

# **Past, Present and Future Advancements in Methods for Detecting Hydrocarbon Seepage after 75 Years\***

**John V. Fontana<sup>1</sup> and David Seneshen<sup>1</sup>**

Search and Discovery Article #41412 (2014)\*\*

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## **Abstract**

It has been over 75 years since German and Russian scientists first identified anomalous methane seeps above gas fields in the mid-1930's. In the United States a few years later, Rosaire and Horvitz extracted hydrocarbon gases from soil samples over oil and gas deposits. Leo Horvitz, a pioneer in the field of near-surface geochemical prospecting for oil and gas, presented his final paper titled "Hydrocarbon Geochemical Exploration after Fifty Years" at the Symposium on Unconventional Methods in Exploration for Petroleum held by the Institute for Earth and Man, Southern Methodist University in 1985. At the same symposium Leigh Price discussed the now abundant evidence and compared the many theories that attempted to explain vertical migration, concluding with a now generally agreed upon gravity driven micro-bubble theory. This theory best explained the near vertical outline of most anomaly patterns found over petroleum deposits and the vertical migration "chimney" seen by both chemical and geophysical methods. Klusman modeled these migration mechanisms and calculated the rate of ascent of gases, which further confirmed the vertical nature of micro-seepage. Higher resolution geophysical data has confirmed the presence of the migration paths to the surface. Two AAPG Hedberg Research Conferences have been held presenting many of the theories, methods and debates on the topic. While some of the theories and techniques were controversial in the first half of the 20th century, vertical migration and micro-seepage is now widely accepted and many geochemical and remote sensing exploration methods are applied by the exploration industry to confirm the presence of hydrocarbon charged.

## References Cited

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<http://www.searchanddiscovery.com/pdfz/documents/2009/090806etiope/images/etiope.pdf.html>.
- Groth, P.K.H., 1988, Bibliography for near surface prospecting methods: Association of Petroleum Geochemical Explorationists, Denver, CO, 244 p.
- Hamid, H., and I.B. Morozov, 2005, Mapping of Salt Dissolution Edge of Prairie Evaporite in South-Central Saskatchewan: 2005 CSEG National Convention, Evolving Geophysics Through Innovation, Web Accessed August 3, 2014.  
[http://cseg.ca/assets/files/resources/abstracts/2005/047S0131-hamid\\_Mapping\\_of\\_Salt\\_dissolution.pdf](http://cseg.ca/assets/files/resources/abstracts/2005/047S0131-hamid_Mapping_of_Salt_dissolution.pdf).
- Horvitz, L., 1969, Hydrocarbon prospecting after thirty years, in W.B. Heroy, ed., Unconventional methods in exploration for petroleum and natural gas: Dallas, Texas, Southern Methodist University Press, p. 205-218.
- Klusman, R. 1993, Soil gas and related methods for natural Resource Exploration: John Wiley & Sons, Inc., New York, 496 p.
- Klusman, R.W., and K.J. Voorhees, 1983, A new development in petroleum exploration technology: Mines Magazine, v. 73/3, March.
- Laubmeyer, G., 1933, A new geophysical prospecting method, especially for deposits of hydrocarbons: Petroleum, v. 29/18, p. 1-4.
- Link, W.K., 1952, Significance of oil and gas seeps in world oil exploration: AAPG Bulletin, v. 36, p. 1505–1541.
- Potter II, R.W., P.A. Harrington, A.H. Sulliman, and J.H. Viellenave, 1996, Significance of geochemical anomalies in hydrocarbon exploration, *in* D. Schumacher and M. A. Abrams, eds., Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 431-439.

Saunders D.F., K.R. Burson, and C.K. Thompson, 1999, Model for Hydrocarbon Microseepage and Related Near-Surface Alterations: AAPG Bulletin, v. 83/1, p. 170-185.

Schumacher, D., and M.A. Abrams., 1994, Hydrocarbon Migration and Its Near-Surface Expression: AAPG Memoir 66, Tulsa, OK, 446 p.

Schumacher, D., and L.A. LeSchack, 2002, Surface Exploration Case Histories: Applications of Geochemistry, Magnetism, and Remote Sensing: AAPG Studies in Geology No. 48/SEG Geophysical References Series No. 11, Tulsa, OK, 500 p.

Sokolov, V.A., 1933, The gas survey as a method of prospecting for oil and gas formations: Technika, p. 1.

# Past, Present and Future Advancements in Methods for Detecting Hydrocarbon Seepage after 75 Years

**John V. Fontana<sup>1</sup>, PG and  
David M. Seneshen<sup>1</sup>, PhD**

***Rocky Mountain Section AAPG Annual Meeting***

**Session Title: Reservoir Characterization Blending**

**Conventional and Emerging Technologies**

**Session Chairs: Marianne Rauch-Davies and John Fontana**

**Tuesday, July 22, 2014**



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Golden, CO, USA;**

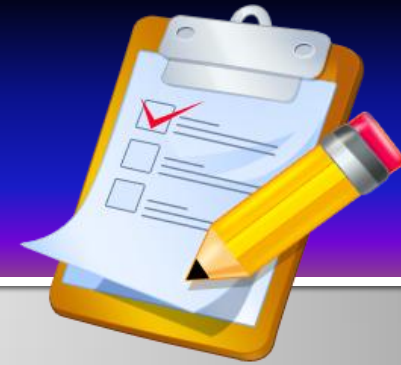
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# Outline



## ■ **PAST**

- **Macroseep vs. Microseep**
- **First Known Methods – Russia & Germany**
- **The American Pioneers**
- **Methods & the Sensitivity Issue**

## ■ **PRESENT**

- **Landmark Symposiums & Publications**
- **The Theory of Vertical Migration**
- **Direct Detection vs. Indirect Detection Methods of Seepage**
- **Methods of Sampling & Analysis**
- **Modern Methods of Seep Detection**
- **Analysis of an Anomaly**

## ■ **FUTURE**

# The Past



**Signal Hill oil field at Atlantic and 28th Streets,  
Long Beach, CA, circa 1930. *Courtesy of the  
Long Beach Public Library Collection.***

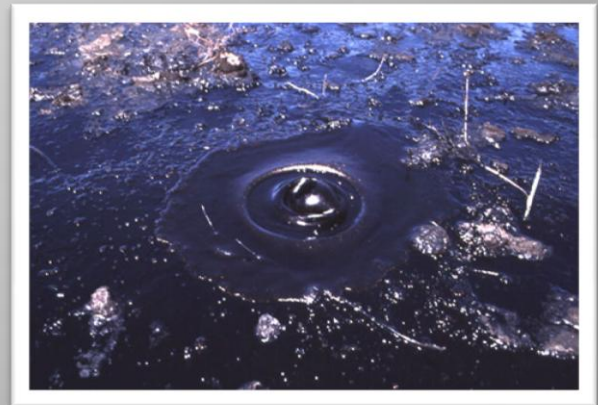
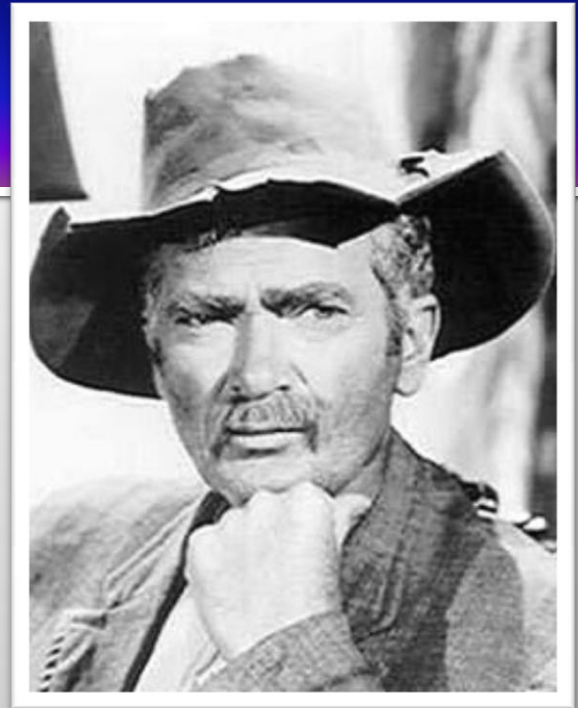
# "Practical Oil Geology"



- **4<sup>th</sup> Edition Textbook by Dorsey Hager, McGraw Hill Book Company, 1926. (Original Ed. 1918)**
  - **Foreword: Oil Geology – Applied Common Sense:**
  - ***"There is at present a rather vague idea in the minds of many men as to just what constitutes an oil geologist. Some people associate him with the 'crooked stick' or 'peach tree twig' men, other think he used hocus-pocus, and as yet, comparatively few of the operators see the geologist as a clean-cut, clear-thinking engineer who is just as much an expert in his line as is the driller or railroad surveyor."***
- ***Geochemistry – Yet to be discovered as a tool?!***

# Or... Were Geochemical Exploration Methods in Use Already?

- Was Jed Clampett the original exploration geochemist?
- Drilling next to a visible oil seep (**a macroseep**) was the earliest method used to find oil traps.
- Today – Near surface exploration geochemistry methods use sensitive instrumentation to detect *invisible* **microseeps**.





# Macroseep vs. Microseep

- **Macroseeps**

- **Jed Clampett Style**
- **Strong Gas/Petroleum Flux**
- **Visible Expressions or.....**
- **Measured in Field or by Remote Sensing Methods**

- **Microseeps**

- **Direct Detection Methods**
  - Sensitive Laboratory or Field Methods
- **Indirect Detection Methods**
  - Alterations Due to Bacterial & Red-Ox Changes
  - Gases or Elements Related to the Reservoir
  - Remote Sensing for Alteration



# Mud (and Methane) Volcanoes of Azerbaijan





# Marcroseeps Seen from Space



*NASA satellite photograph showing oil slicks from natural seeps in the Gulf of Mexico, offshore Louisiana. (NASA)*

# Less Obvious Macroseeps





# The First



- **First Geochemical Survey Done in Germany, 1929, Published by G. Laubmeyer in 1933**
  - Laubmeyer, G., "A New Geophysical Prospecting Method, Especially for Deposits of Hydrocarbons," Petroleum, 1933.
  - *Measured methane using microcalorimeter.*
- **Russian paper in the same year.**
  - Sokolov, V. A., "The Gas Survey as a Method of Prospecting for Oil and Gas Formations," Informatsionnyl Sbmik, Neftyanogo Gedogo Razvedochnogo Instituta, Union of Soviet Publishing Houses (ONTI), 1933.
  - *Sokolov was able to measure methane and ethane.*

# American Pioneers (1930's - 1940's)

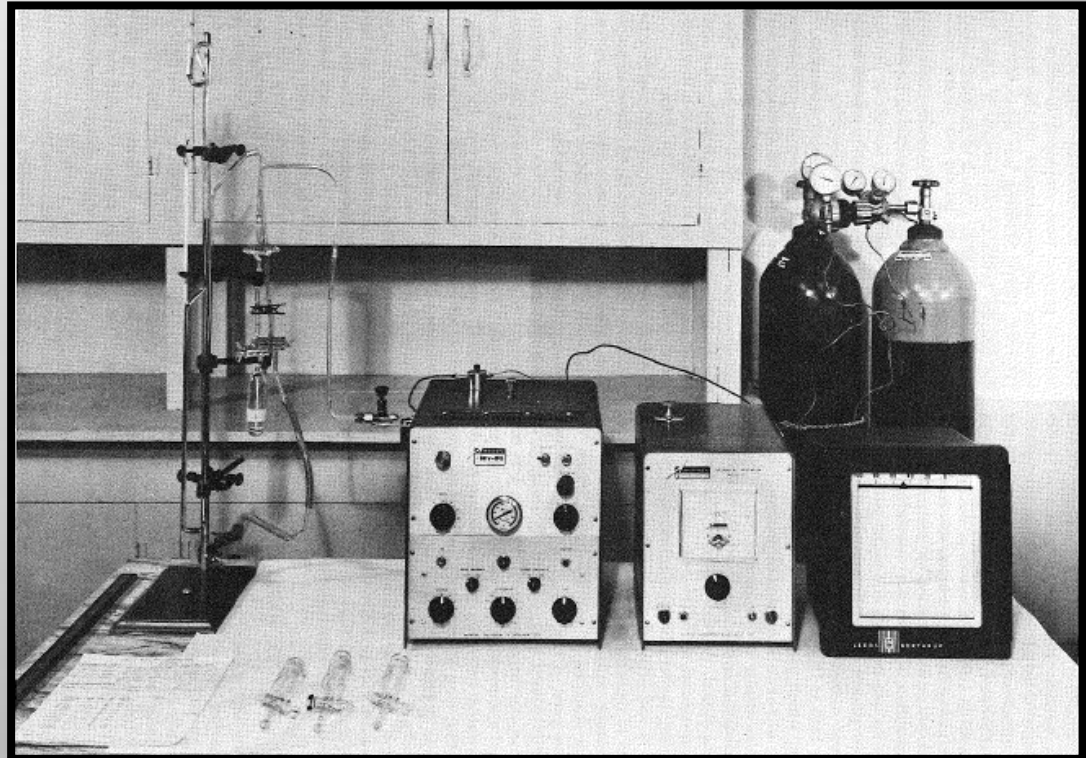
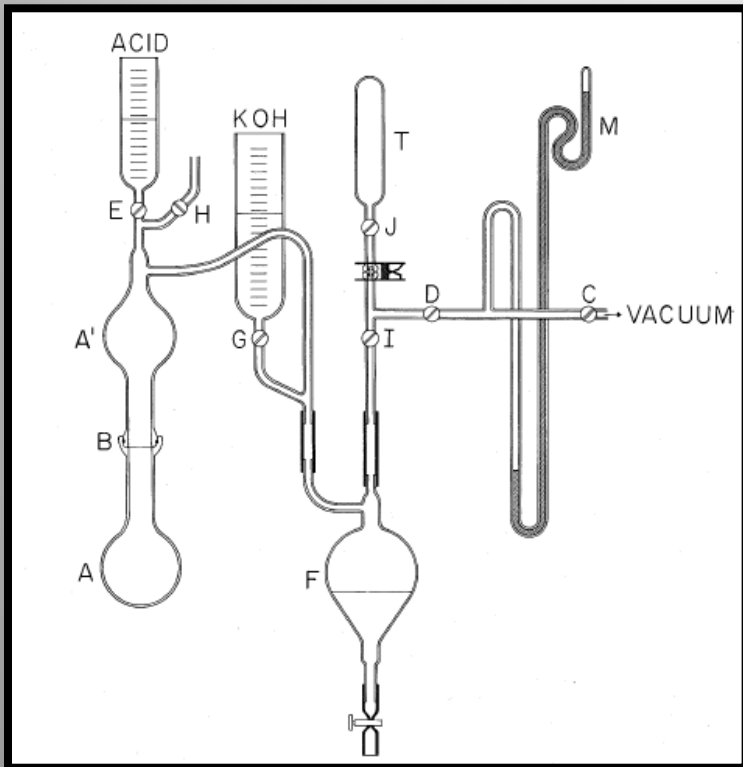
- **Ludwig W. Blau of Humble Oil & Refining Co., (now ExxonMobile)**
  - *Contended many geophysical highs were velocity anomalies from alteration and was opposed to using reflection seismography.*
- **Eugene Rosaire & Eugene McDermott noted unique mineralization above Texas fields.**
  - *Both Geophysicists and pioneers in seismography, were so convinced they started a geochemical service company.*
- **Leo Horvitz developed innovative hydrocarbon detection methods**
  - *Developed an acid extraction method to measure adsorbed (or occluded) gases and concentrate the gases to enable analysis of C<sub>1</sub>-C<sub>4</sub> hydrocarbons.*

# Early Methods Limitations

- **Mainly Direct Detection of Hydrocarbons**
- **Methane, Ethane, & Other Gases as Technology/Methods Improve**
  - **Instrument Sensitivity was Limiting**
- **Visible Alterations from Gas Seepage**
  - **Reducing & pH Conditions**

# The Sensitivity Issue

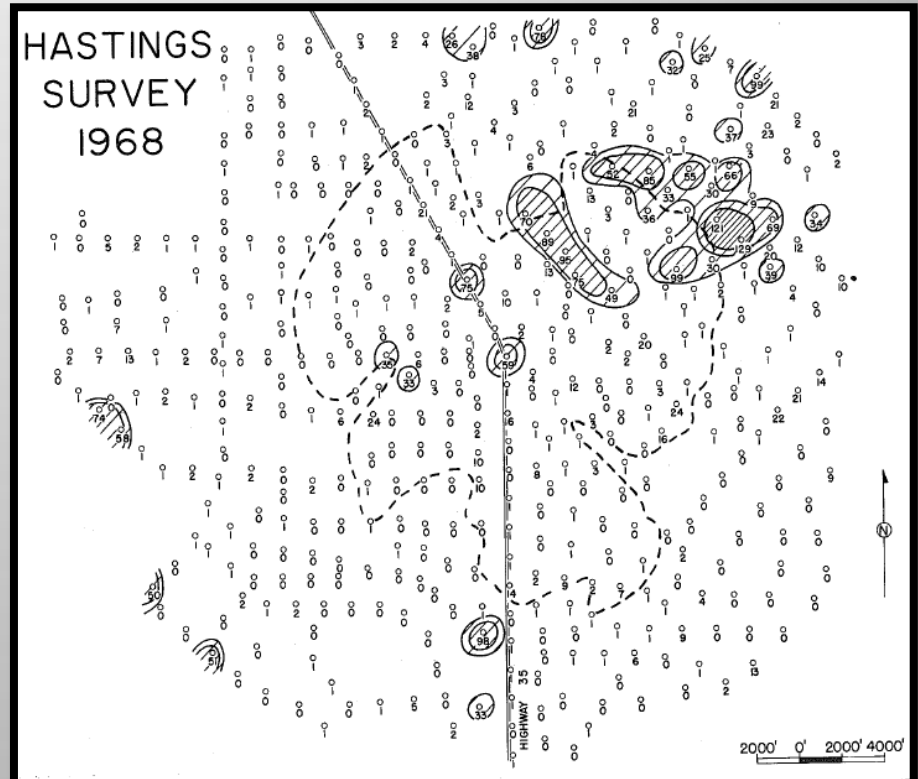
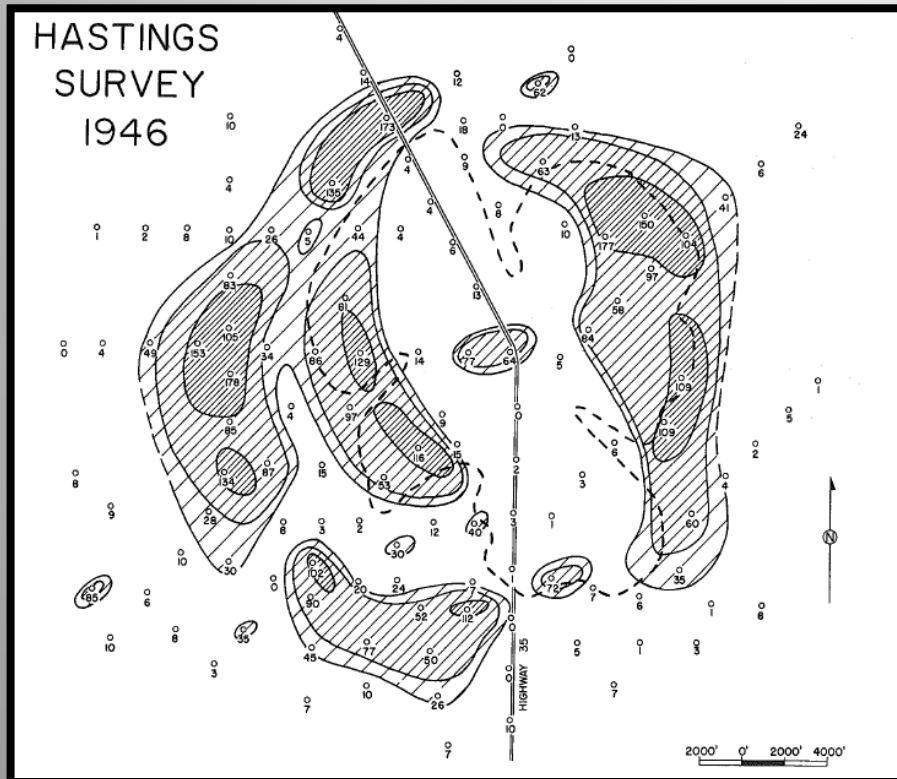
- Extracting and concentrating gases increased sensitivity.



From Leo Horvitz, 1969

# Repeated Surveys Yielded Evidence Seeps are Live

- Surveys in Texas field 22 years apart, 34 years after production started & 375,000 bbls produced.



From Leo Horvitz, 1969



# Landmark Symposiums and Publications

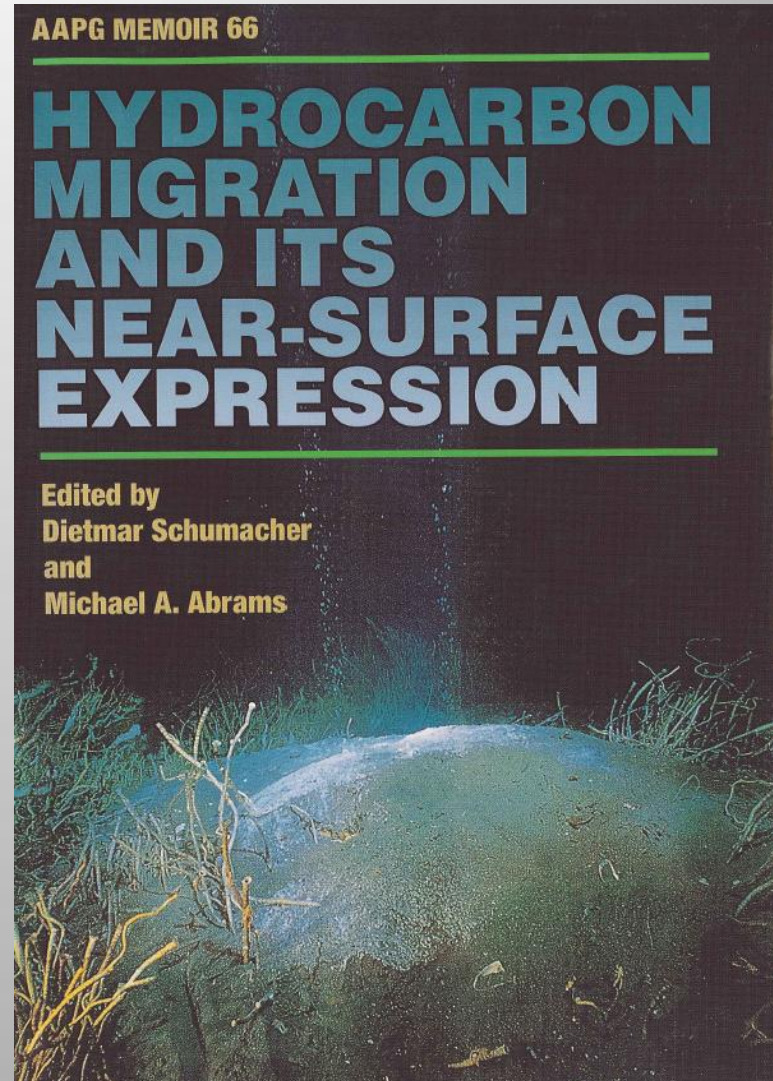
- **Unconventional Methods in Exploration for Petroleum & Natural Gas**
  - Four Meetings Held, 1968 – 1985
  - Institute for the Study of Earth & Man at Southern Methodist University
  - Four Proceeding Volumes Published
  - Ed. Heroy, Gottlieb, Davidson
- **1984, AAPG - Joint NASA/Geosat Test Case Project,**
  - Jet Propulsion Laboratory, California Institute of Technology
  - Ed. Michael Abrams

# Landmark Symposiums and Publications

- **Bibliography for Near Surface Prospecting Methods**
  - APGE Special Publication No. 2
  - 1988, Peter K. H. Groth,
- **Soil Gas & Related Methods for Natural Resource Exploration**
  - 1993, Ronald Klusman (Colorado School of Mines)
- **Surface Exploration Case Histories; Applications of Geochemistry, Magnetism and Remote Sensing**
  - AAPG Studies in Geology No. 48 and SEG Geophysical Reference Series No. 11:
  - 2002, Editors D. Schumacher and L. LeSchack

# Landmark Symposiums and Publications

- **AAPG Hedberg Research Conferences**
  - 1994, Hydrocarbon Microseepage and Its Near-Surface Expression
  - 2002, Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates
  - 1996 Publication: AAPG Memoir 66; Hydrocarbon Migration and Its Near-Surface Expression. (from the 1994 conf.)
  - Editors D. Schumacher, M. Abrams





# Theory of Vertical Migration & Microseepage

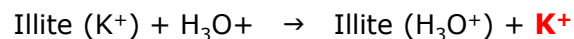
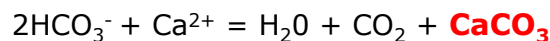
- **Diffusive - Effusive – Gravity – Buoyancy?**
- **Effusion is responsible for the “Escape.”**
- **Gravity and Buoyancy best explain the near vertical migration to the surface.**
- **Diffusion does not explain the patterns we see but is more likely a part of the equation above the water table (vadose zone.)**

Heavy C<sub>6</sub>+  
alkanes &  
aromatics

Light C<sub>1</sub>-C<sub>4</sub>  
alkanes,  
H<sub>2</sub>, He

Geomorphic Anomaly

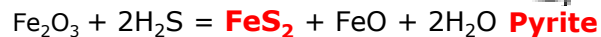
Secondary Mineralization



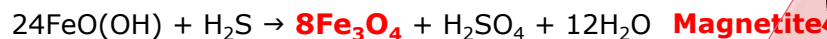
Carbonate  
and silica

Potassium Loss

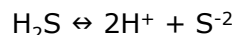
Hydrogen Sulphide Alterations



Pyrite

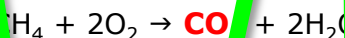


Magnetite



Uranium

Aerobic



Anaerobic



PETROLEUM

Faster Micro or  
Macro Seepage

Slower  
Microseepage

# Evidence of Alteration


## Bleaching of Red Sandstone, East Texas Basin



1999, Saunders, D.F., et. al.,



# The Present



A camouflaged rig  
on Island Grissom,  
a man-made drilling  
island near Long  
Beach, CA.  
*Photo by J. Jepson.*

# Documented Macroseeps



- **Link, W.K., 1952, Significance of Oil and Gas Seep in World Exploration.** AAPG Bulletin 36, 1505-1540.
- **Simon Petroleum Technology, 1992, Hydrocarbon Seeps. A Global Digital Database.** Non-exclusive Data Product
  - **>10,000 Macroseeps Documented Worldwide**
- **Etiope, Giuseppe, 2009, GLOGOS, A New Global Onshore Gas-Oil Seeps Dataset**
- ***If we have documented this many visible macroseeps, how many microseeps are there?***

# Seep Detection Methods

## ■ Direct Methods

- Detects actual migrated hydrocarbon species that have seeped from the reservoir and accumulated in the near surface.
- Today, Comparing Reservoir Fluid and Gas Composition to Seep Composition is Possible

## ■ Indirect Methods

- Detects visible, chemical and biological alterations from migrating hydrocarbons caused by altering redox conditions, mineralization, microbial activity, etc..

# Direct vs. Indirect

## ■ Direct Methods

- **Ambient Air Seeps**
  - Infra-Red Spectrometers
  - Portable Gas Detectors
- **Soil Gas Hydrocarbons**
  - Interstitial, Occluded or Adsorbed Gases
  - Passive Soil Gas Collection
- **Liquid Hydrocarbons**
  - Solvent Extracted Oils
  - Scanning Fluorescence
  - Extended GC or GC-MS
  - Satellite or Fluorescence Imaging
- **Offshore**
  - Subsurface “Sniffers”

## ■ Indirect Methods

- **Remote Sensing**
- **Geomorphology**
- **Mineral Alterations**
- **Trace Metals**
- **Radon, Radiometrics**
- **Iodine**
- **Microbial**
- **Helium**
- **Botanical Stress**
- **Geophysical Methods**
  - Magnetics
  - Velocity Changes
  - Sonar Images (offshore)



# Finding the Less Obvious

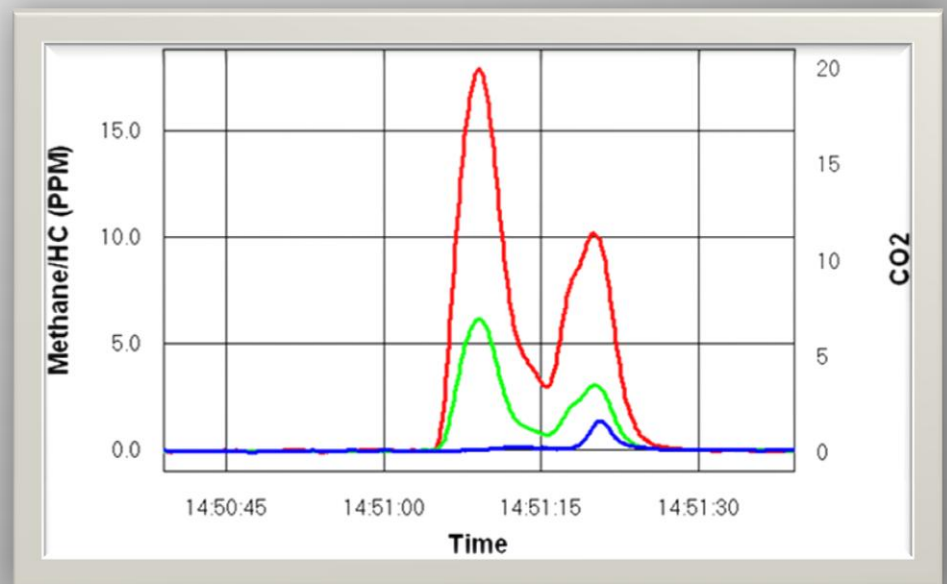
- **Ambient Air IR Surveys**
  - Truck, ATV, Boat or Helicopter Mounted
  - Rapid data collection system
  - Detects gas seep “plumes”
  - Locates infrastructure leaks.



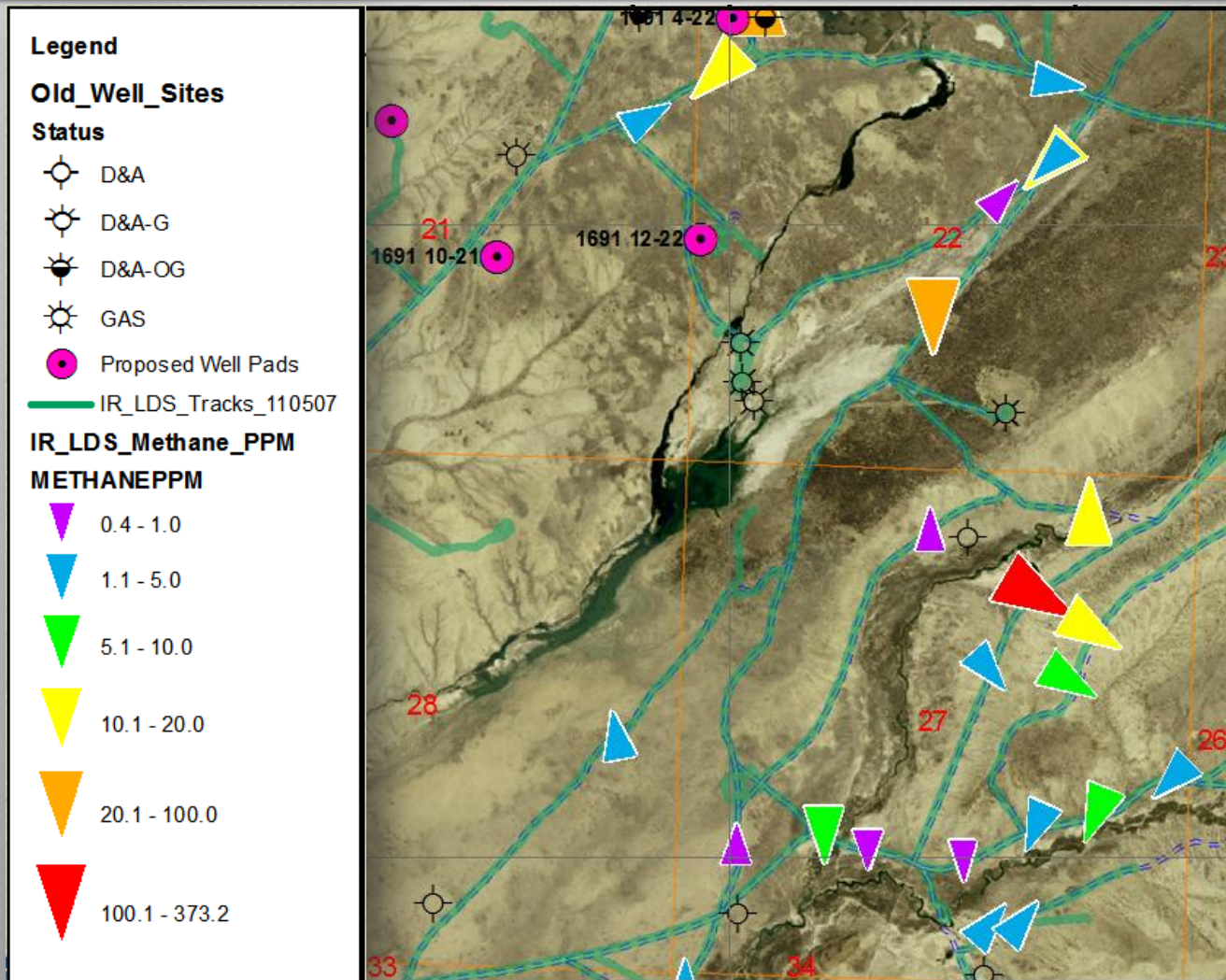


# Ambient Air IR Survey Real Time Results

- CH<sub>4</sub>, CO<sub>2</sub> and Heavier (C<sub>2</sub>+) Hydrocarbons
- <1 ppm Sensitivity for Methane
- Continuous GPS/GIS Enabled Acquisition
- Wind (Gas Plume) Direction Recorded



# Ambient IR Road Survey Intensity & Wind Direction





# Portable FID/PID on Foot Surveys Locate Gas Seeps

- **Flame Ionization (FID)**
  - Detects Hydrocarbon Gases
  - 1ppm CH<sub>4</sub> Sensitivity
- **Photo Ionization (PID)**
  - Heavies & Aromatics
  - 0.1ppm Sensitivity
- **Continuous Surface measurements**
- **Calibrated Detectors**



# Improvements in Sensitivity

- **Gas Chromatography**
  - PPB or PPT Sensitivity
- **Stable Isotope Analysis**
- **Satellite & Remote Sensing**
- **Portability**



# Trace Analysis Methods

## ■ Gas Range (Light) C<sub>1</sub>-C<sub>6</sub> Hydrocarbons

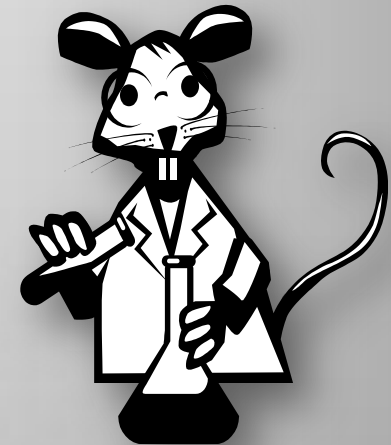
- Parts Per Billion (ppb) Levels
- Free Gas or Head-Space Gas
- Thermally Desorbed (low & high temp)
- Acid Extracted
- Adsorbents (Passive Soil Gas)

## ■ Liquid Range (C<sub>6</sub>+) Hydrocarbons

- PPB and Parts Per Million (ppm) Levels
- Solvent Extracted
  - Spectral Fluorescence
  - High Resolution GC-FID
- Thermally Desorbed
  - High Resolution GC/FID or GC/MS
  - Adsorbents (Passive Soil Gas)

## ■ Trace Metals

- Acid Extracted Soils - ICP/MS





# Sampling Media Available for Geochemical Analysis

**Shallow Soils**



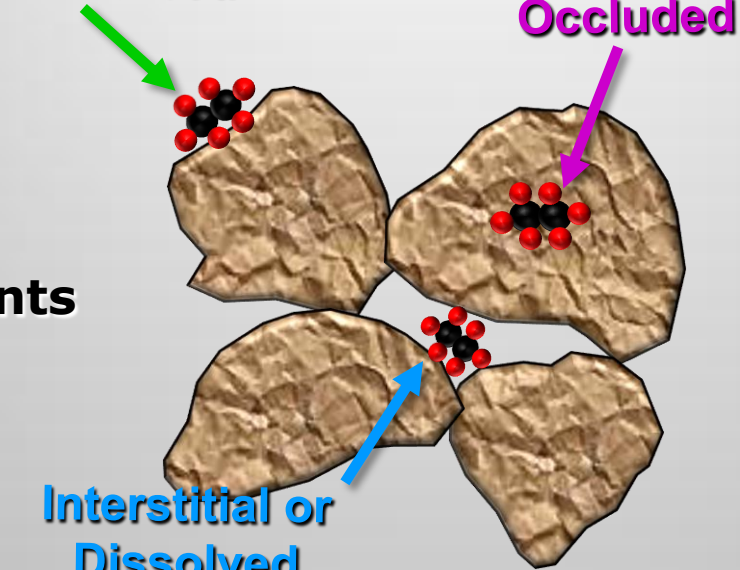
**Free Soil Gas**



**Adsorbed**

**Occluded**

**Interstitial or  
Dissolved**



**Ground or Sea Water**



**Shot-hole Sediments**



**Lake Sediments**



**Vegetation**



**Deep Soils**



# Passive Soil Gas Methods

- **Invented at Colorado School of Mines,**
  - Klusman & Voorhees, 1980's
- **Also called “Integrative” Soil Gas**
- **Activated Adsorbents Buried in Soil/Sediments**
- **Concentrates Gases and Smooths Variations**
- **Detects C<sub>2</sub> – C<sub>20</sub> Hydrocarbons**
- **Thermal Desorption GC and GC/MS**
- **Independent of the Matrix**





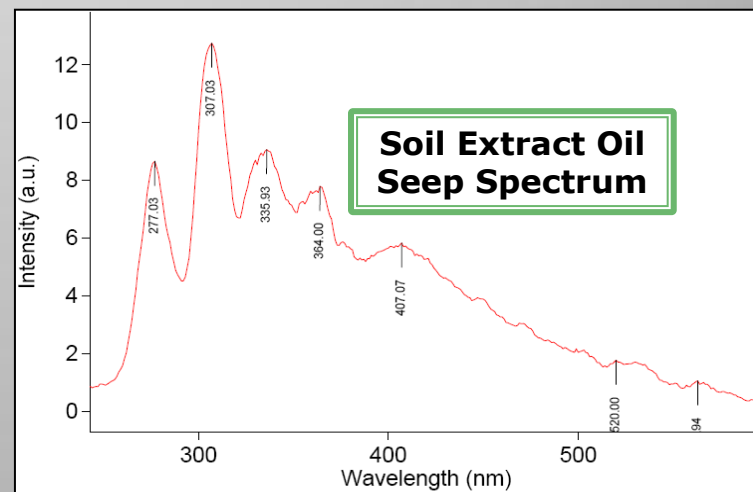
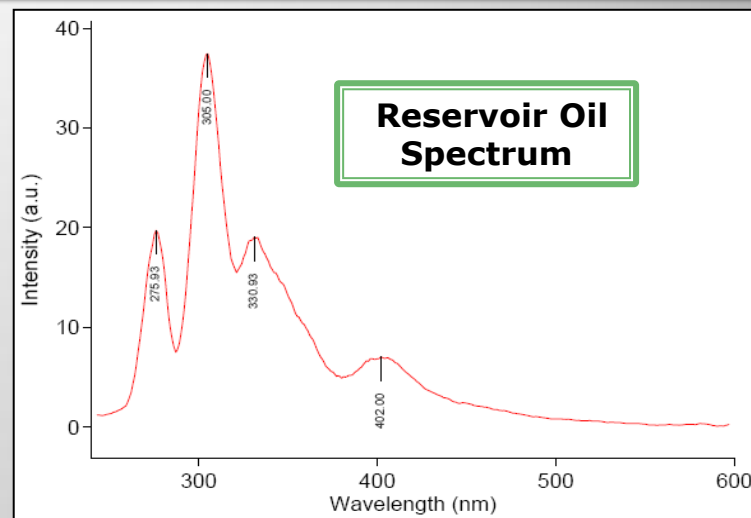
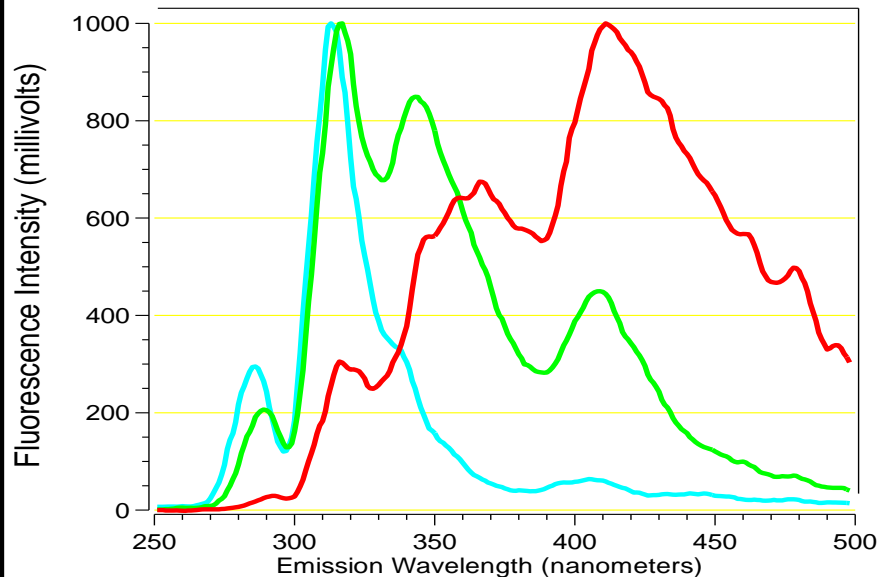
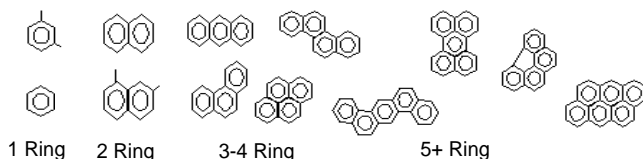
# Oil Micro-Seeps Seen by SSF

## SYNCHRONOUS SCANNED UV-FLUORESCENCE

### Spectra of Three Oils with Different Gravities

- High Gravity Cretaceous Condensate
- Medium Gravity Cretaceous Oil, Colorado
- Low Gravity Paleozoic Oil, Nevada

#### Aromatic Hydrocarbon Groupings





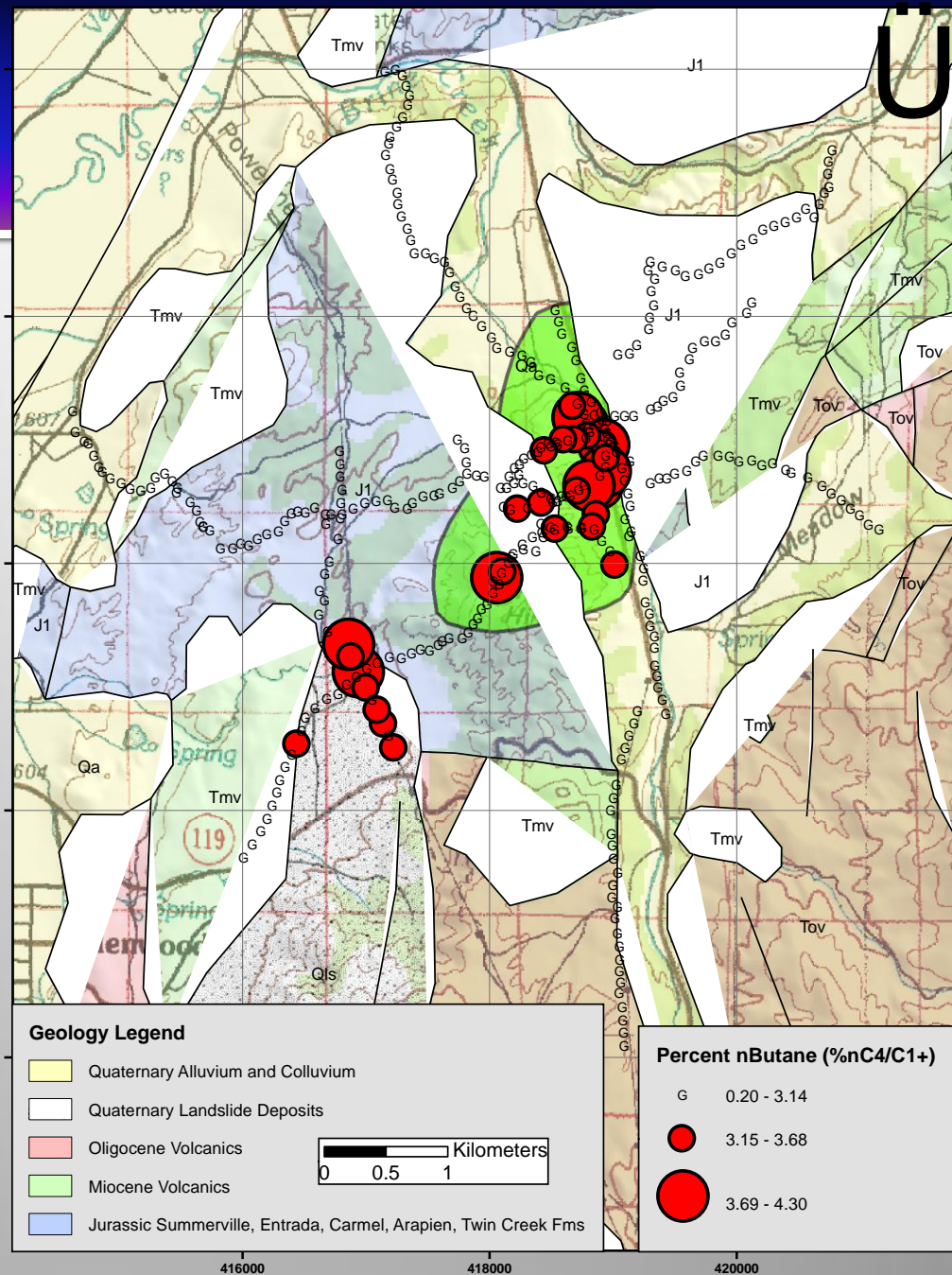
# Analysis of an Anomaly

- **Historically, a Detection WAS an Anomaly!**
- **Lower Sensitivities Mean We Can Now Detect Background Everywhere**
- **Isotopes ( $\delta^{13}\text{C}$ ,  $\delta\text{D}$ ) of Larger Seeps**
- **To Distinguish Background from Anomaly:**
  - **Fingerprinting Reservoir Gases and Fluids**
  - **Adequate Sample Density**
  - **Multivariate Statistical Analysis**
  - **Integration with Other Methods**

# Covenant Field

## Light Hydrocarbons

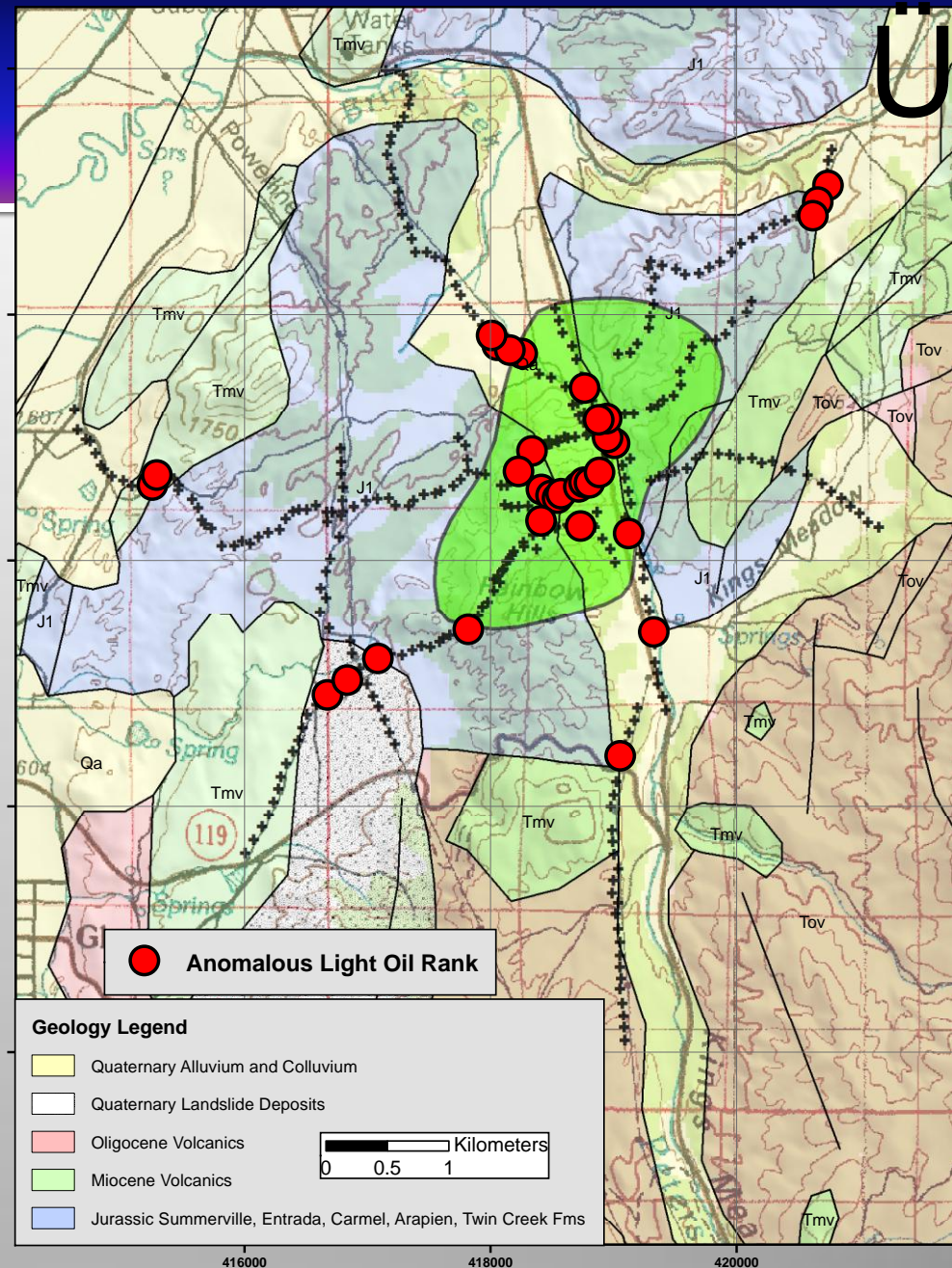
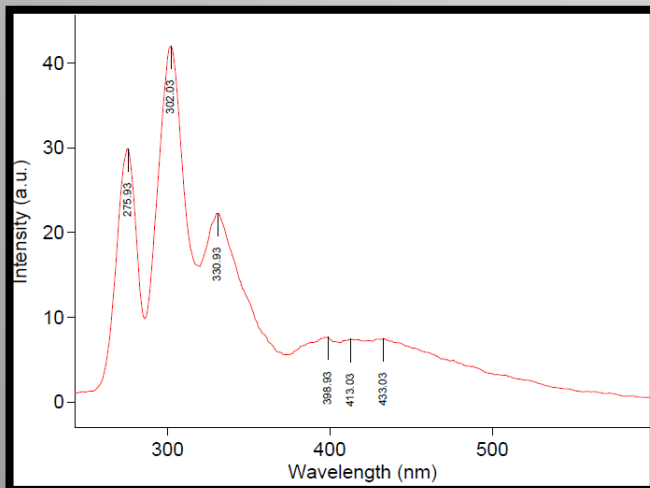
- Prospect Scale Survey
- Utah Overthrust
- HTTD Method
- Wet Gas Ratio in Desorbed Soil Gas
  - %  $nC_4/C_1$
- Apical & Fault Related Anomalies



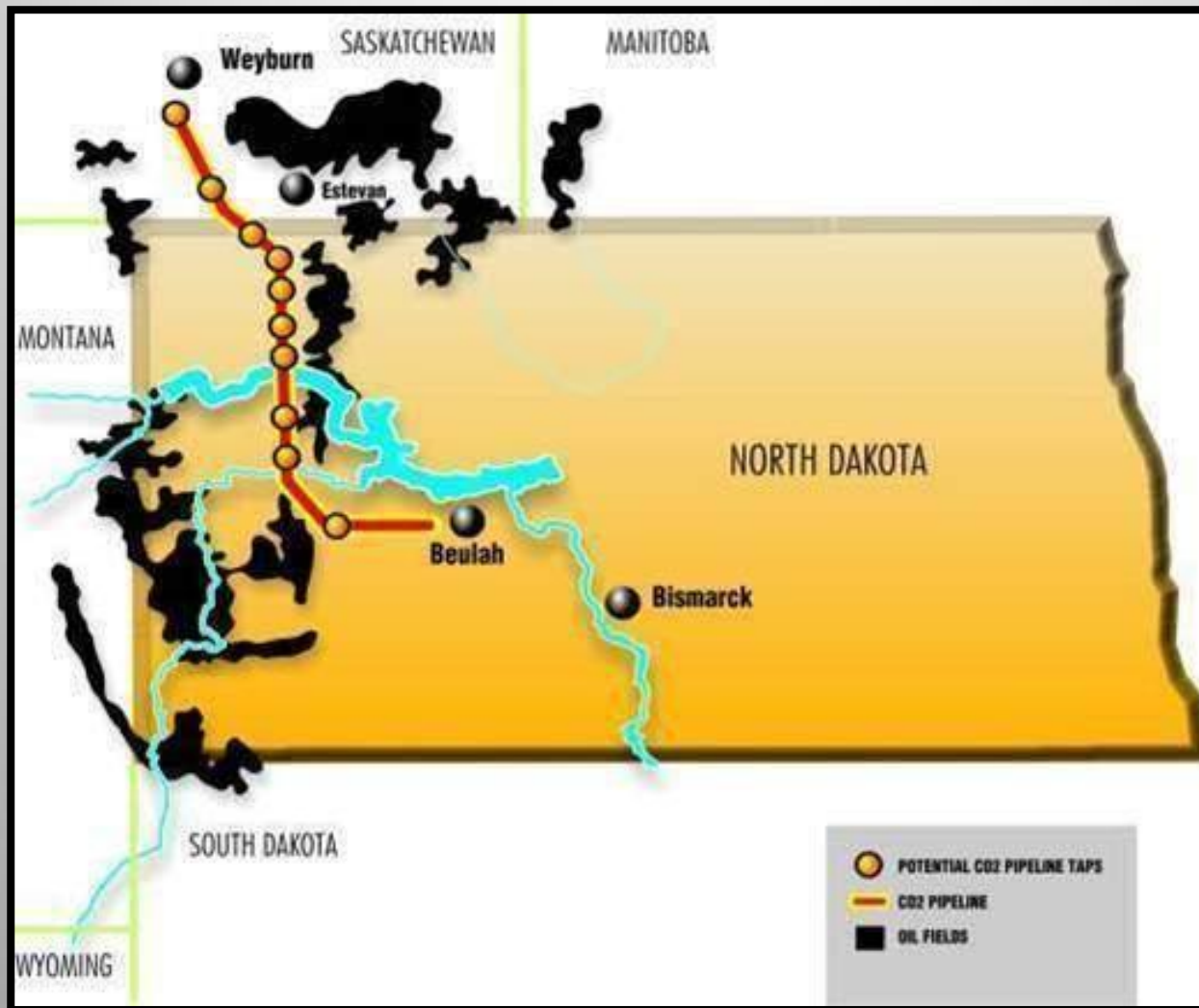


# Covenant Field Fluorescence

- Synchronous Scanned Fluorescence (SSF)
- Trace Light Oils (Spectral Similarity)
- Apical & Fault Anomalies



# Bakken Prospecting: Regional Geochem Surveys





P3 (333nm) Peak Intensity for Light Oil Rank >79

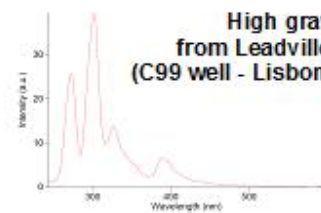
◆ 1 - 3

● 4

● 5 - 7

● 8 - 11

High gravity oil  
from Leadville Formation  
(C99 well - Lisbon Oil Field, Utah)



P3 (333nm) Peak Intensity for Medium Oil Rank >73

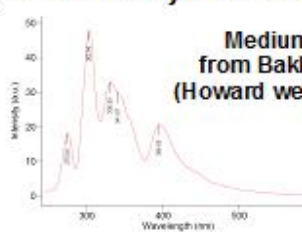
◆ 2 - 3

● 4

● 5 - 9

● 10 - 91

Medium gravity oil  
from Bakken Formation  
(Howard well - 2-26-8-10 W2)



P3 (333nm) Peak Intensity for Heavy Oil Rank >68

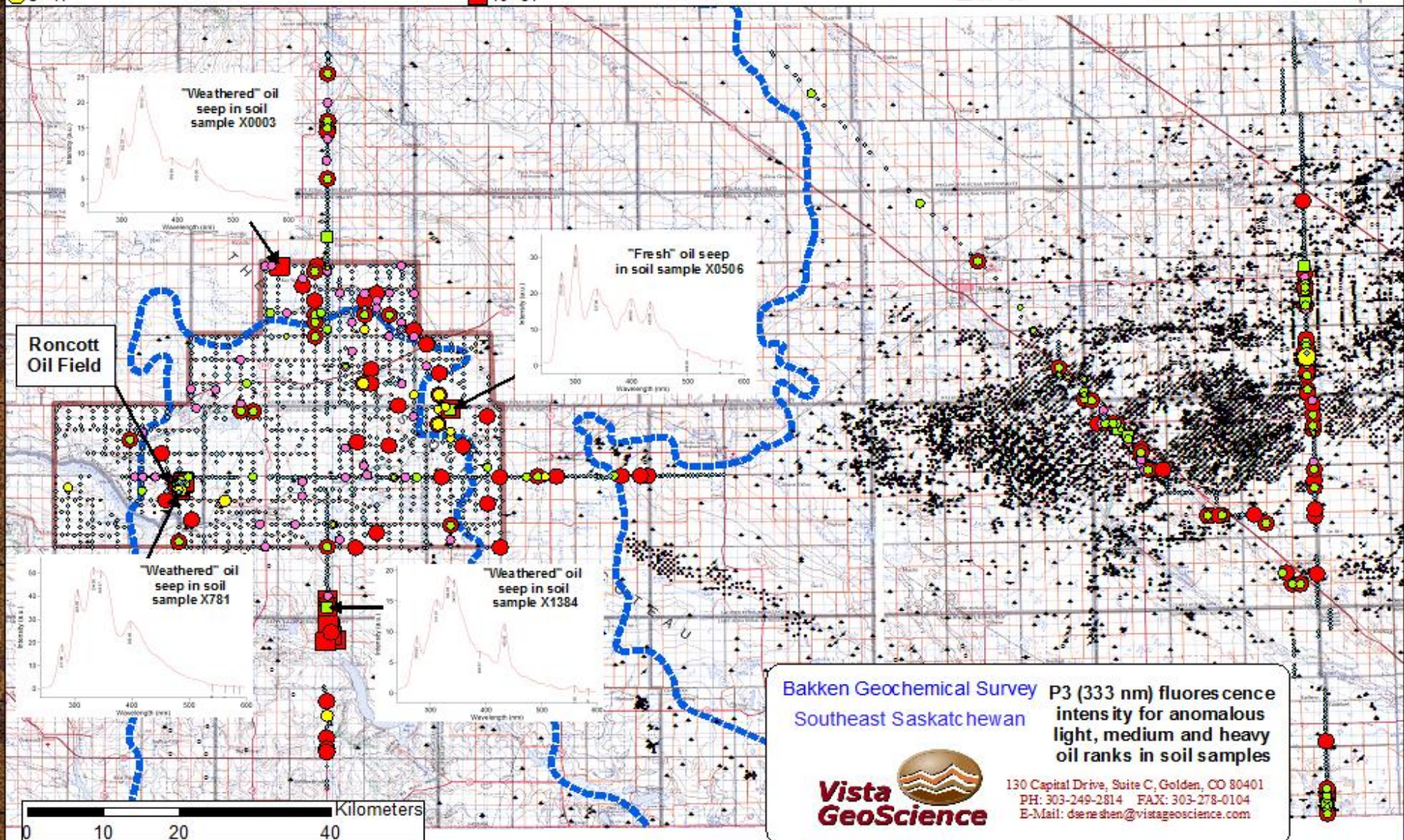
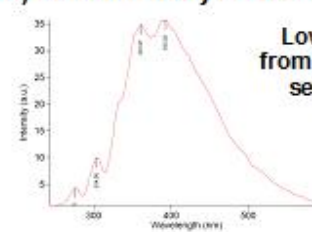
◆ 3

● 4

● 5 - 10

● 11 - 91

Low gravity oil  
from weathered oil  
seep in Belize



Bakken Geochemical Survey  
Southeast Saskatchewan

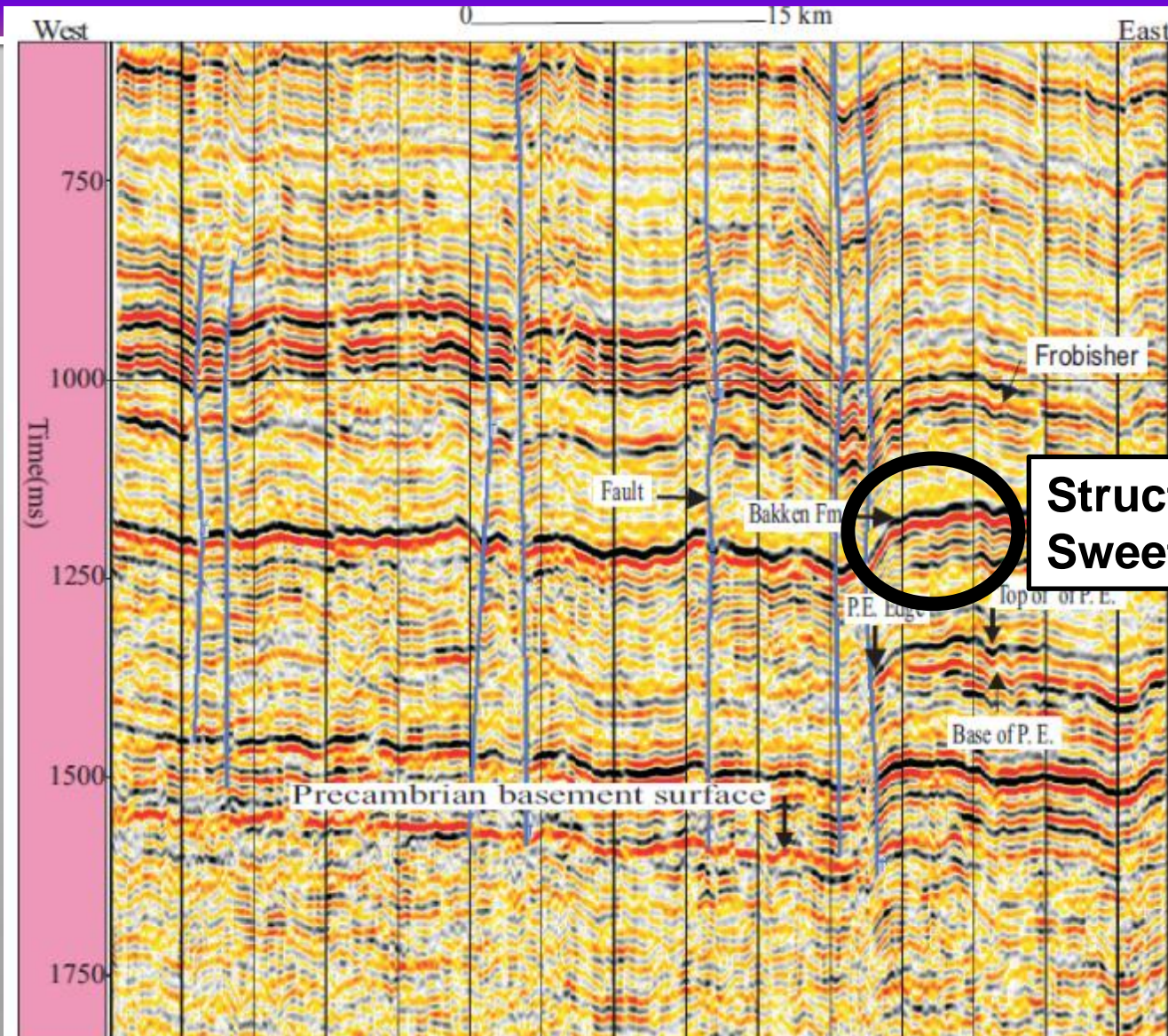
P3 (333 nm) fluorescence  
intensity for anomalous  
light, medium and heavy  
oil ranks in soil samples



130 Capital Drive, Suite C, Golden, CO 80401  
PH: 303-249-2814 FAX: 303-278-0104  
E-Mail: dsenehen@vistageoscience.com



# Recent salt dissolution disturbs all overlying strata (Hamid et al., 2005)

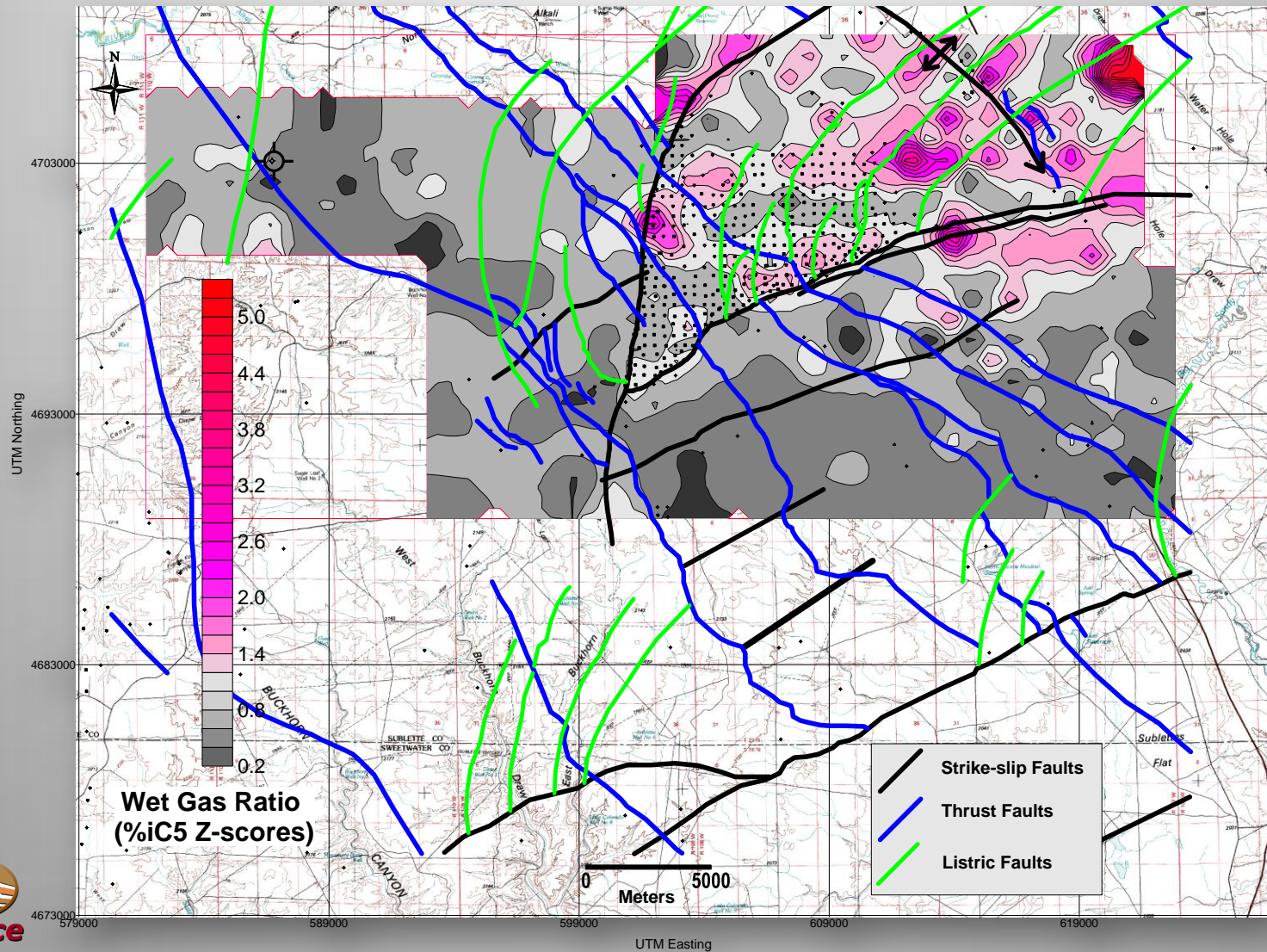


**Structural  
Sweetspot?**



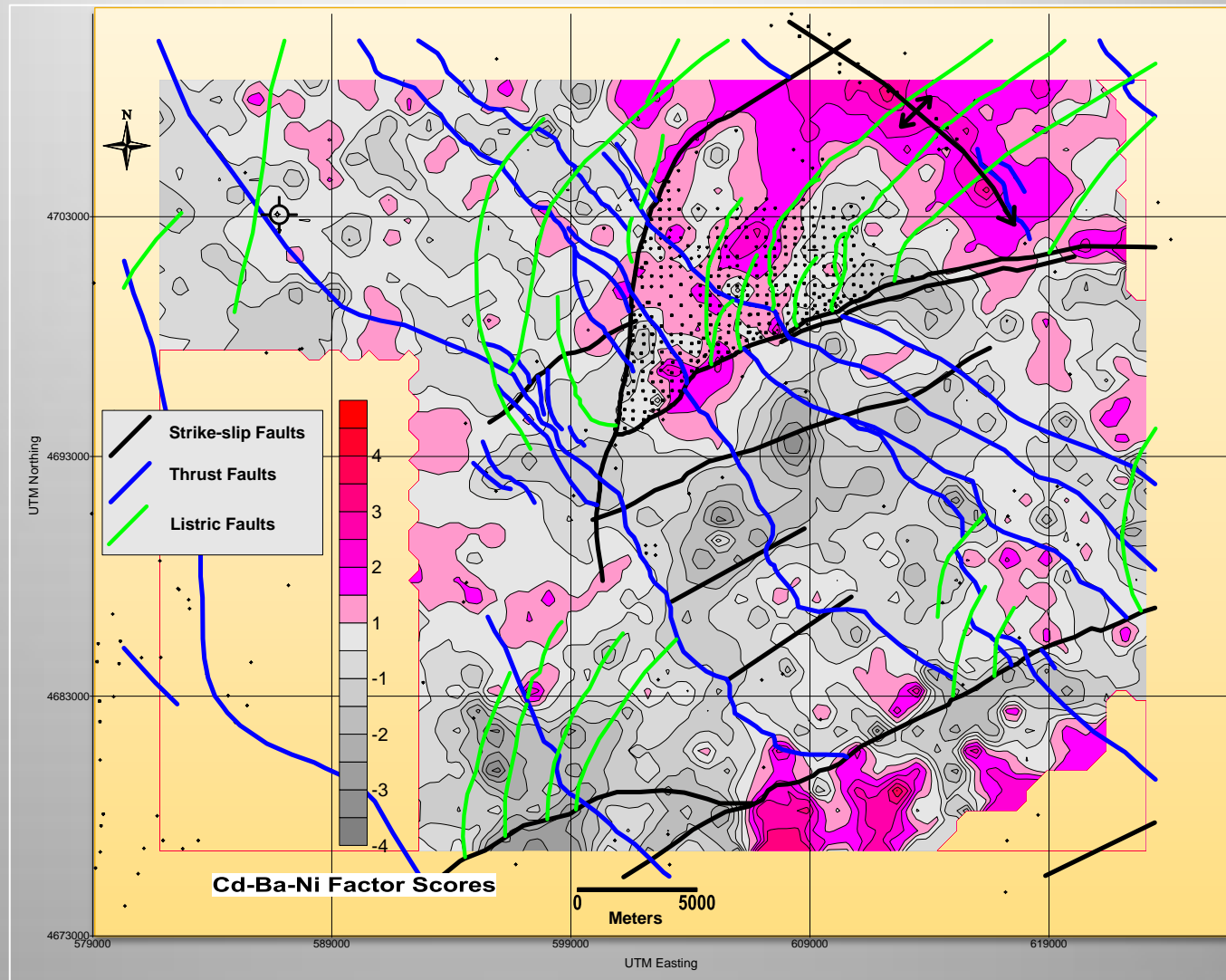
# Jonah & Pinedale Tight Gas

Light Hydrocarbon Gases      Regional Scale Sampling



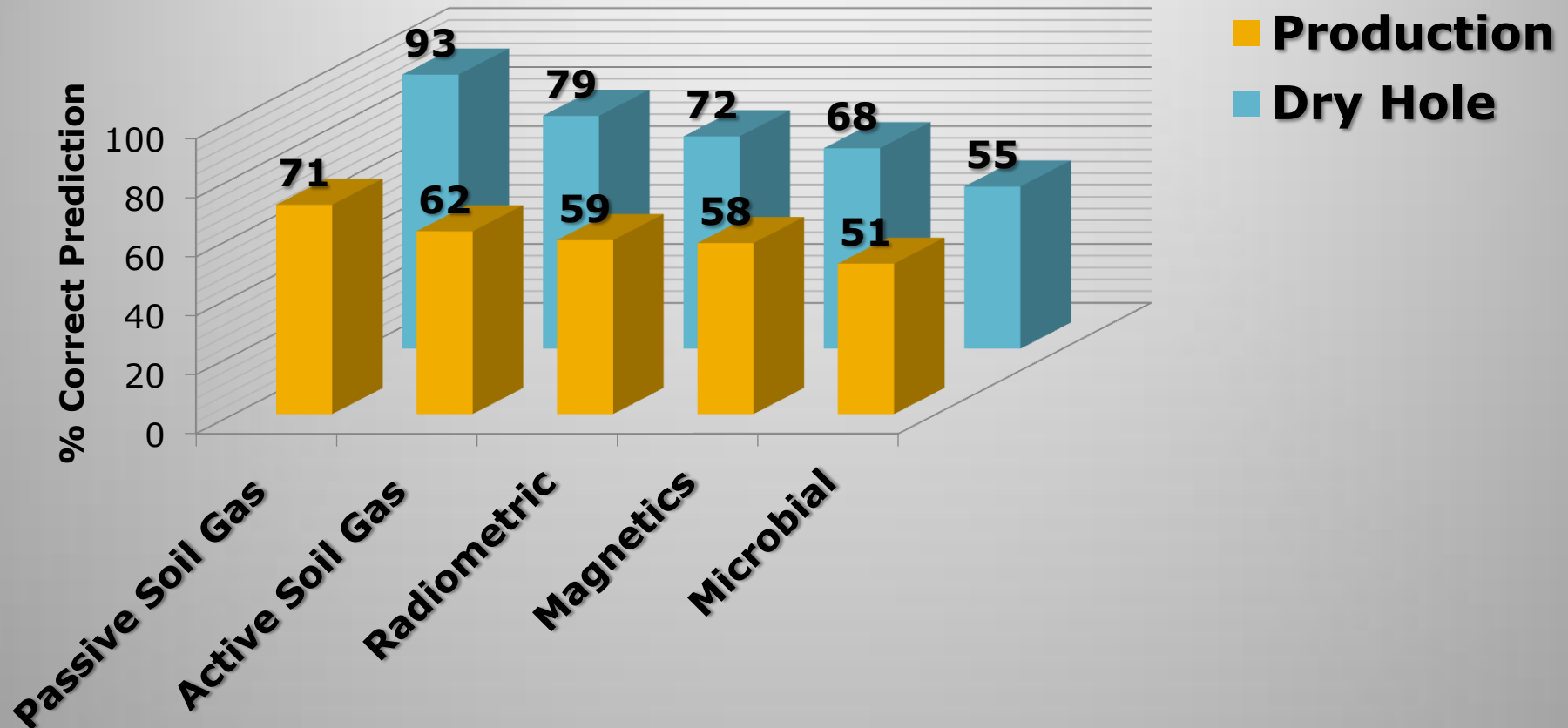
# Trace Metals in Sagebrush

## Cadmium, Nickel, Barium Factor



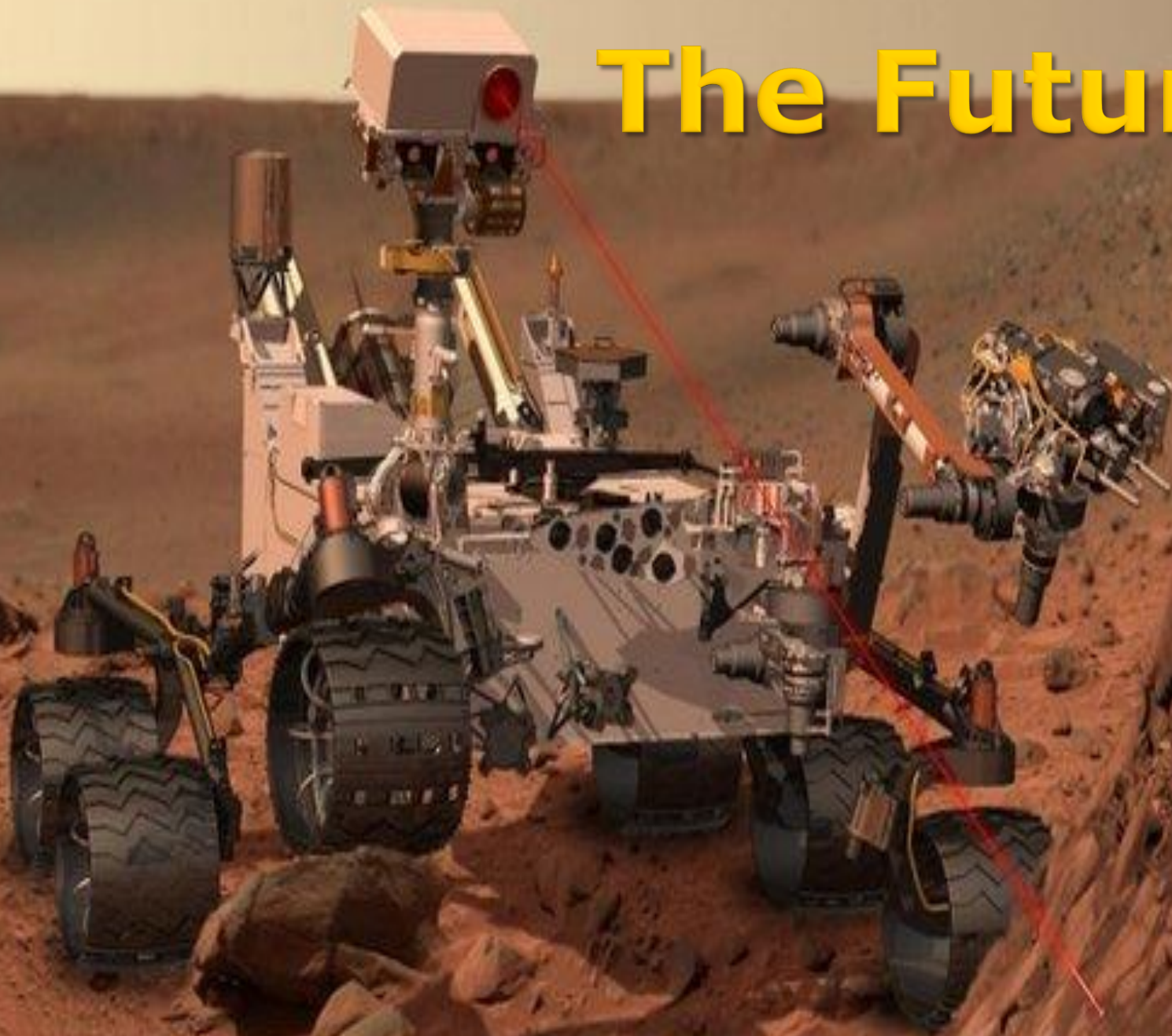


# Success of Geochemical Exploration Methods



Robert Potter II, et. al. (1994) Santa Fe Minerals Inc.  
Chapter 33 in AAPG Memoir 66

# The Future?



# What Will Change?

- **Continued Improvements in Technology & Sensitivity**
- **Ability to Measure Stable Isotopes at Low Concentrations**
- **Ability to Process More Data & Variables**
- **Improved Remote Sensing Technologies**
- **Better Understanding of Seep and Migration Mechanisms**

# Summary

- **Geochemical Methods...**
  - **Have Been Historically Successful in Reducing Exploration Risk, Especially Dry Holes**
  - **Geochemical Methods are a General Underutilized Tool**
  - **Can be Used on Regional and Prospect Scales Programs, Onshore and Offshore**
  - **Can be Used to Compare Reservoir-Seep Composition**
  - **Are Best Utilized Combined with Multiple Methods to Reduce Risk and False Positives**
  - **Should be Implemented with Adequate Sample Size and Spacing**
  - **Will Expand in Capabilities Due to Technology Improvements and Sensitivity**



# *Questions?*



***Please Drive & Drill Responsibly!***



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