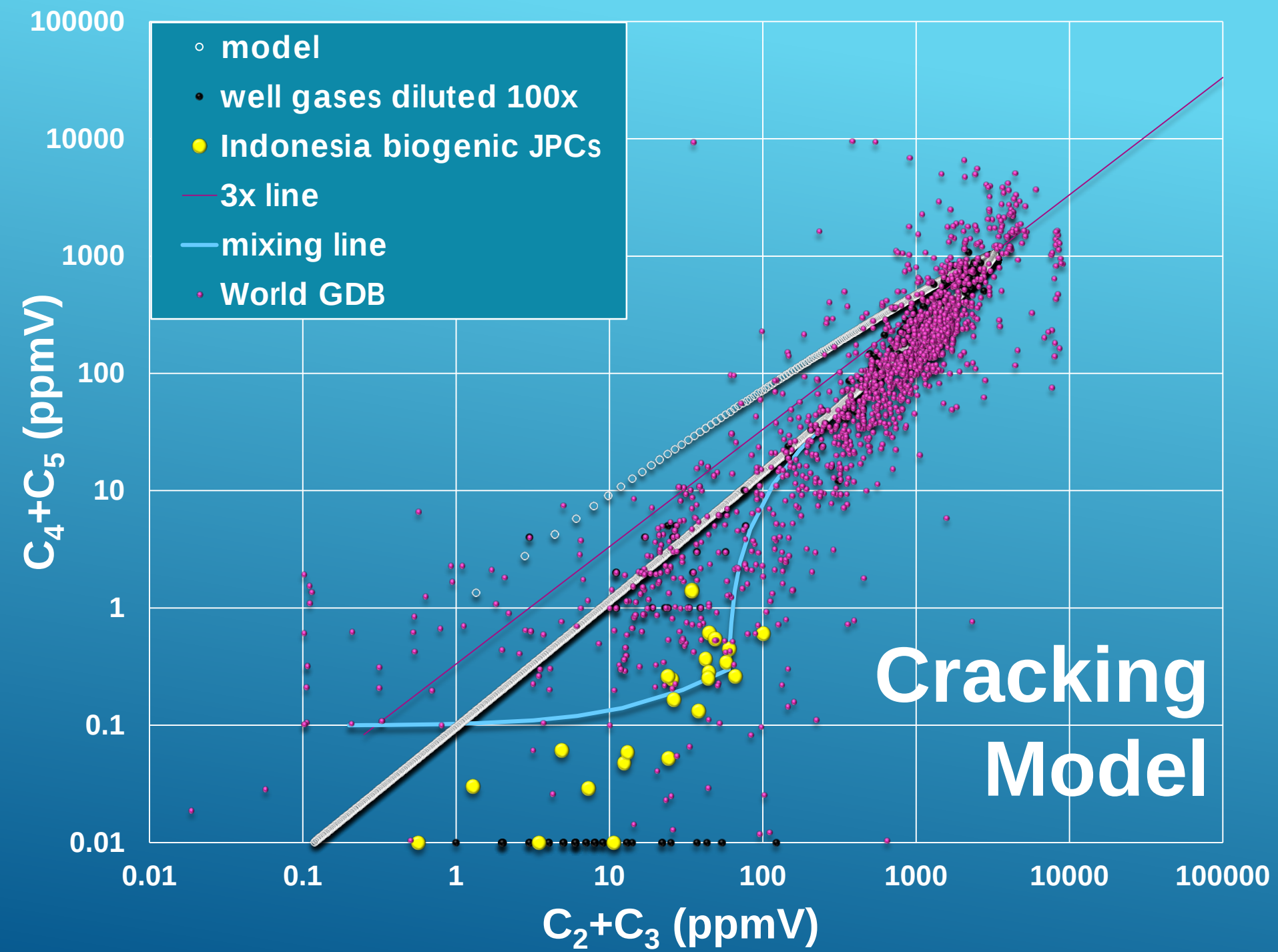
cumulate each daughter produced &
decayed with each iteration



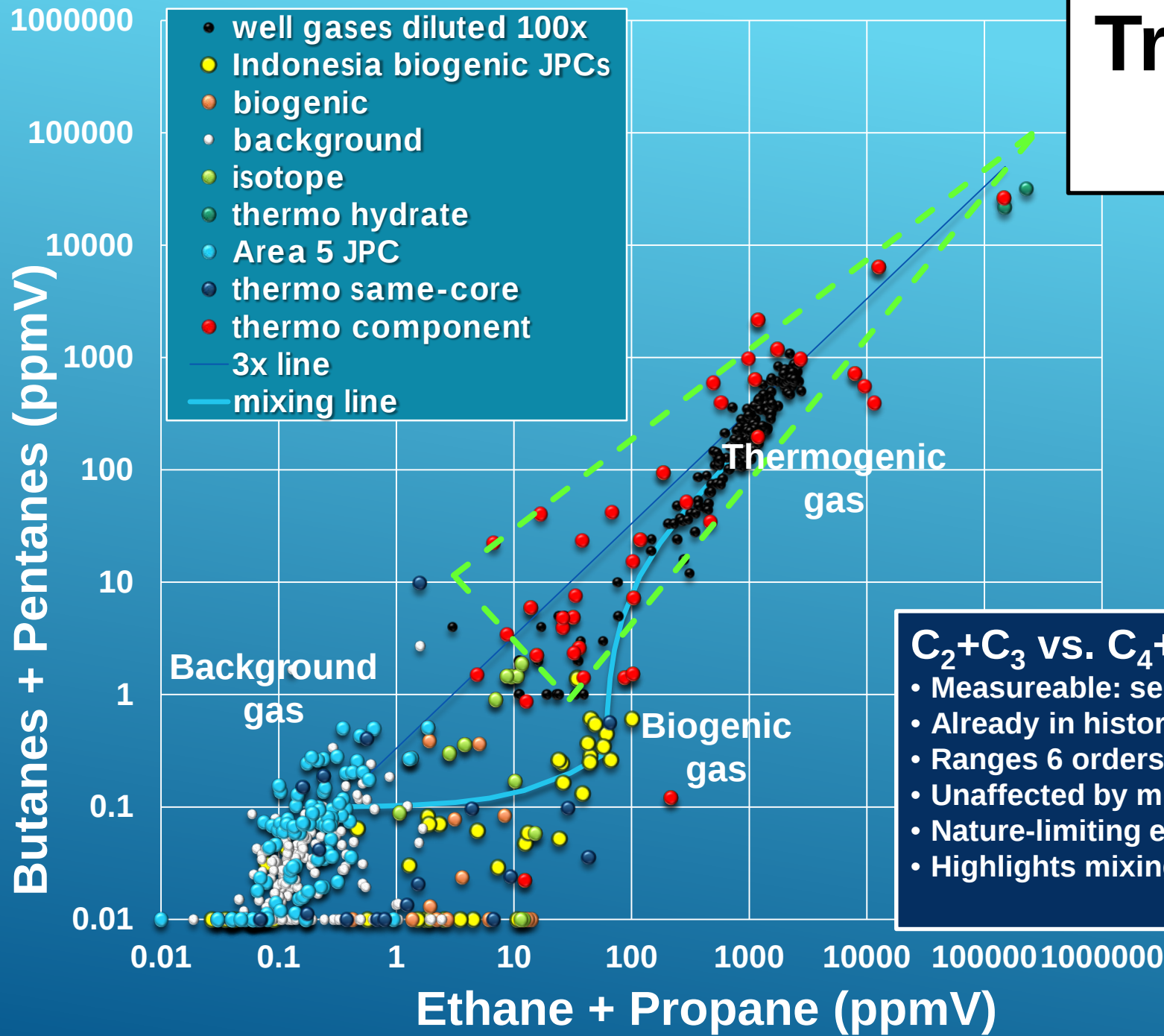






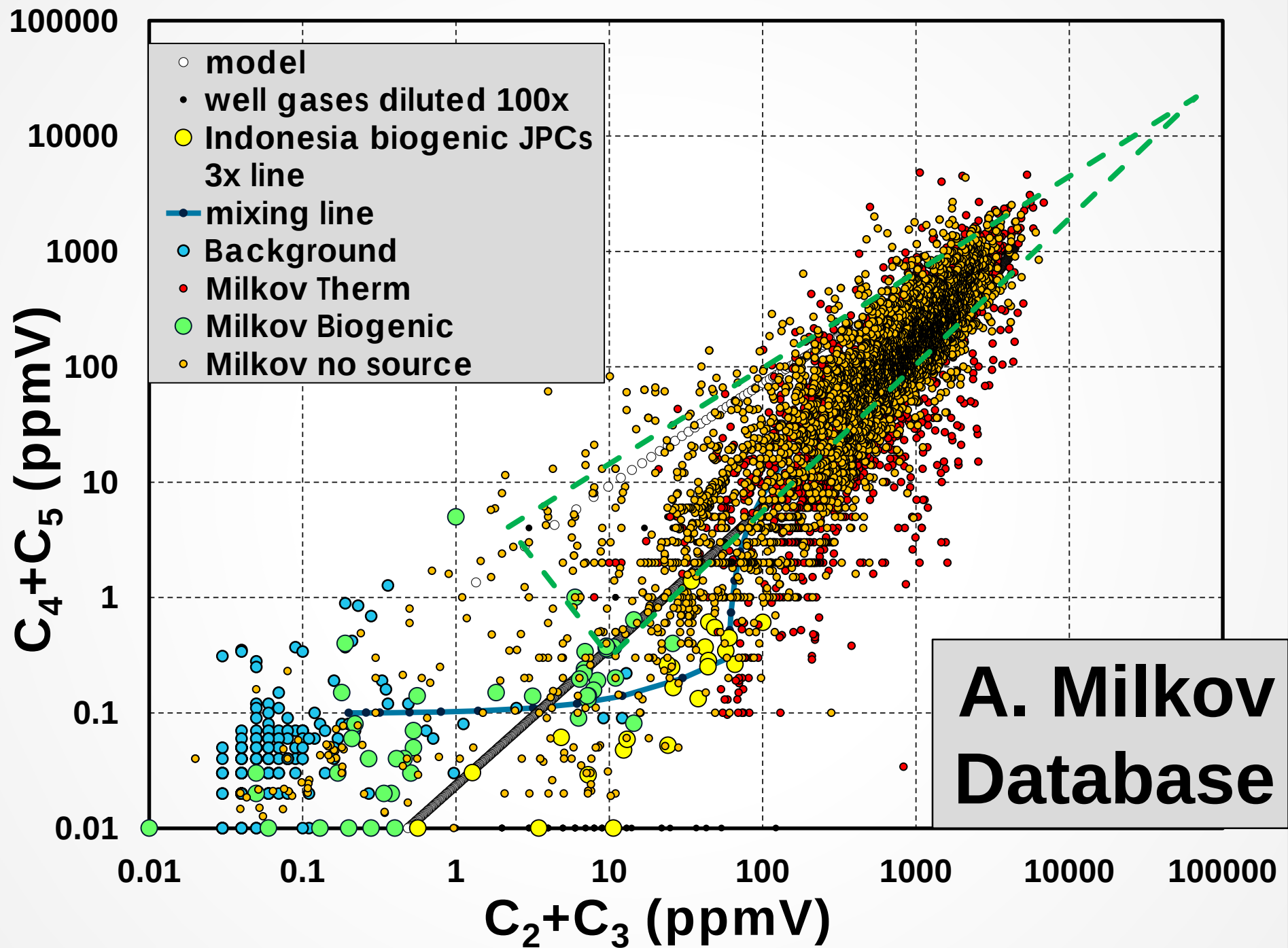


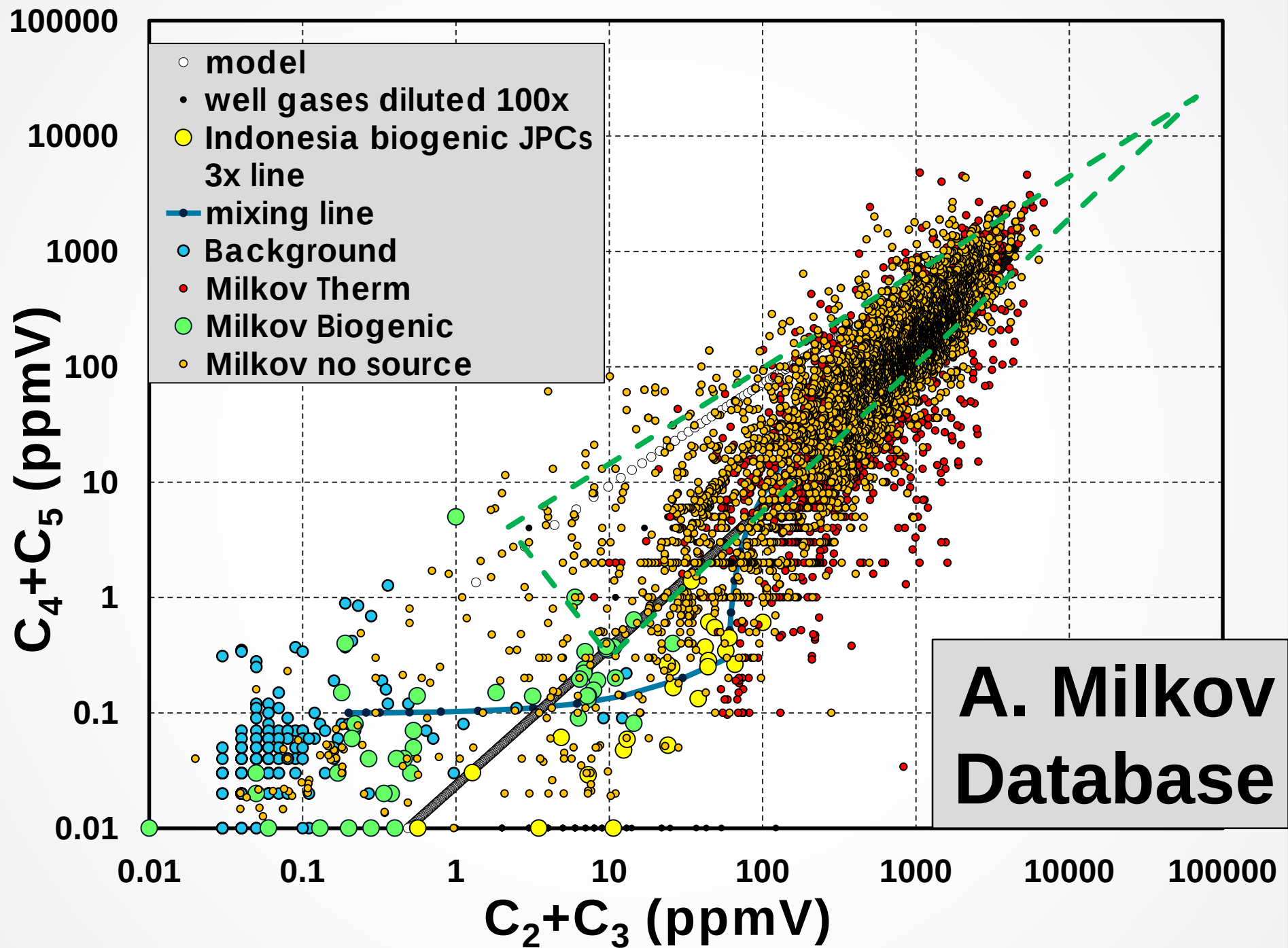
Triangle Plot

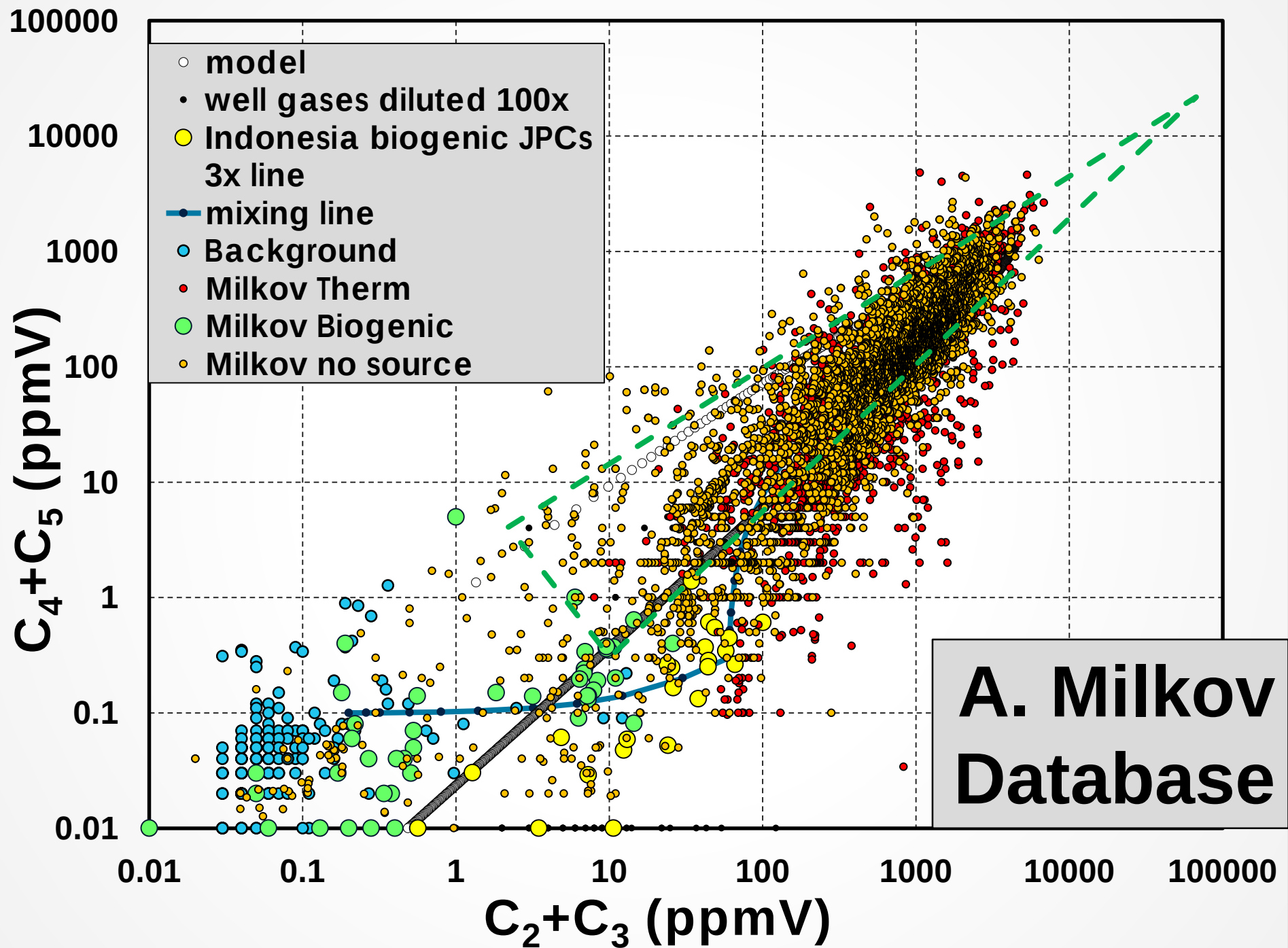


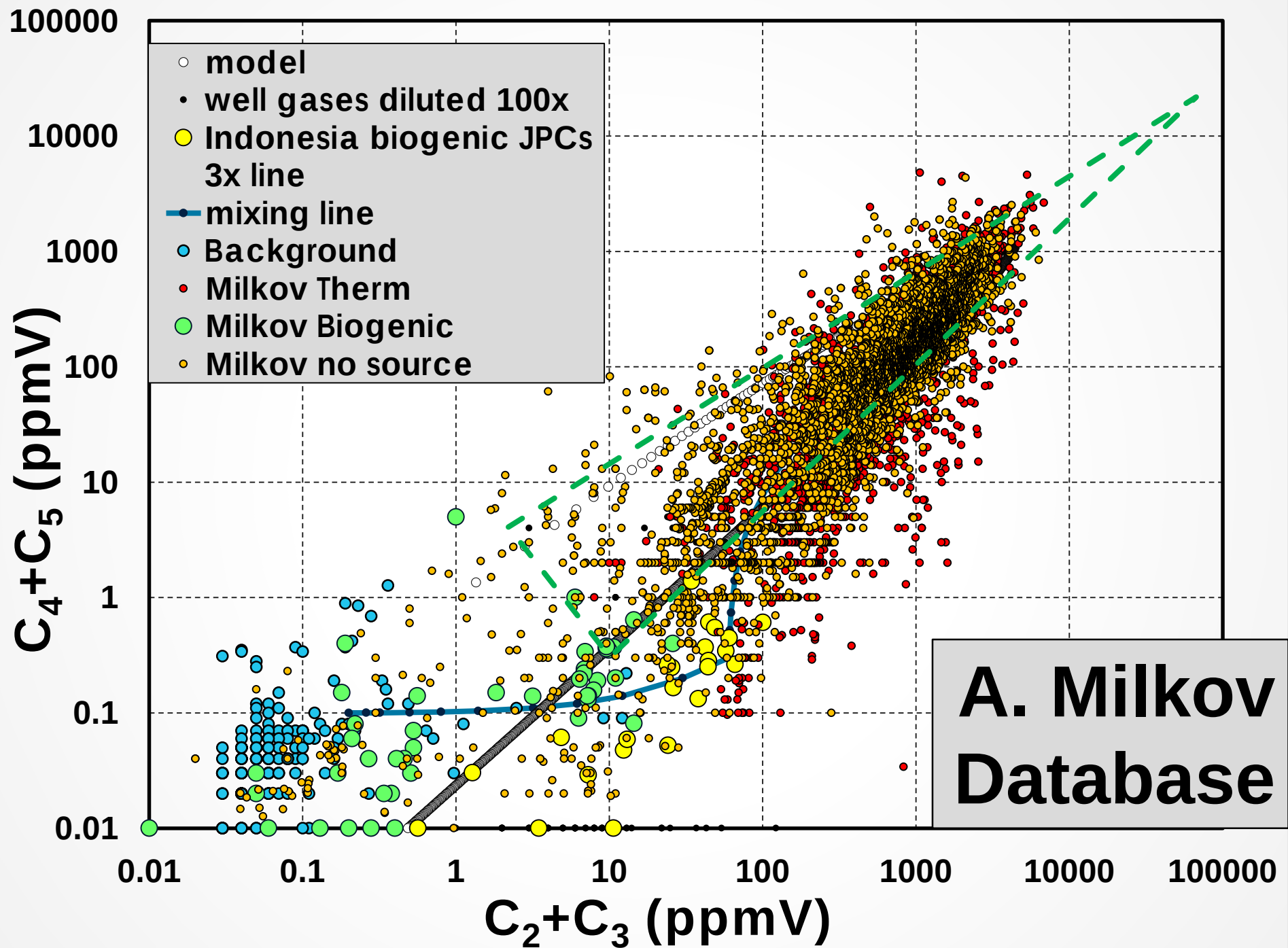
C_2+C_3 vs. C_4+C_5

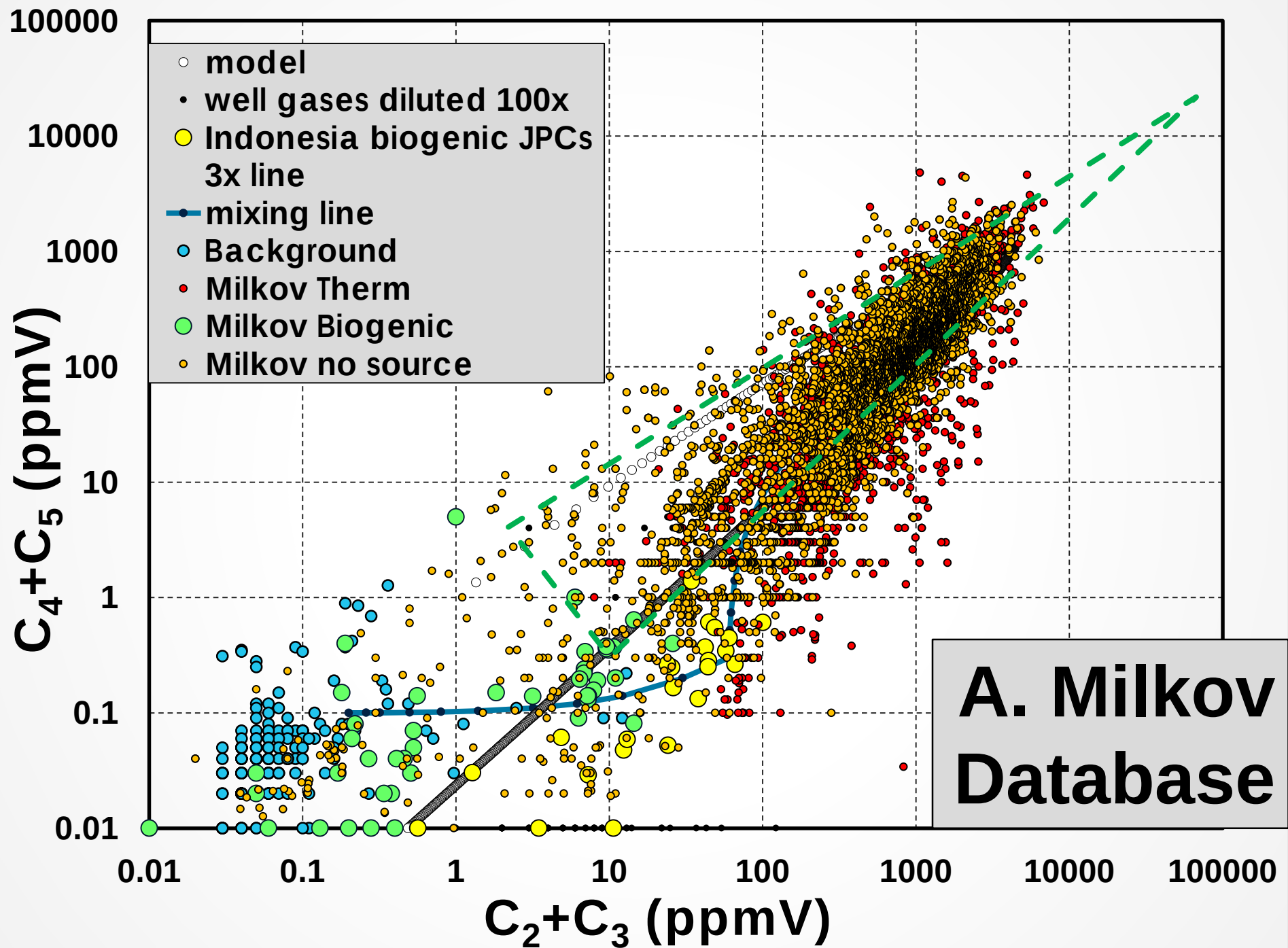
- Measureable: sed, seeps, wells
- Already in historic databases
- Ranges 6 orders of magnitude
- Unaffected by migration
- Nature-limiting end-members
- Highlights mixing & fractionation

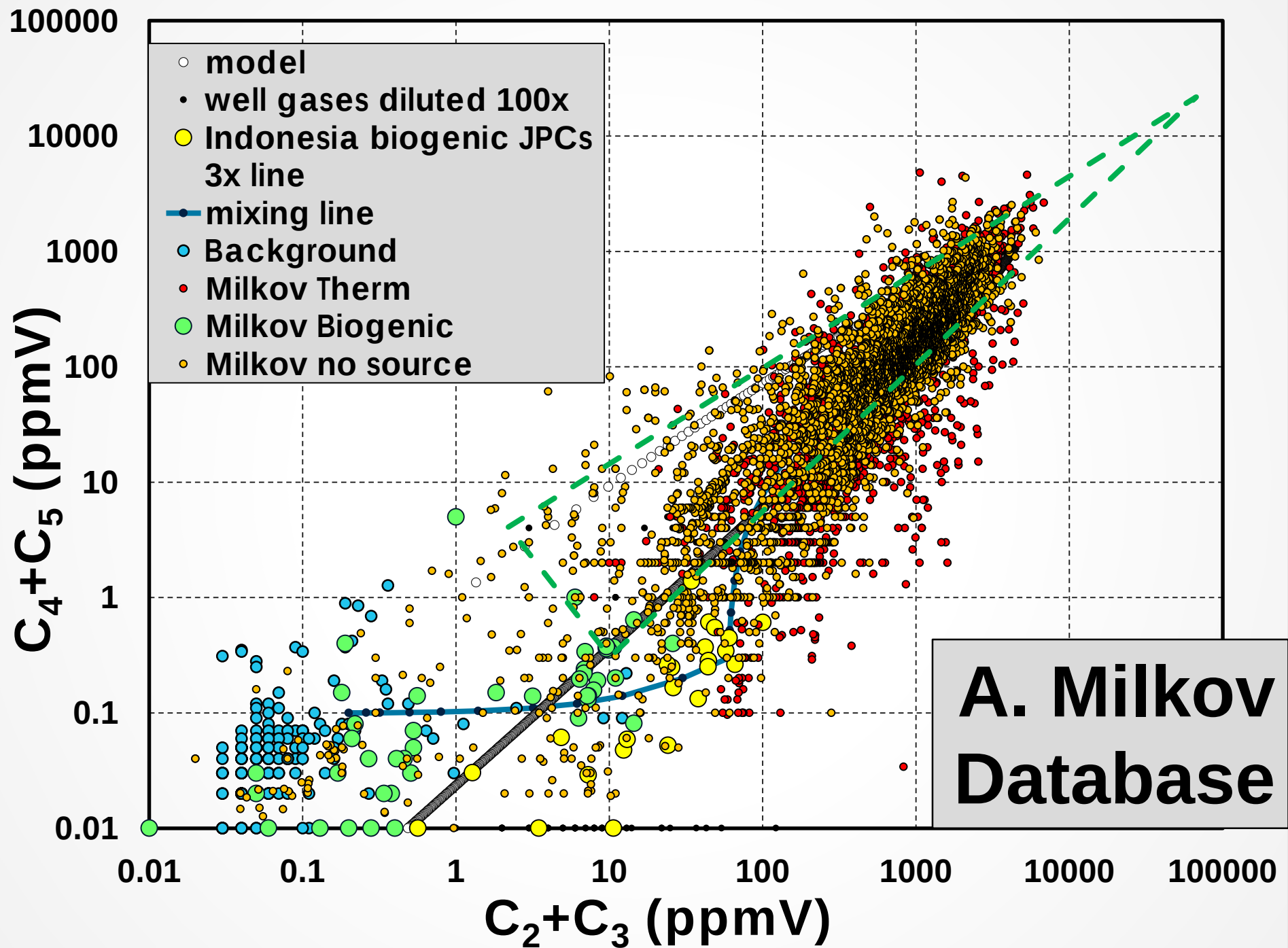


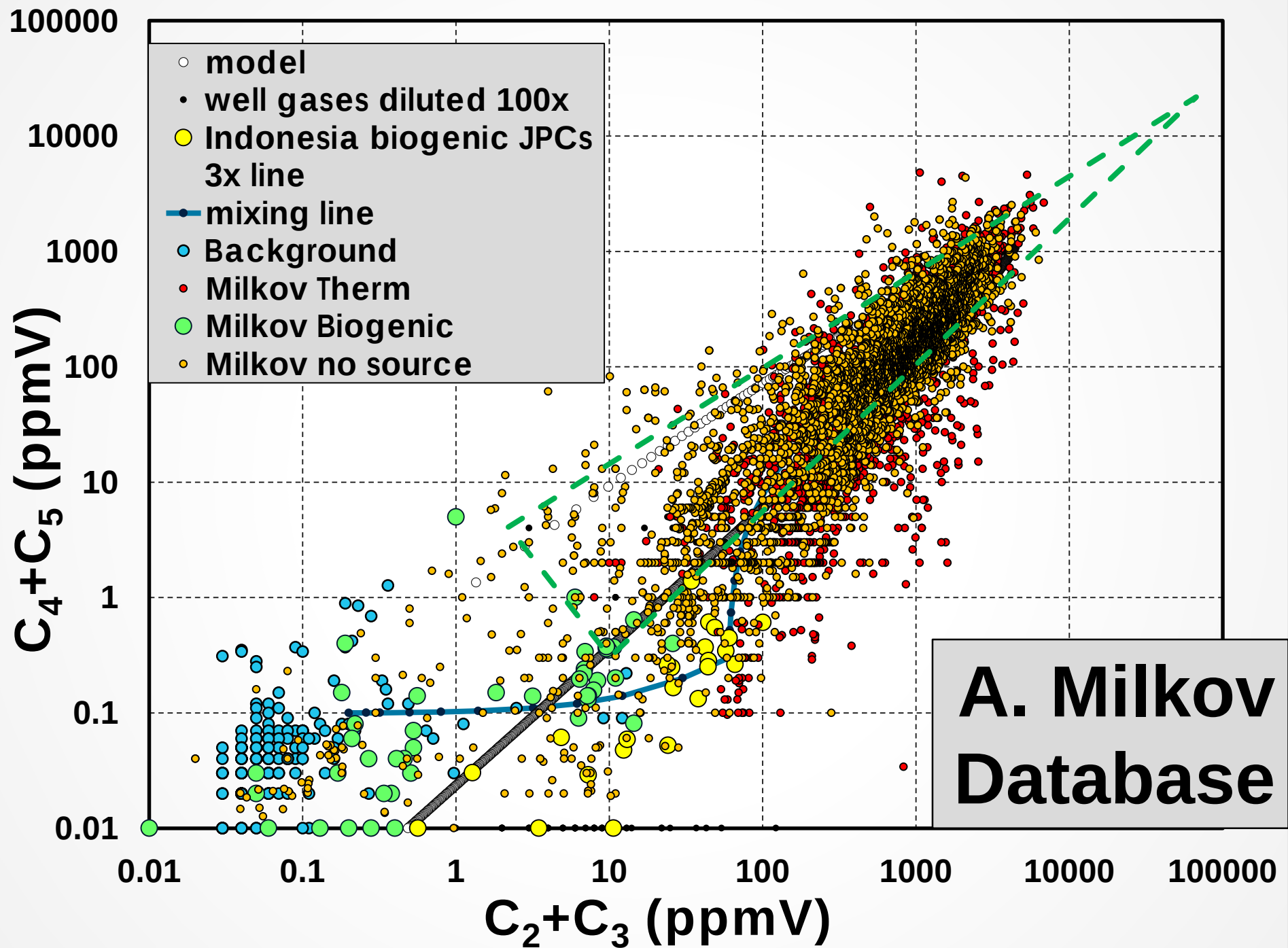


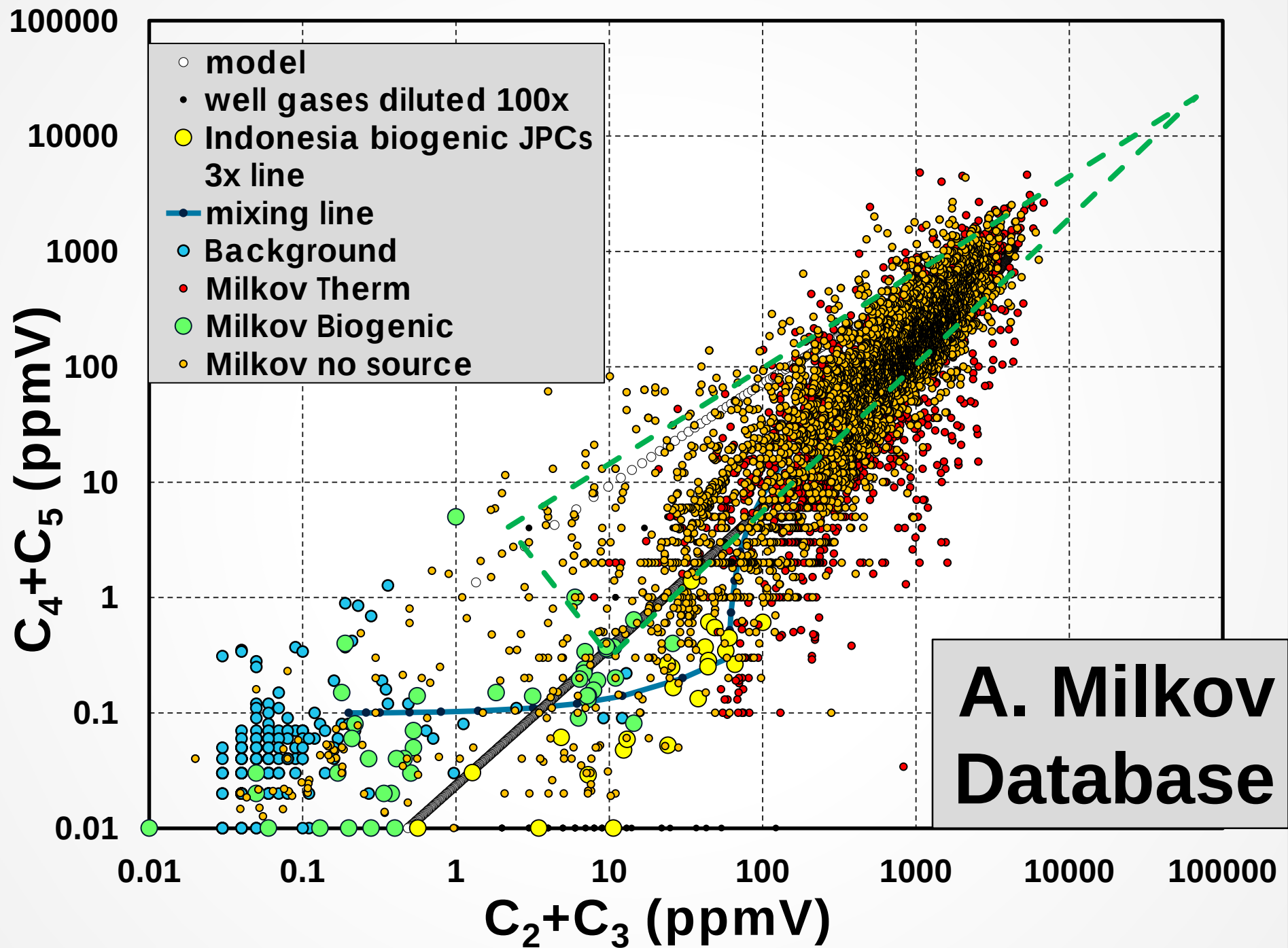




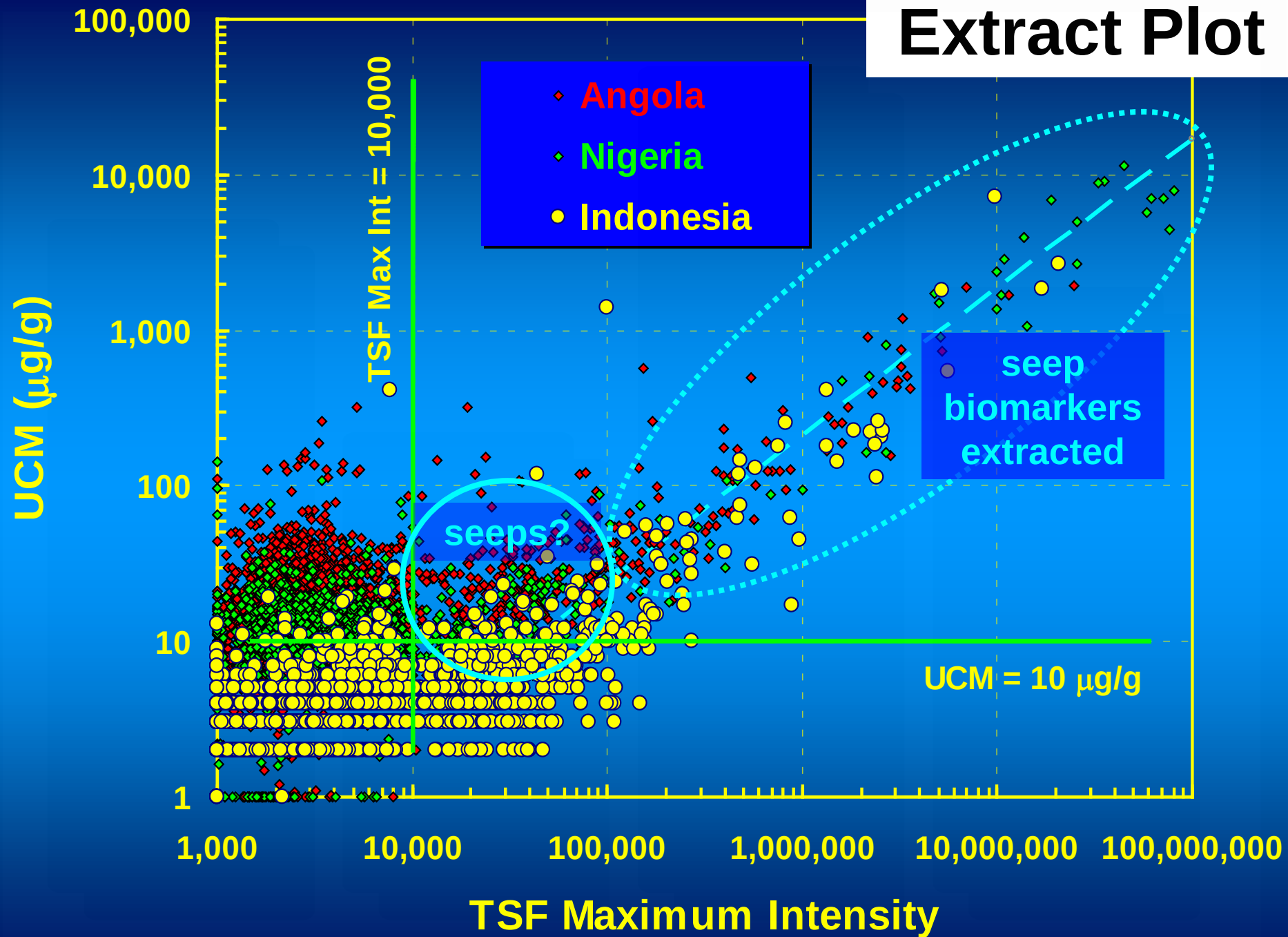


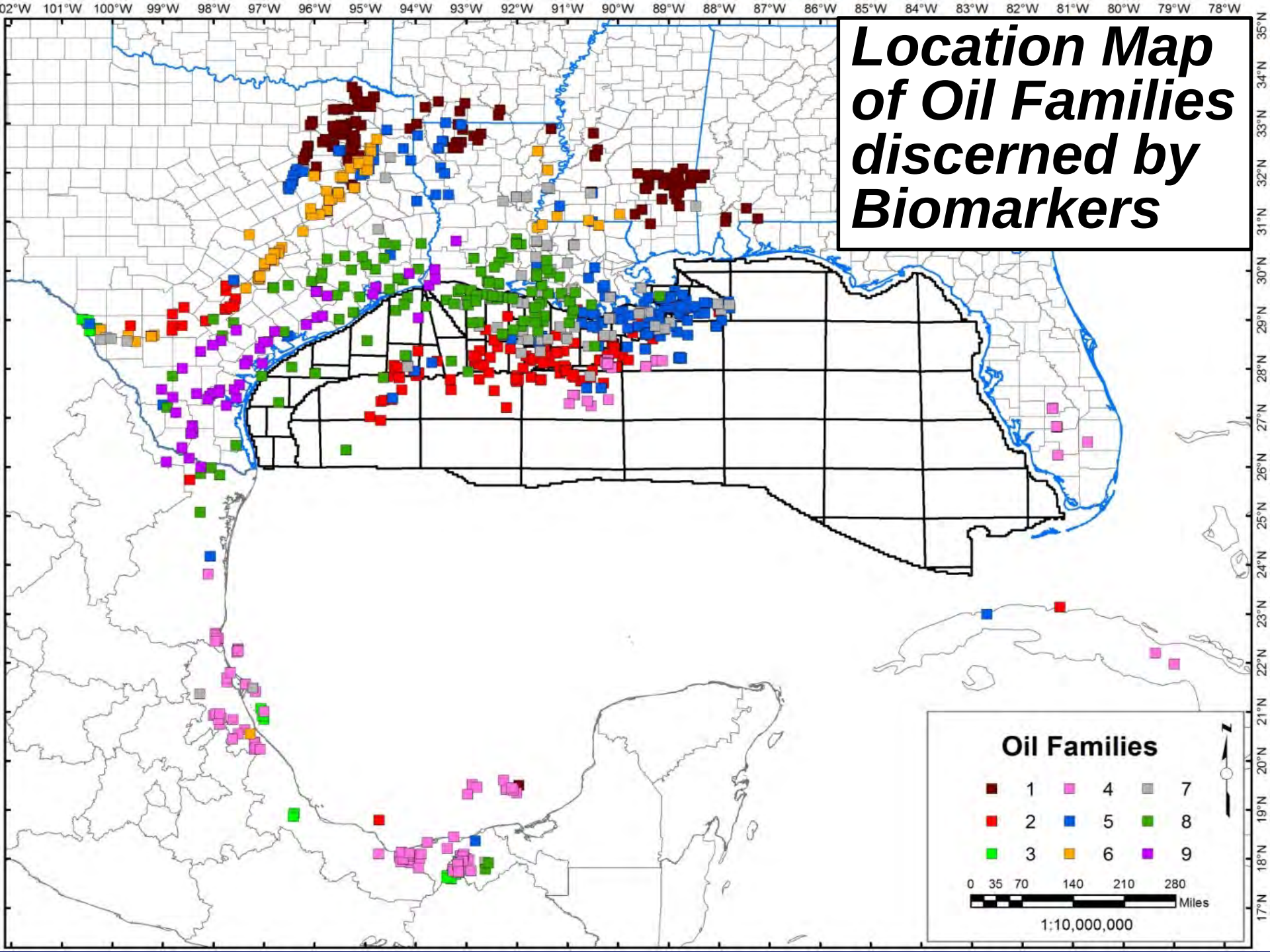


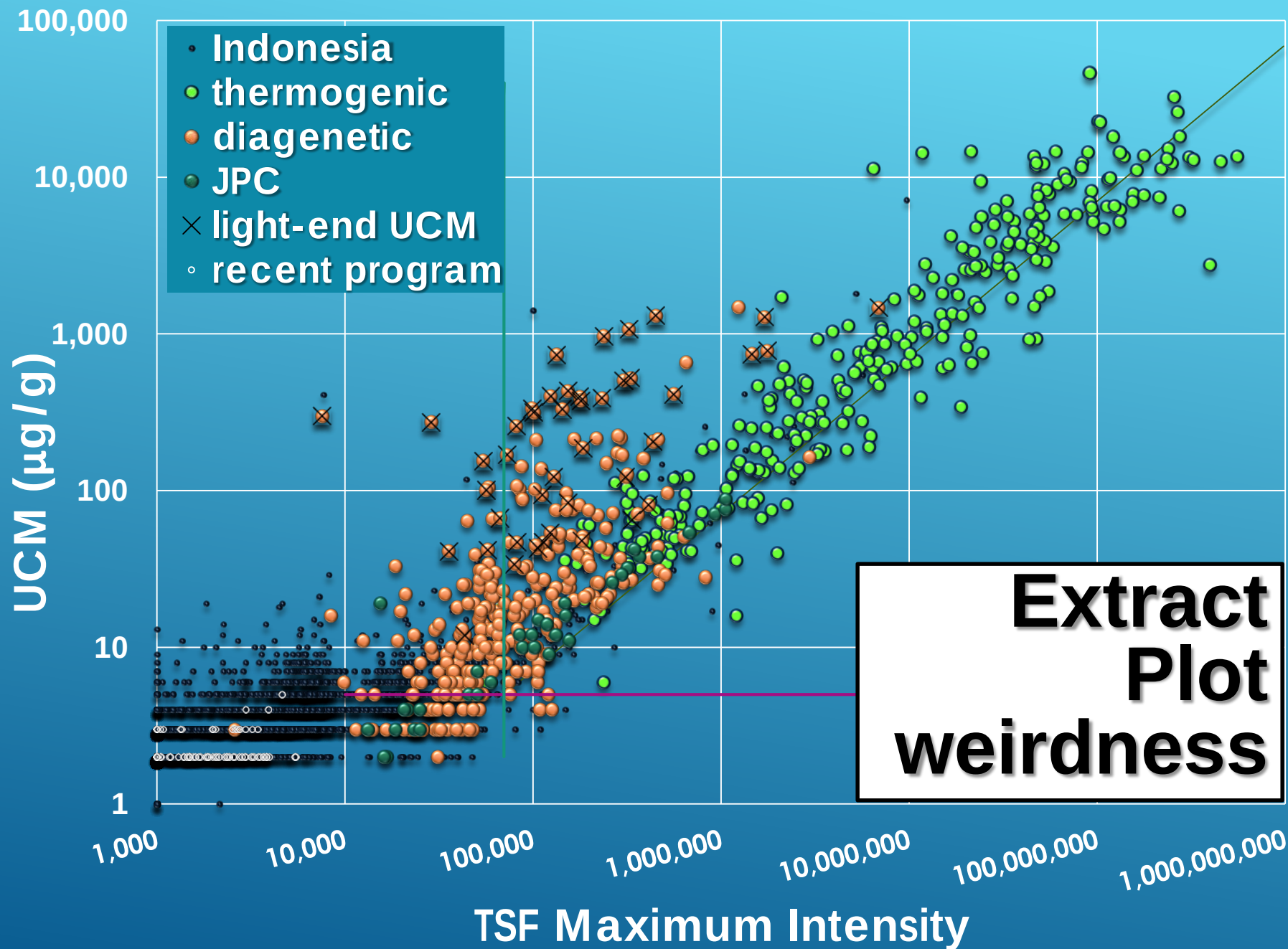




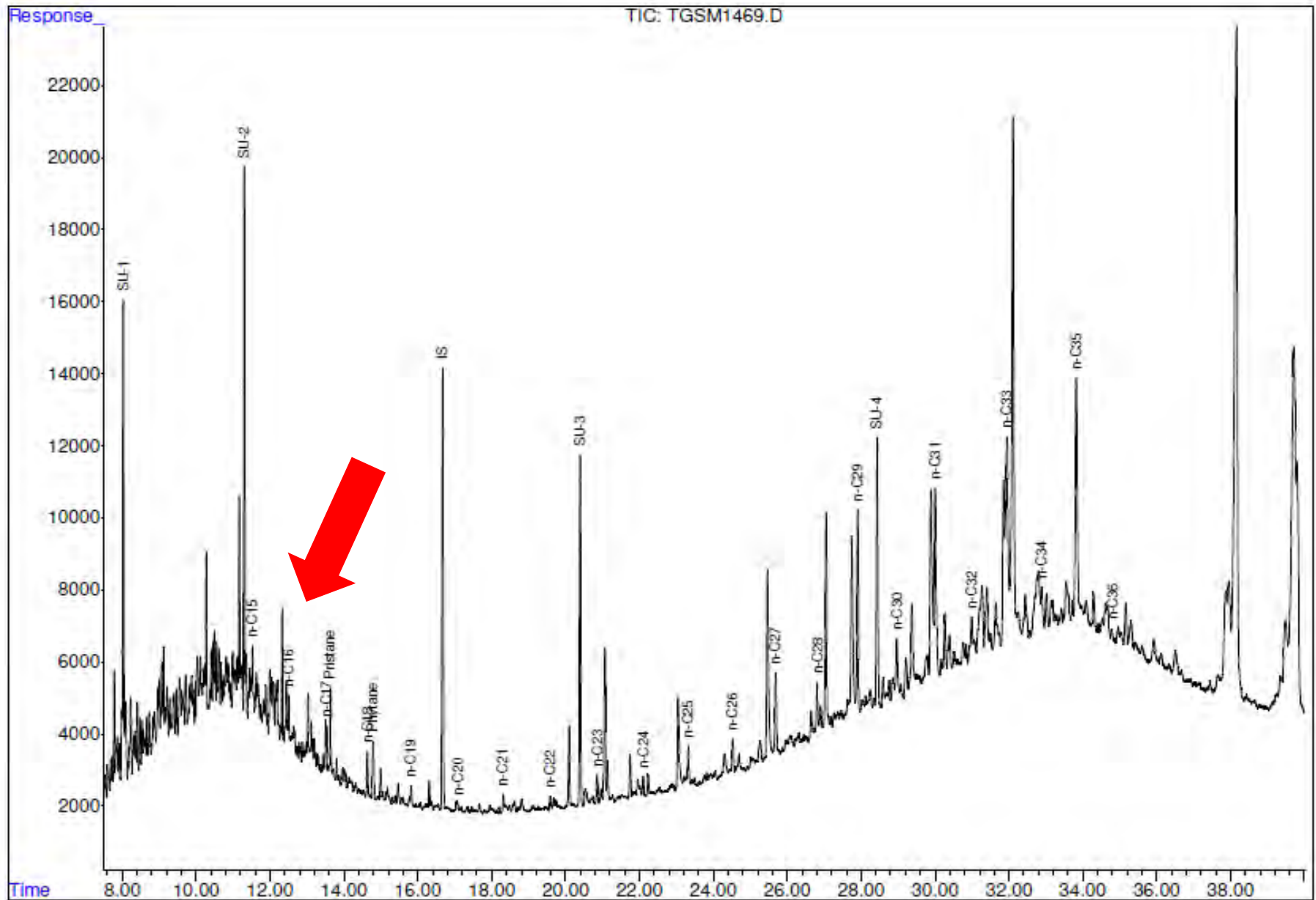
Extract Plot



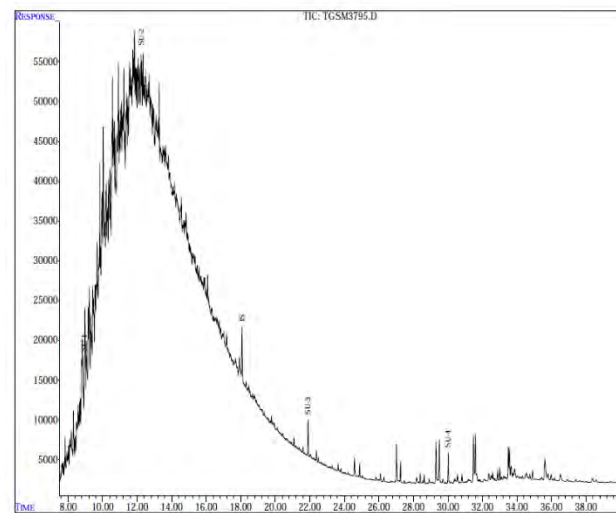
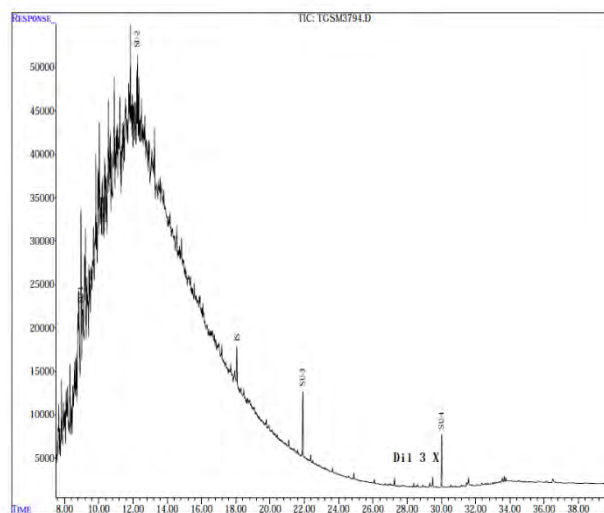
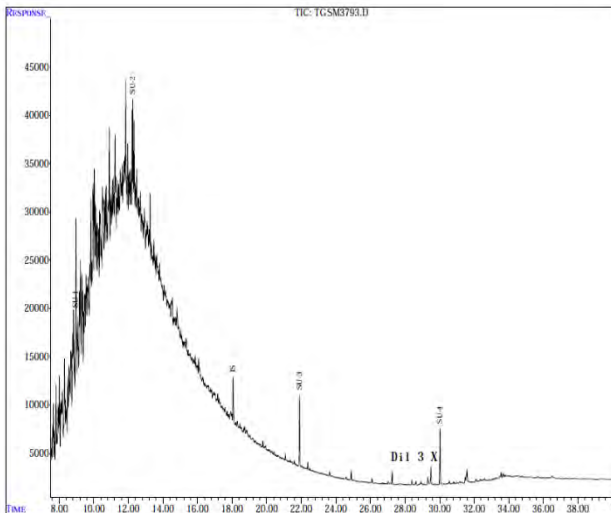
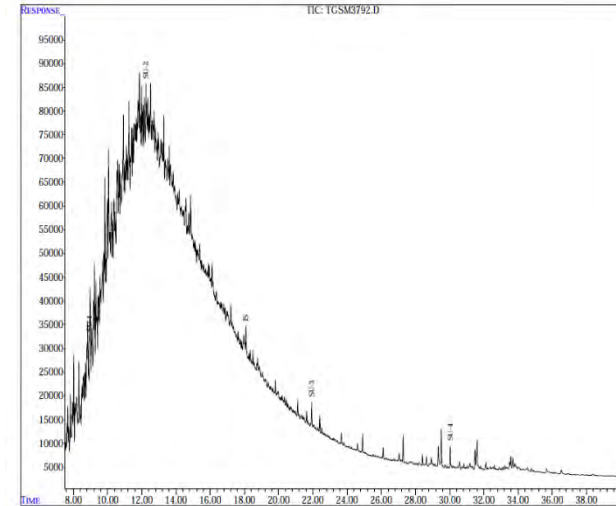
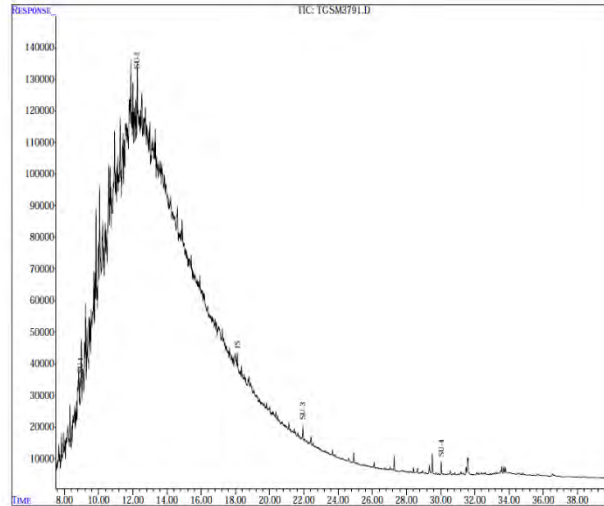
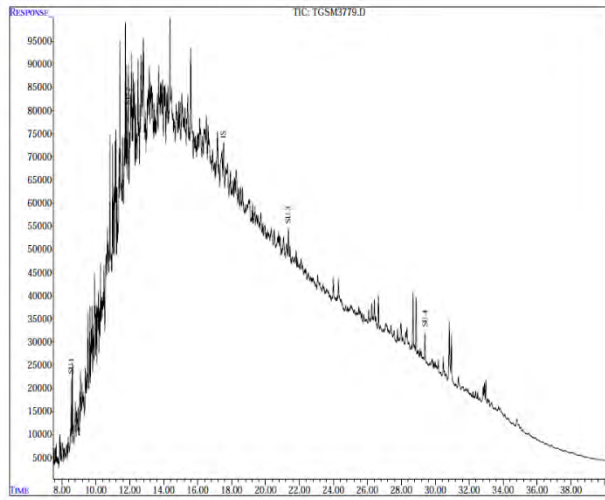




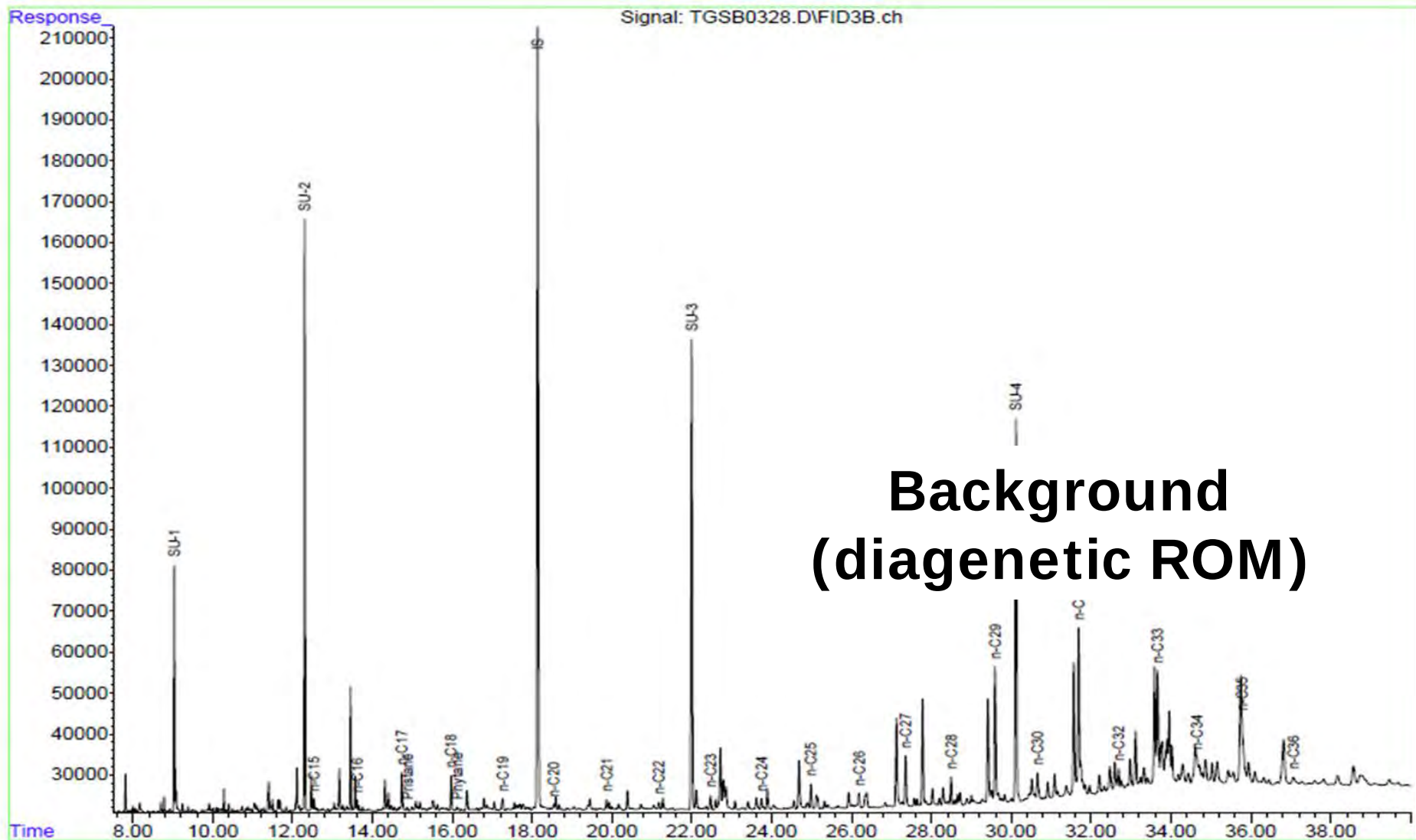
Light-end UCM hump (contamination?)



Light-end UCMs associated with thermogenic gas seepage (!)



Anomalous influences to HC background



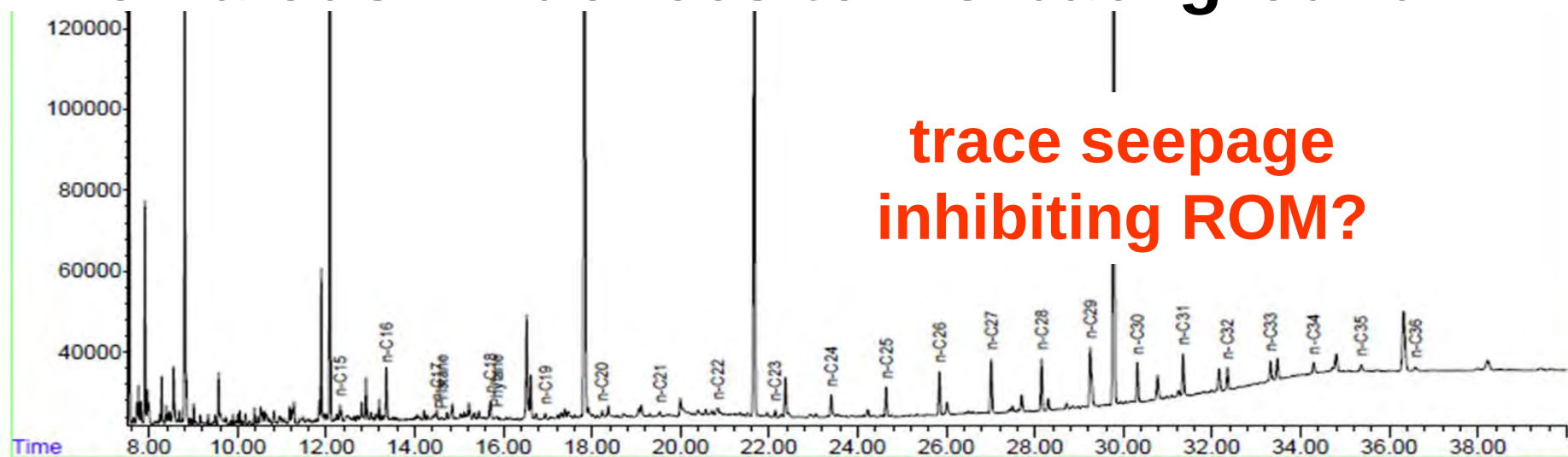
Sample: TBZ105/16

Method: FID60002C10B.M

Injection date: 08-Sep-2018, 08:36

File: TGSB0328.D

Anomalous influences to HC background

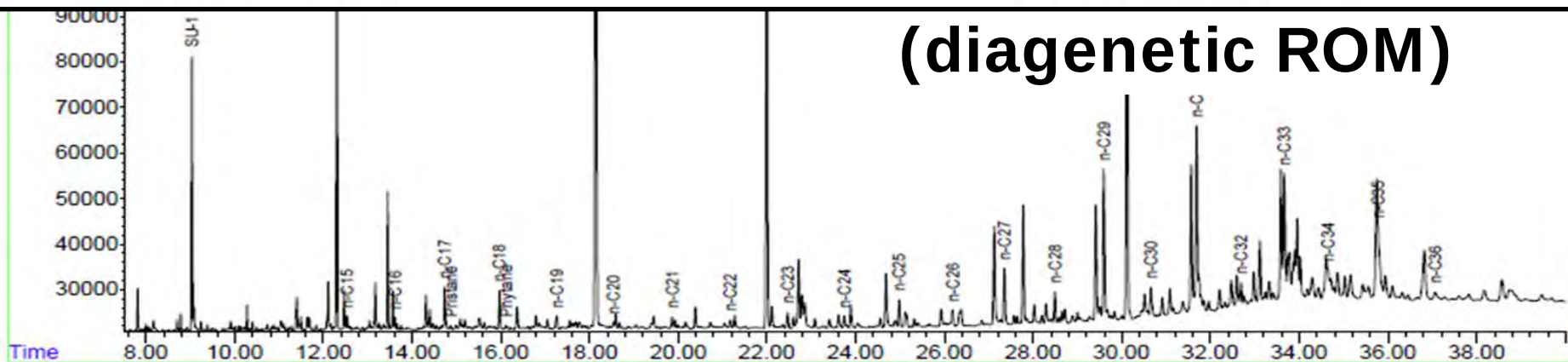


Sample: TBZ183/17

Injection date: 12-Nov-2018, 08:51

Method: FID60001C10F.M

File: TGSB0695.D



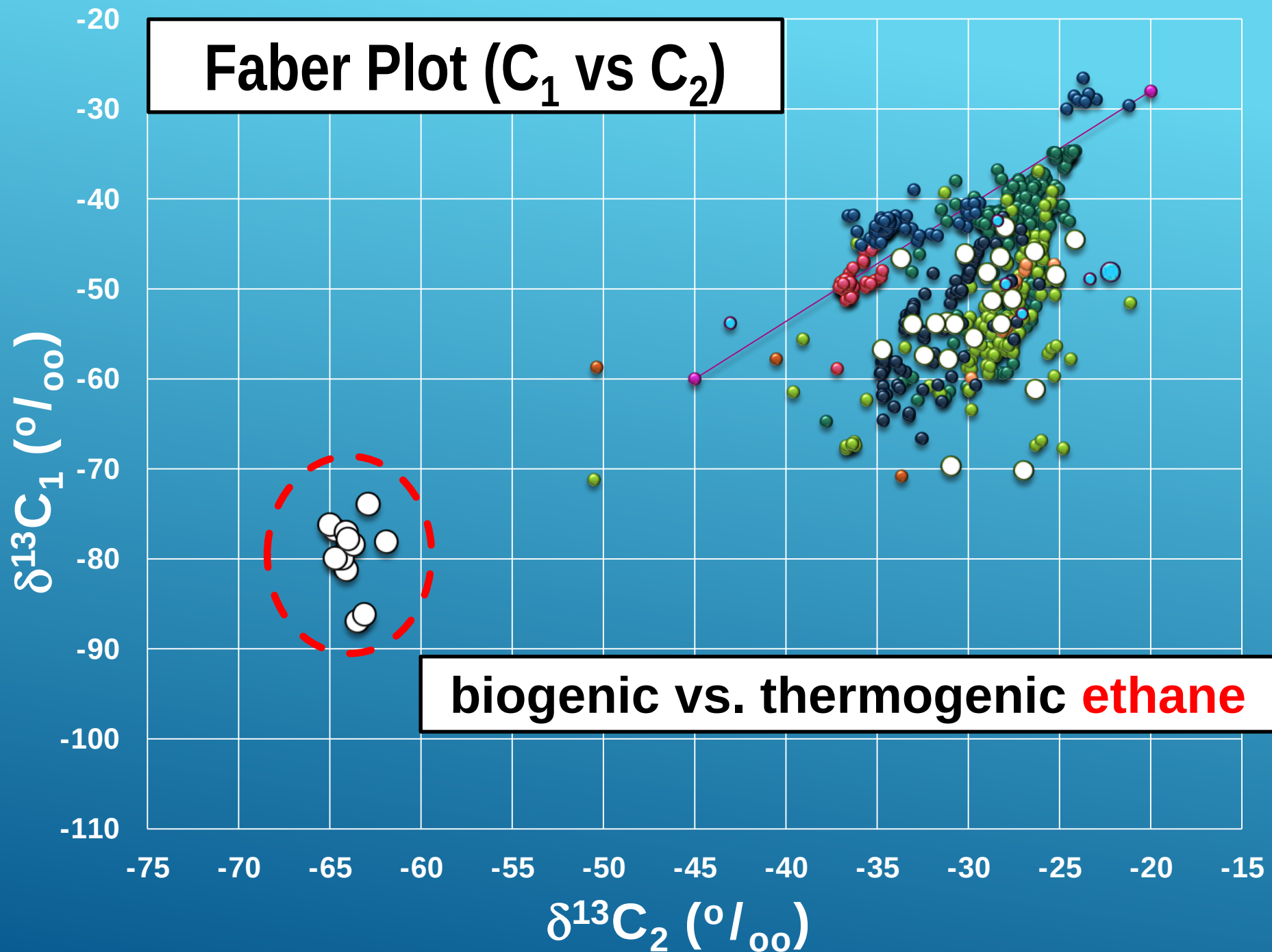
Sample: TBZ105/16

Injection date: 08-Sep-2018, 08:36

Method: FID60002C10B.M

File: TGSB0328.D

Faber Plot (C_1 vs C_2)



Data Stewardship (Jayme McBee)

- Data are abundant, but often exist in inconsistent formats
- Manual conditioning often necessary to build workable database
- Propose adoption of standardized open file formats/metadata
 - Look to other disciplines: Seg-y file format for Seismic; IOGP Seabed Survey Data Model, FGDC/ISO 19139 metadata format in GIS
 - Will require consensus to determine conceptual framework(s) – must be flexible enough to encompass a wide variety of data types
 - Consider applications beyond initial acquisition and interpretations:
 - *Analytics is reliant on a database built with consistent structure*
 - *Special characters are not database friendly*

Key Points

- on-land prospecting is different from marine
- lots of different marine seep proxies
- marine seep proxies can prove up charge
- macro-seeps can reveal oil age, maturity, depositional environment, quality
- seeps are signals of, not same as in reservoir
- field, lab, interp, data methods still evolving

Legacy

Legacy

