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

John V. Fontana[1] and David M. Seneshen[1]

Search and Discovery Article #41203 (2013)**
Posted October 18, 2013

*Adapted from presentation at History of Petroleum Geology Forum, AAPG Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013

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Summary

Geochemical Methods…

- Have been historically successful in reducing exploration risk, especially dry holes
- Geochemical methods are a general under-utilized tool
- Can be used on regional and prospect scales programs, onshore and offshore
- Can be used to compare reservoir to 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

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

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

John V. Fontana[1], PG and David M. Seneshen[1], PhD

Session Title: History of Petroleum Geology Forum (AAPG)
Sunday, May 19, 2013
Session Chairs: Stephen Testa, Larry Woodfork

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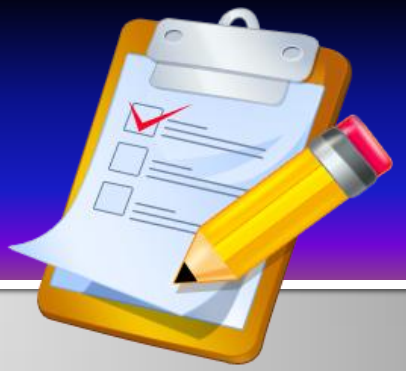
Outline



- 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

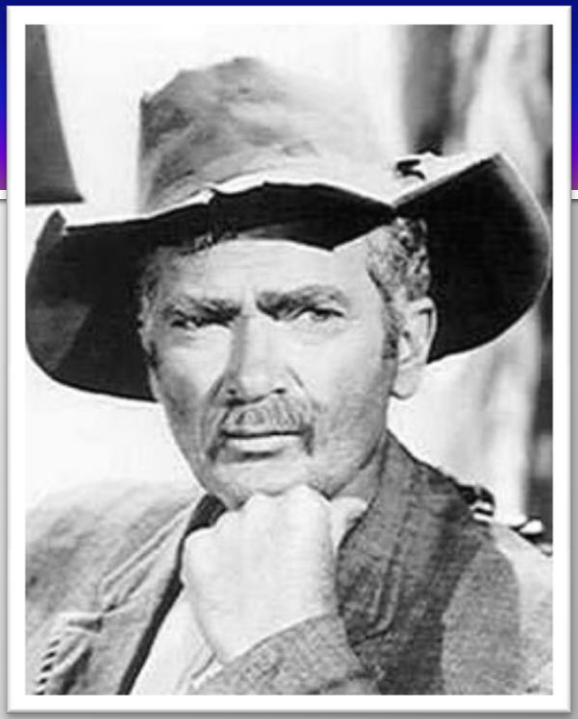
Signal Hill oil field at Atlantic and 28th Streets, Long Beach, CA, circa 1930. *Courtesy of the Long Beach Public Library Collection*.

"Practical Oil Geology"

- **4th Edition Textbook by Dorsey Hager, McGraw Hill Book Company, 1926. (Original Ed. 1918)**
  - **<u>Foreword: Oil Geology – Applied Common Sense:</u>**
  - ***"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, others 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?

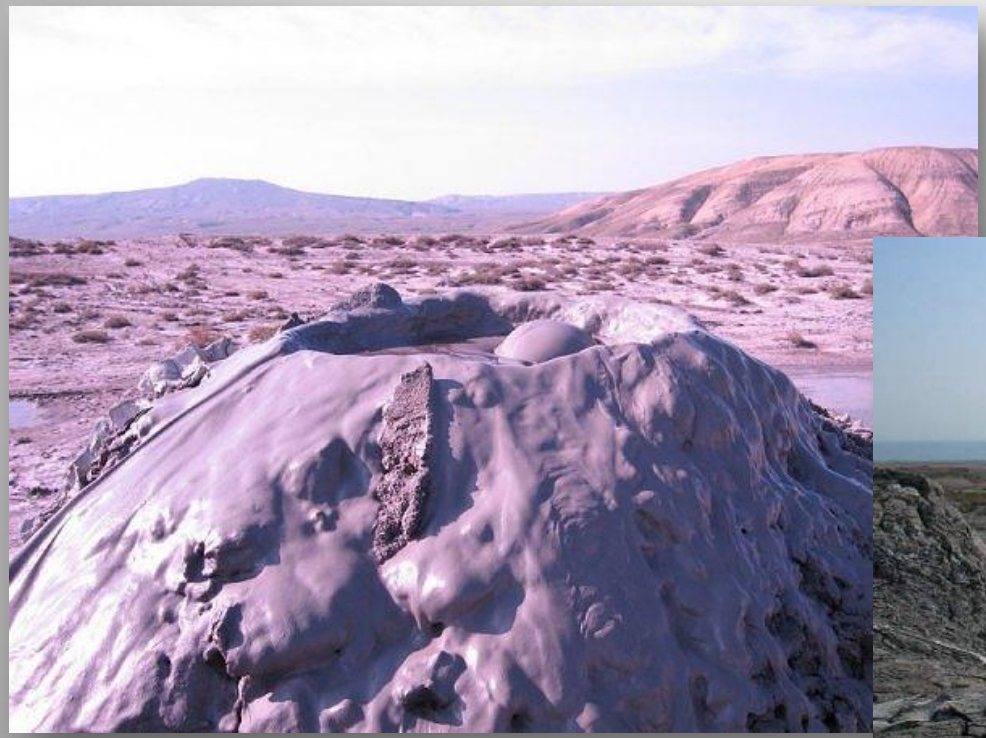
- **Was Jed Clampett the original exploration geochemist?**
- **Drilling next to a visible oil seep (a macroseep) was the earliest method used to find oil traps.**
- **Today – Near-surface exploration geochemistry methods use sensitive instrumentation to detect *invisible* microseeps.**



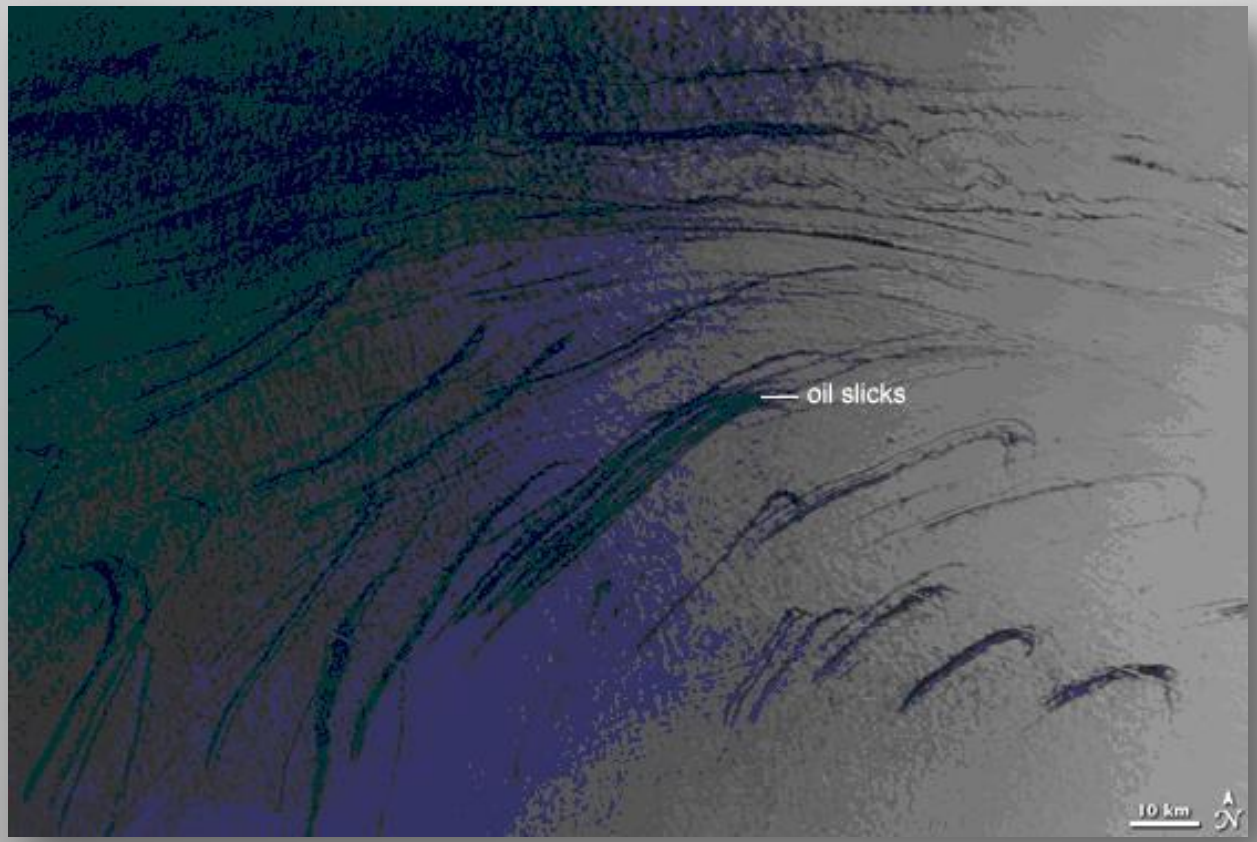
Macroseep vs. Microseep

- **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



Macroseeps 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 Sbomik, 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)

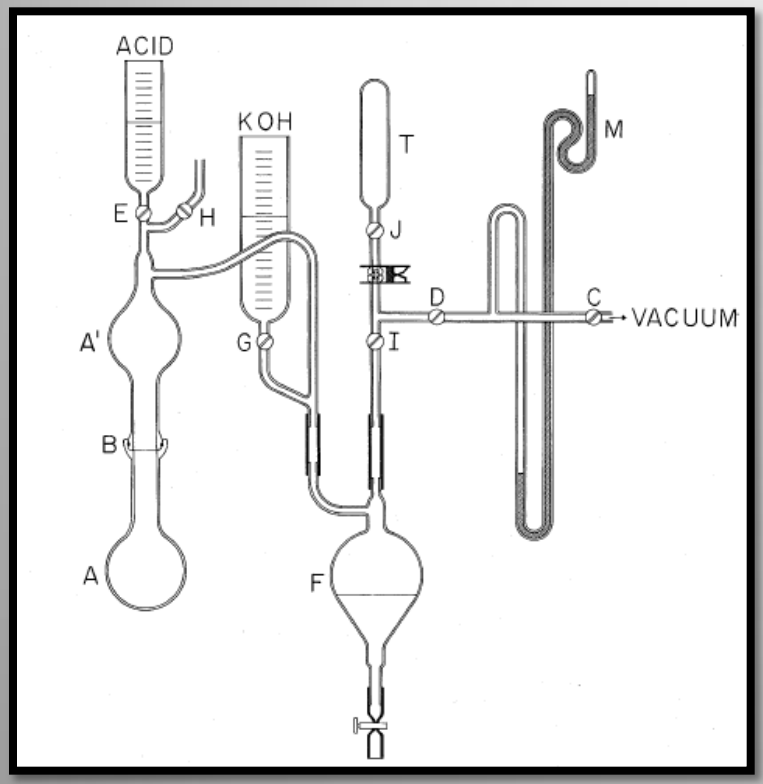
- **Ludwig W. Blau of Humble Oil & Refining Co. (now ExxonMobil)**
  - *Contended many geophysical highs were velocity anomalies from alteration and was opposed to using reflection seismography.*
- **Eugene Rosaire & Eugene McDermott noted unique mineralization above Texas fields.**
  - *Both Geophysicists 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_1-C_4 hydrocarbons.*

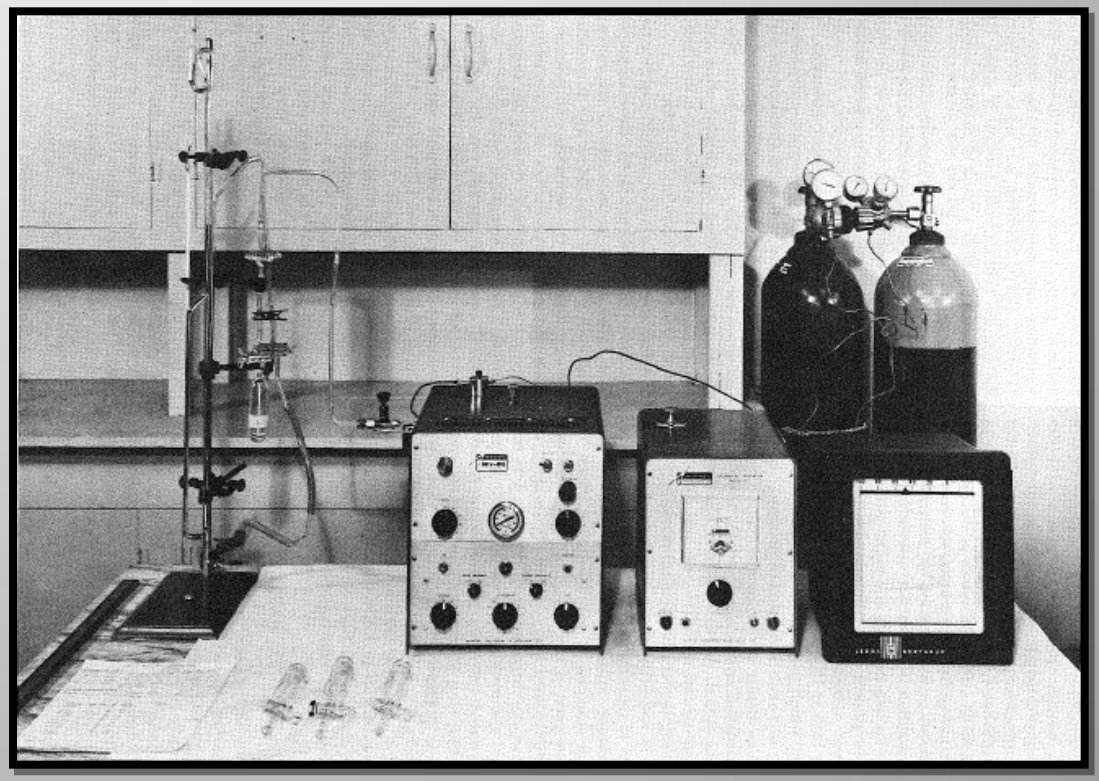
Early Methods Limitations

- 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.**

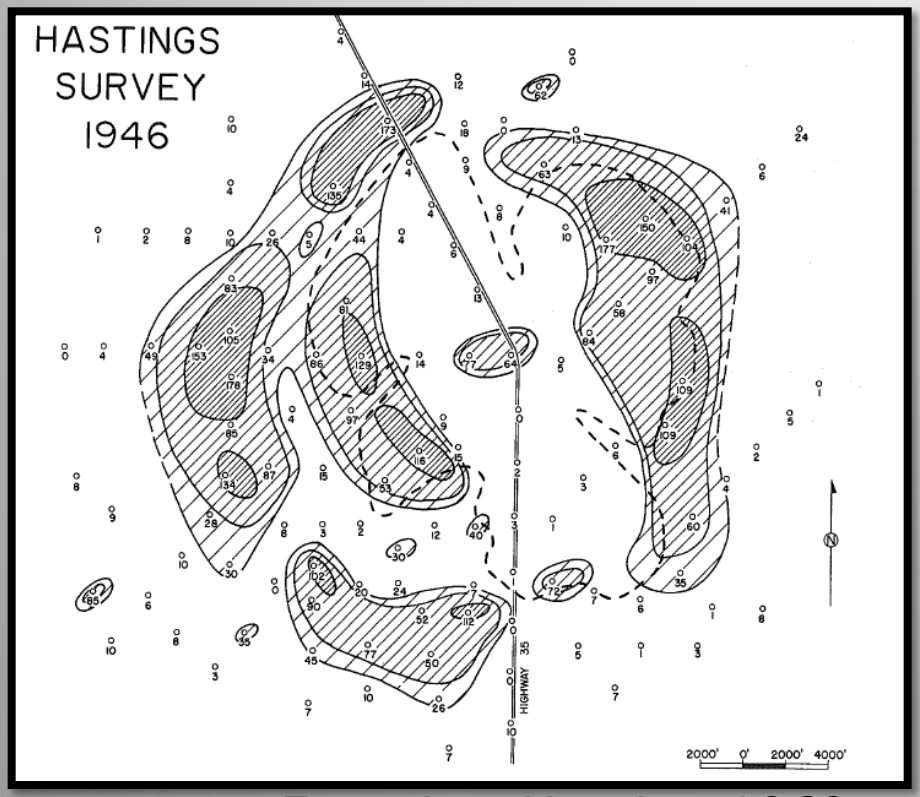


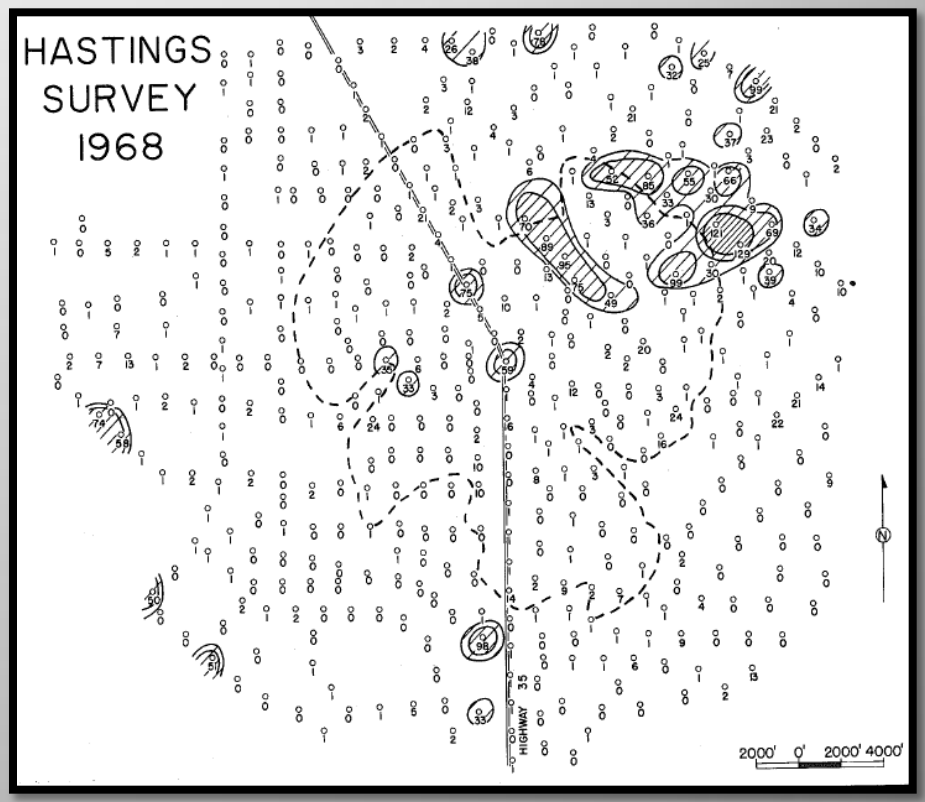


From Leo Horvitz, 1969

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

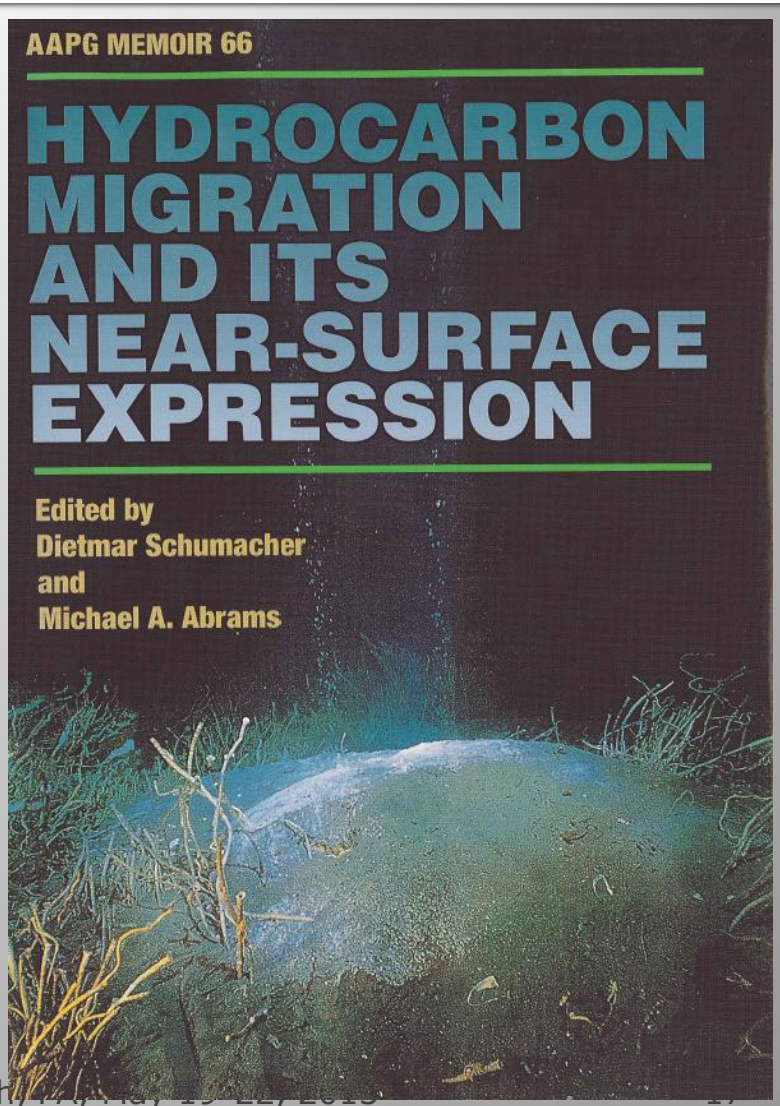
- **Unconventional Methods in Exploration for Petroleum & Natural Gas**
  - Four Meetings Held, 1968 – 1985
  - Institute for the Study of Earth & Man at Southern Methodist University
  - Four Proceeding Volumes Published
  - Eds. Heroy, Gottlieb, Davidson
- **1984, AAPG - Joint NASA/Geosat Test Case 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, Magnetics and Remote Sensing**
  - AAPG Studies in Geology No. 48 and SEG Geophysical Reference Series No. 11:
  - 2002, Editors D. Schumacher and L. LeSchack

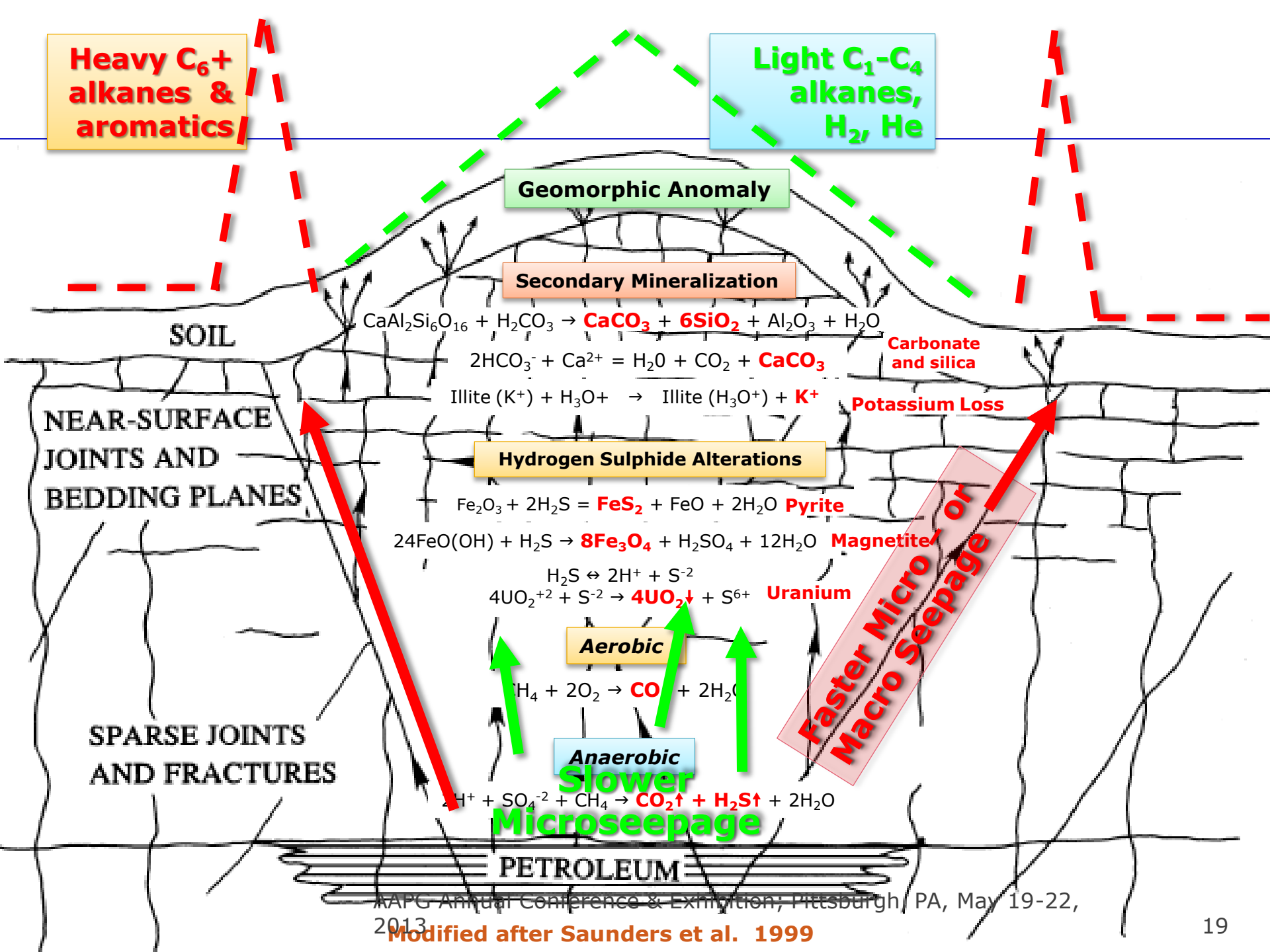
Landmark Symposiums and Publications

- **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_6+ alkanes & aromatics
Light C_1-C_4 alkanes, H_2, He
Geomorphic Anomaly
Secondary Mineralization
$CaAl_2Si_6O_{16} + H_2CO_3 \rightarrow CaCO_3 + 6SiO_2 + Al_2O_3 + H_2O$
$2HCO_3^- + Ca^{2+} = H_20 + CO_2 + CaCO_3$
Carbonate and silica
Illite (K^+) + H_3O+ → Illite (H_3O^+) + K^+
Potassium Loss
SOIL
NEAR-SURFACE JOINTS AND BEDDING PLANES
Hydrogen Sulphide Alterations
$Fe_2O_3 + 2H_2S = FeS_2 + FeO + 2H_2O$ Pyrite
$24FeO(OH) + H_2S \rightarrow 8Fe_3O_4 + H_2SO_4 + 12H_2O$ Magnetite
$H_2S \Leftrightarrow 2H^+ + S^{-2}$
$4UO_2^{+2} + S^{-2} \rightarrow 4UO_2\downarrow + S^{6+}$ Uranium
Aerobic
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Faster Micro / or Macro Seepage
SPARSE JOINTS AND FRACTURES
Anaerobic
Slower Microseepage
$2H^+ + SO_4^{-2} + CH_4 \rightarrow CO_2\uparrow + H_2S\uparrow + 2H_2O$
PETROLEUM

Evidence of Alteration

Bleaching of Red Sandstone, East Texas Basin

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

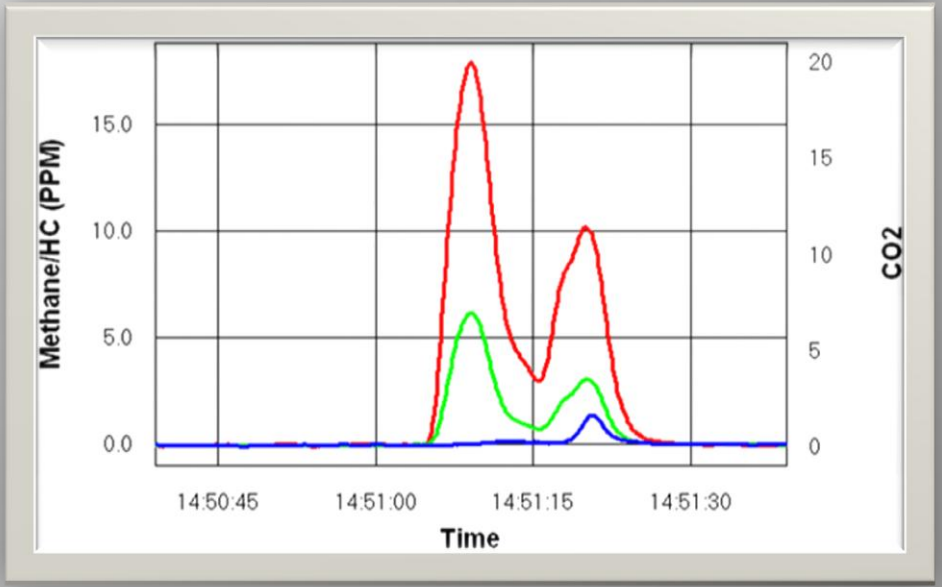
- **Direct Methods**
  - **Ambient Air Seeps**
    - Infra-Red Spectrometers
    - Portable Gas Detectors
  - **Soil Gas Hydrocarbons**
    - Interstitial, Occluded or Adsorbed Gases
    - Passive Soil Gas Collection
  - **Liquid Hydrocarbons**
    - Solvent Extracted Oils
    - Scanning Fluorescence
    - 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

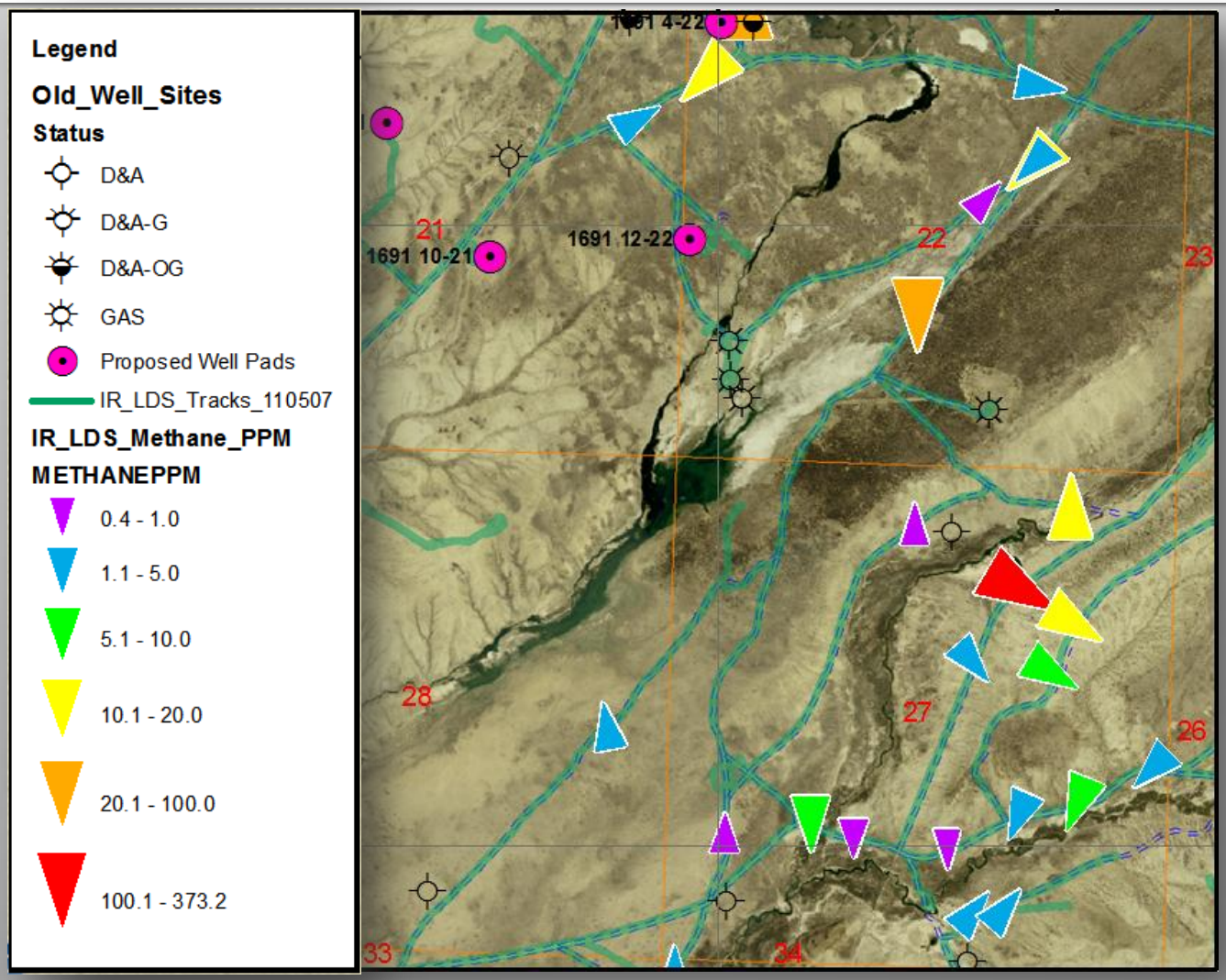
- **Ambient Air IR Survey**
  - **Truck, ATV, Boat or Helicopter-Mounted**
  - **Rapid data collection system**
  - **Detects gas seep "plumes"**
  - **Locates infrastructure leaks.**

Ambient Air IR Survey Real Time Results

- CH_4, CO_2 and Heavier (C_2+) 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_4 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

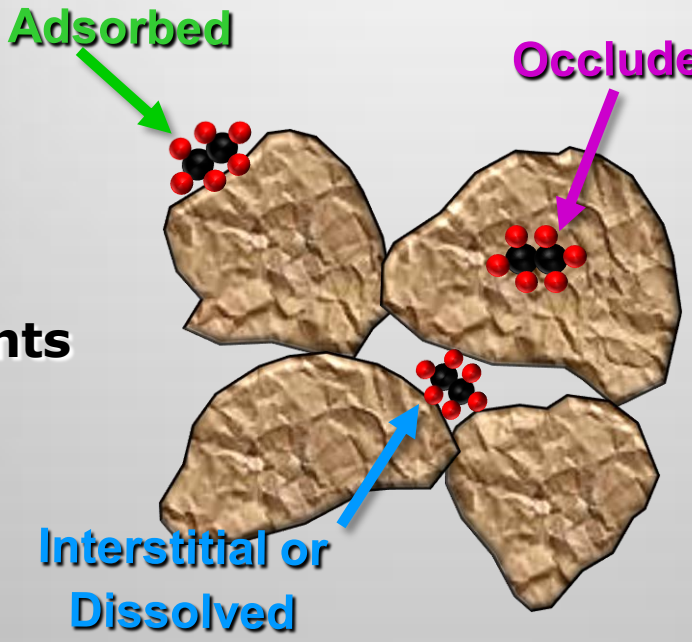
Trace Analysis Methods

- **Gas Range (Light) C_1-C_6 Hydrocarbons**
  - Parts Per Billion (ppb) Levels
  - Free Gas or Head-Space Gas
  - Thermally Desorbed (low & high temp)
  - Acid Extracted
  - Adsorbents (Passive Soil Gas) ng or ppt
- **Liquid Range (C_6+) 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

Shot-hole Sediments



Free Soil Gas

Ground or Sea Water

Lake Sediments

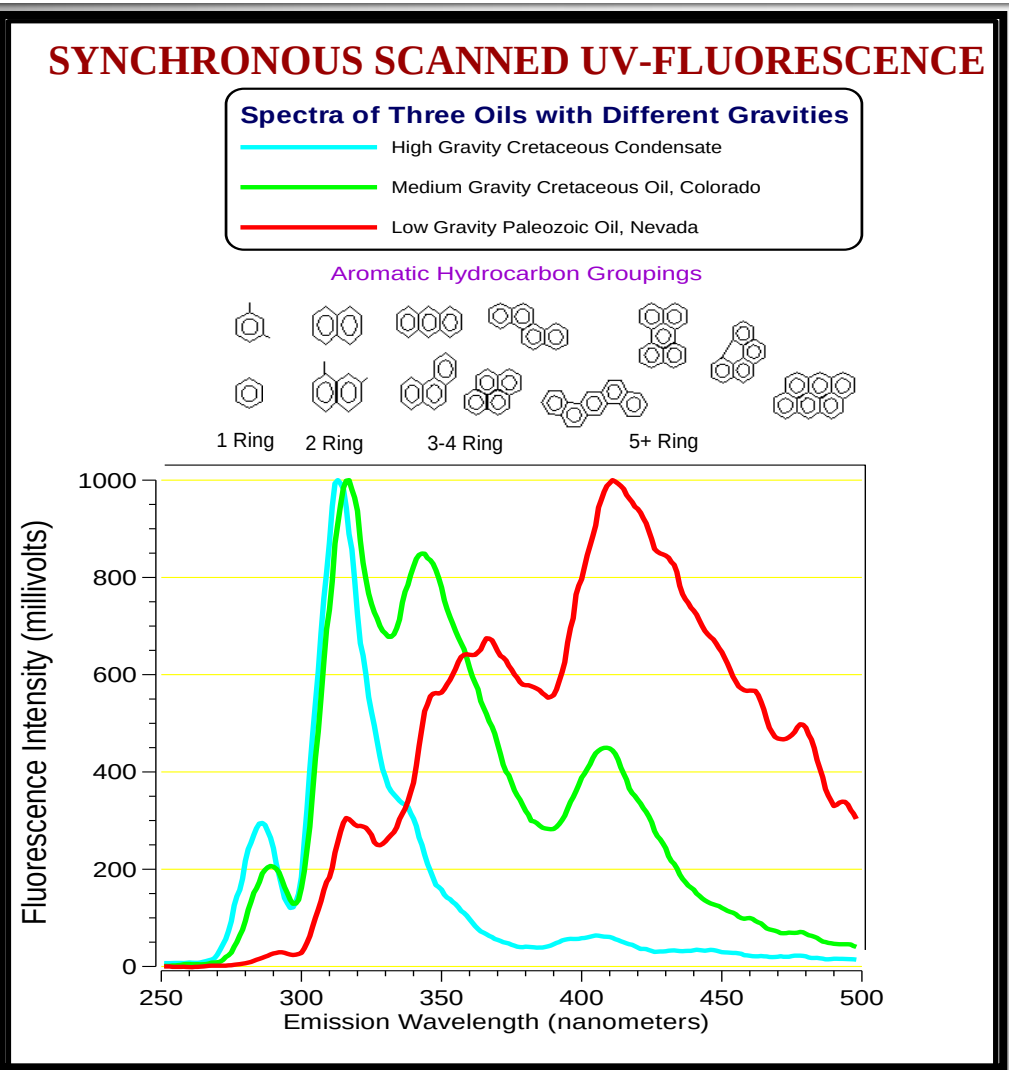
Vegetation

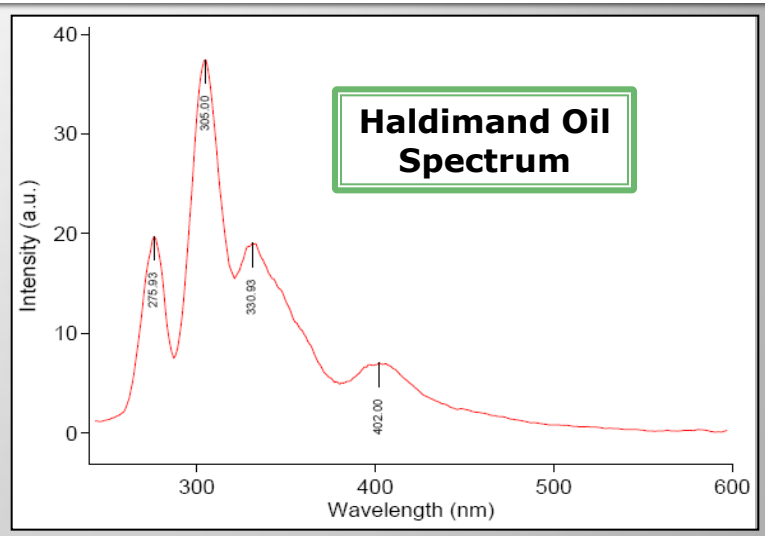
Deep Soils

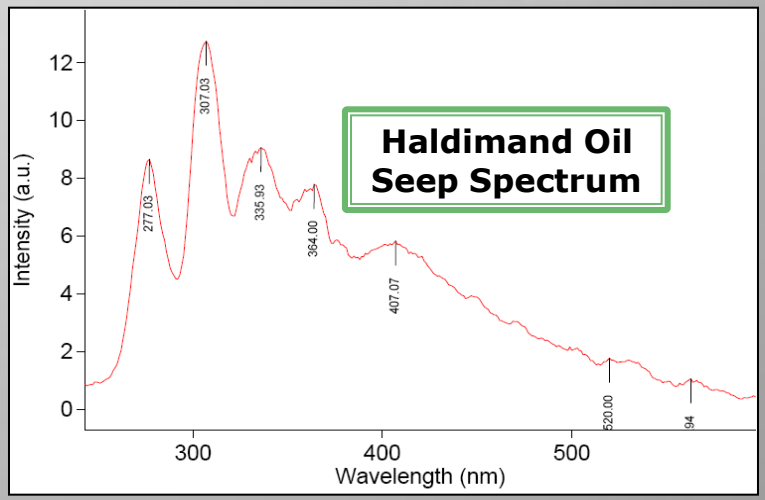
Passive Soil Gas Methods

- **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_2 – C_{20} Hydrocarbons**
- **Thermal Desorption GC and GC/MS**
- **Independent of the Matrix**

Oil Microseeps Seen by SSF
Matching Reservoir & Seep Compostion





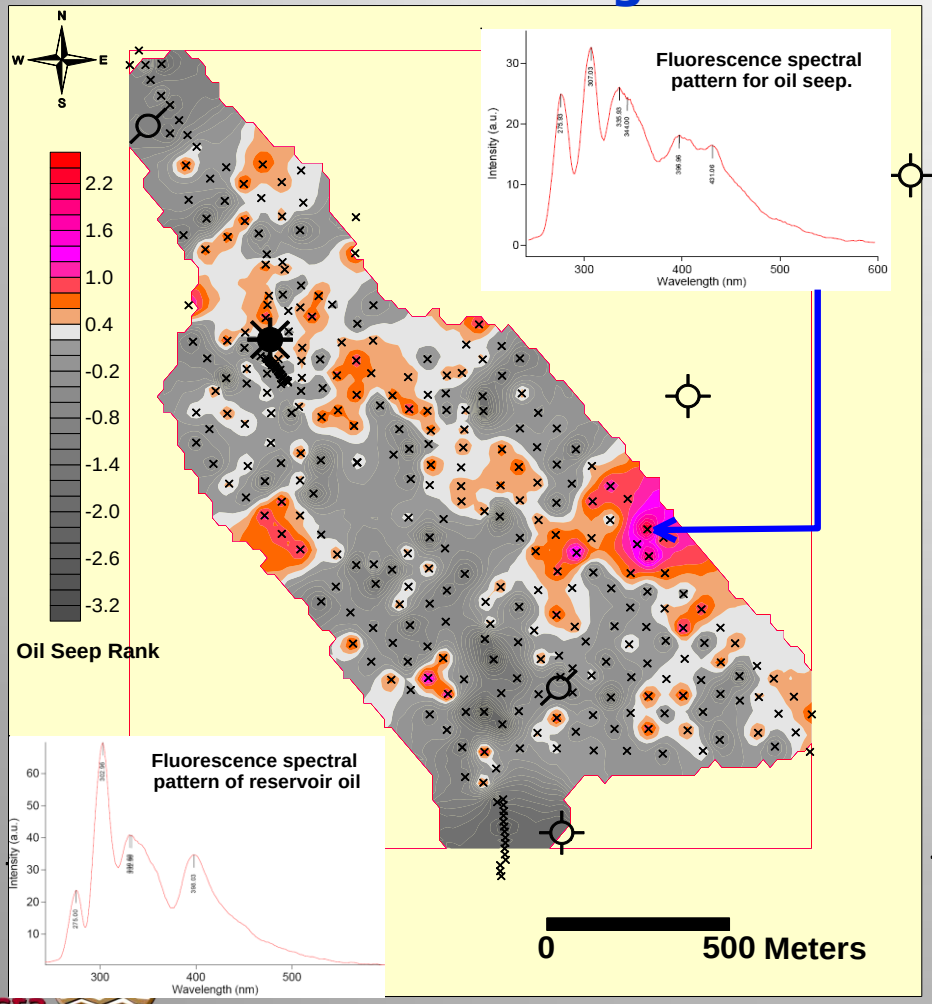


Analysis of an Anomaly

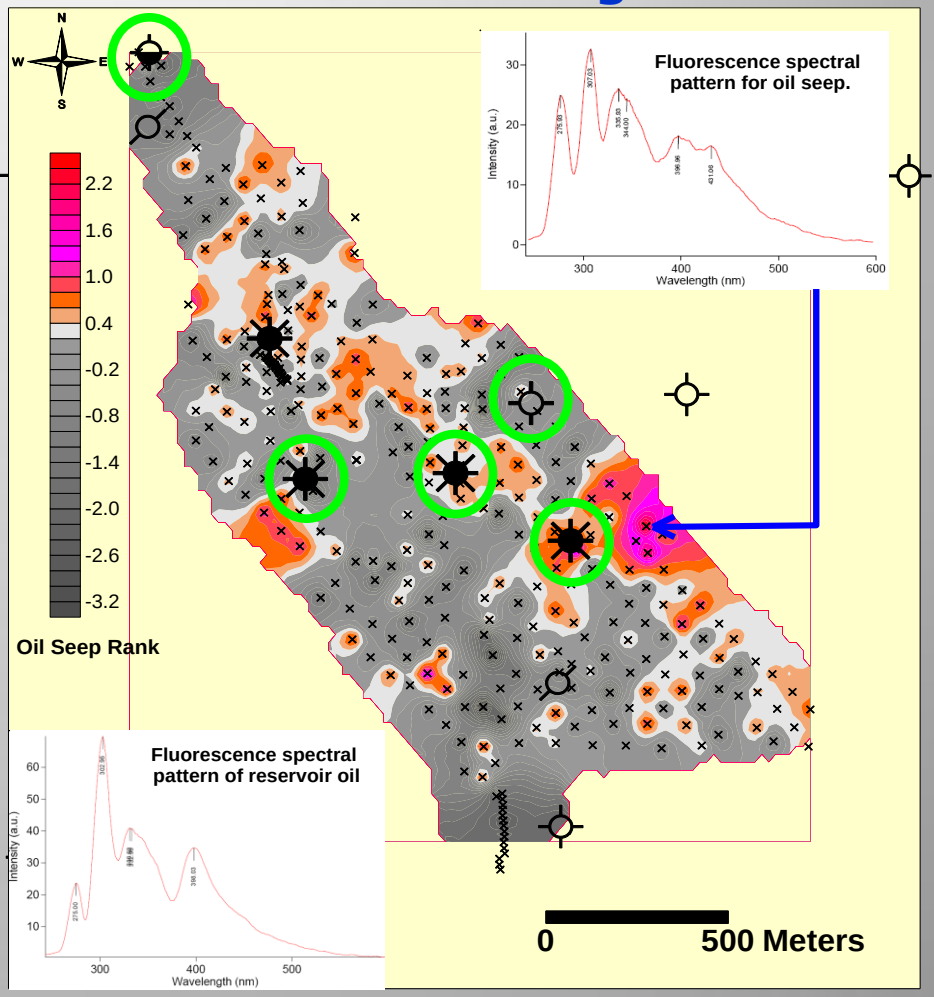
- **Historically, a Detection WAS an Anomaly!**
- **Lower Sensitivities Mean We Can Now Detect Background Everywhere**
- **Isotopes ($d^{13}C$, dD) of Larger Seeps**
- **To Distinguish Background from Anomaly:**
  - **Fingerprinting Reservoir Gases and Fluids**
  - **Adequate Sample Density**
  - **Multivariate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

Liquid Hydrocarbon Seep Anomalies
Albion-Scipio Oil Field
(Prospect Level Sample Spacing)

Before Drilling

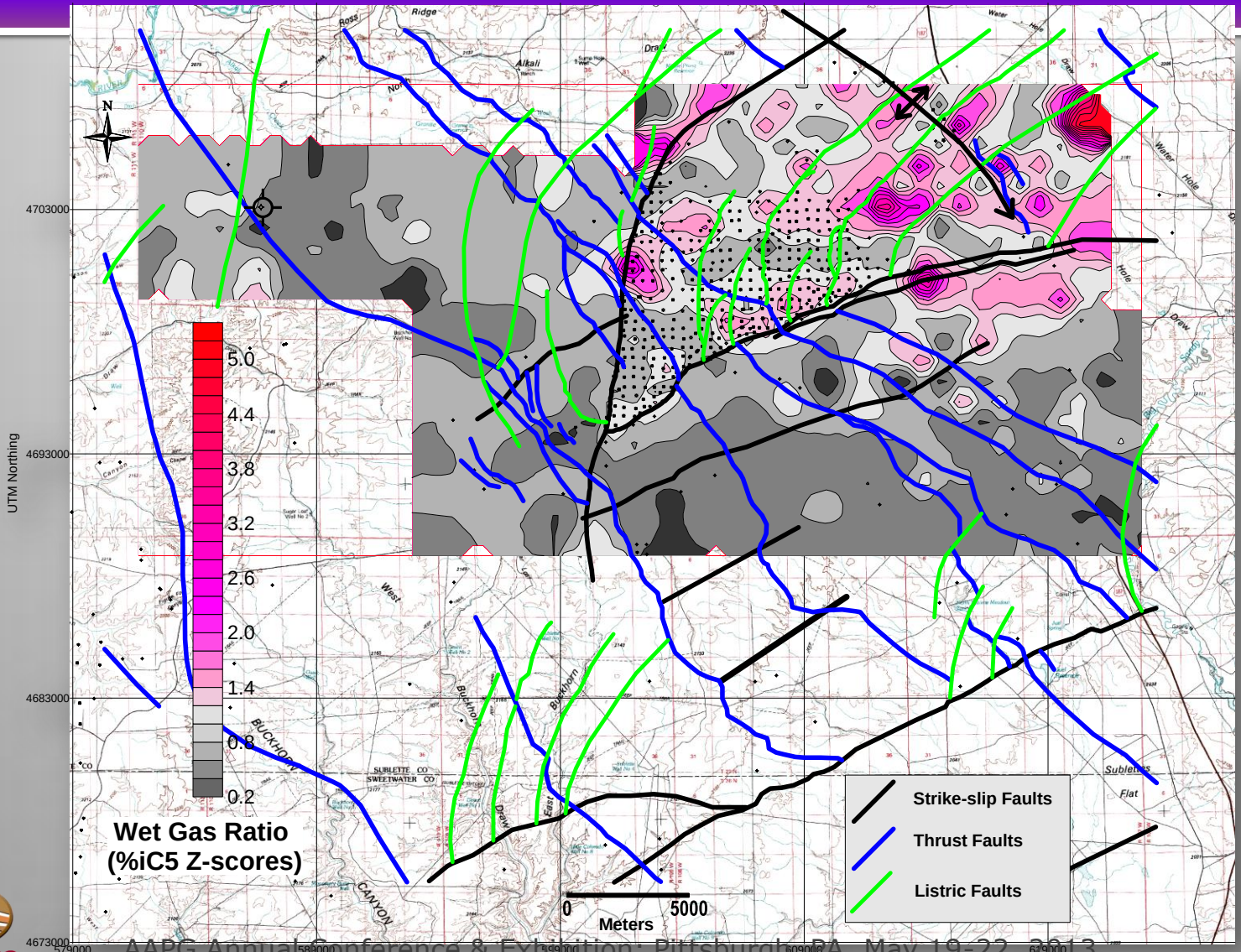


After Drilling

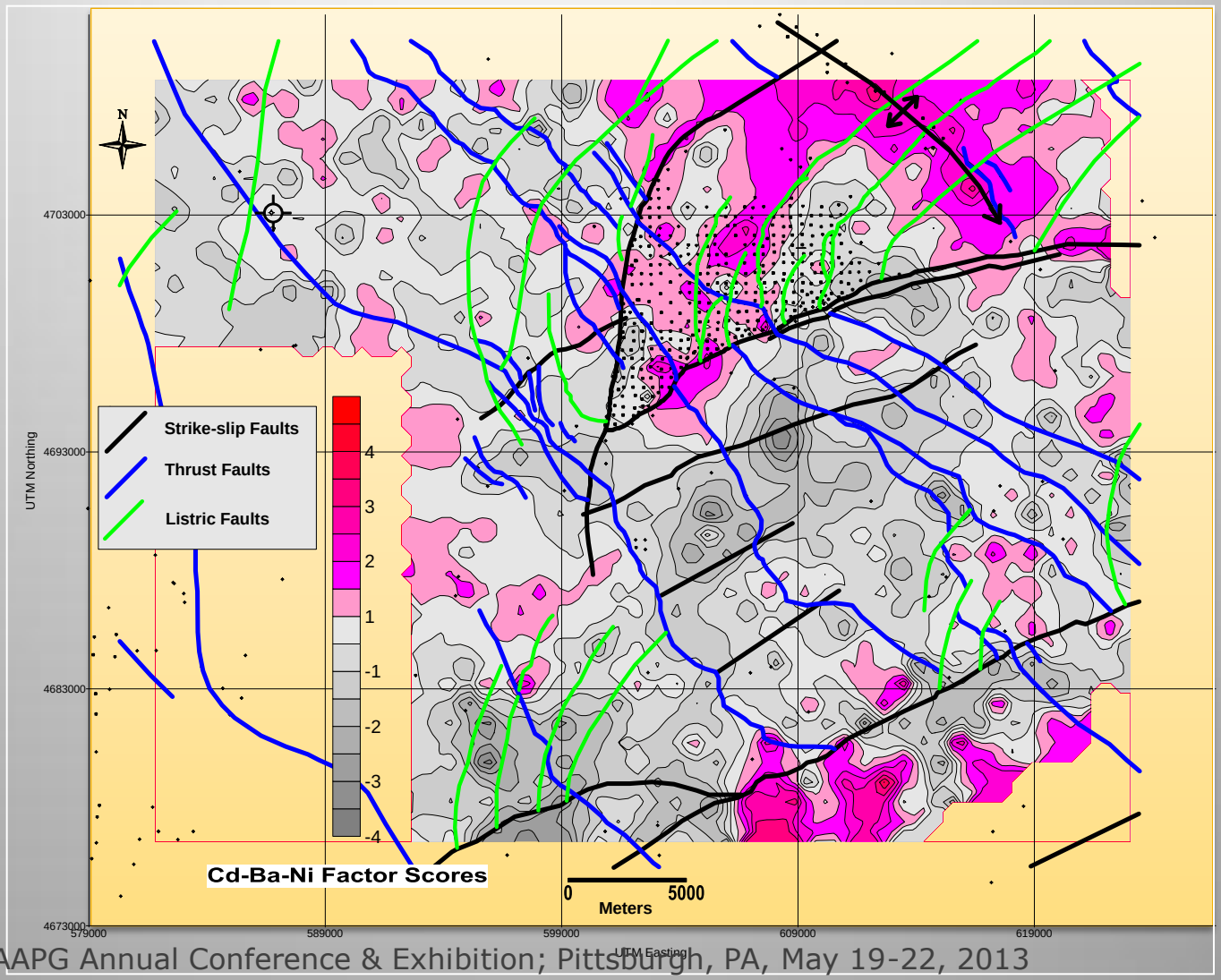


Jonah & Pinedale Tight Gas

Light Hydrocarbon Gases Regional Scale Sampling

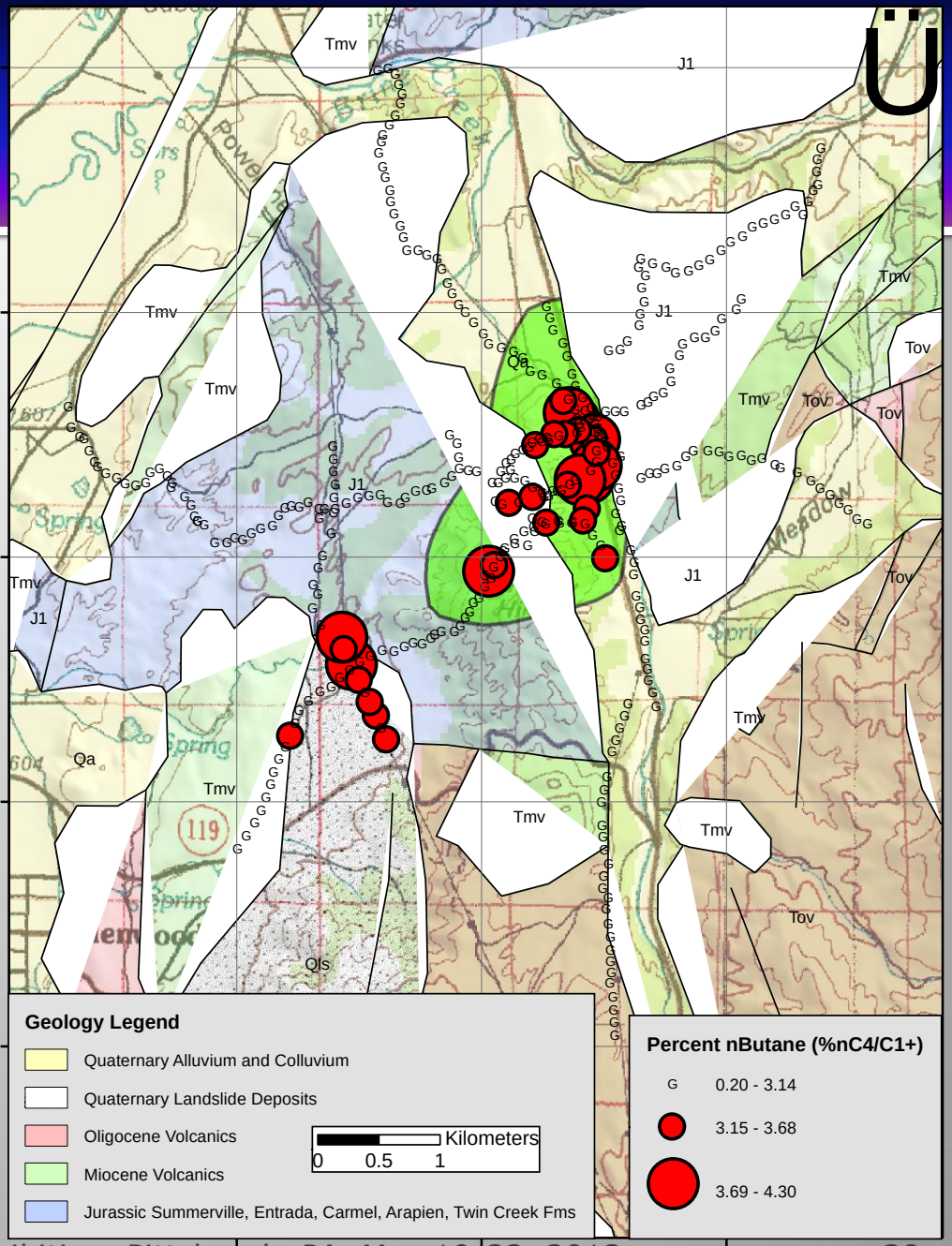


Trace Metals in Sagebrush
Cadmium, Nickel, Barium Factor



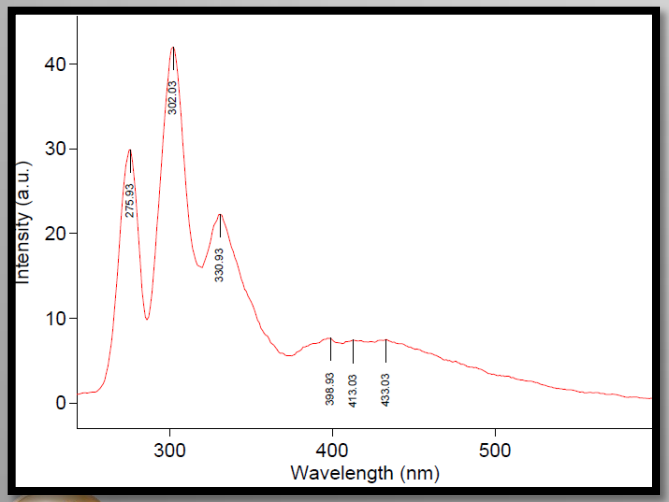
Covenant Field
Light Hydrocarbons

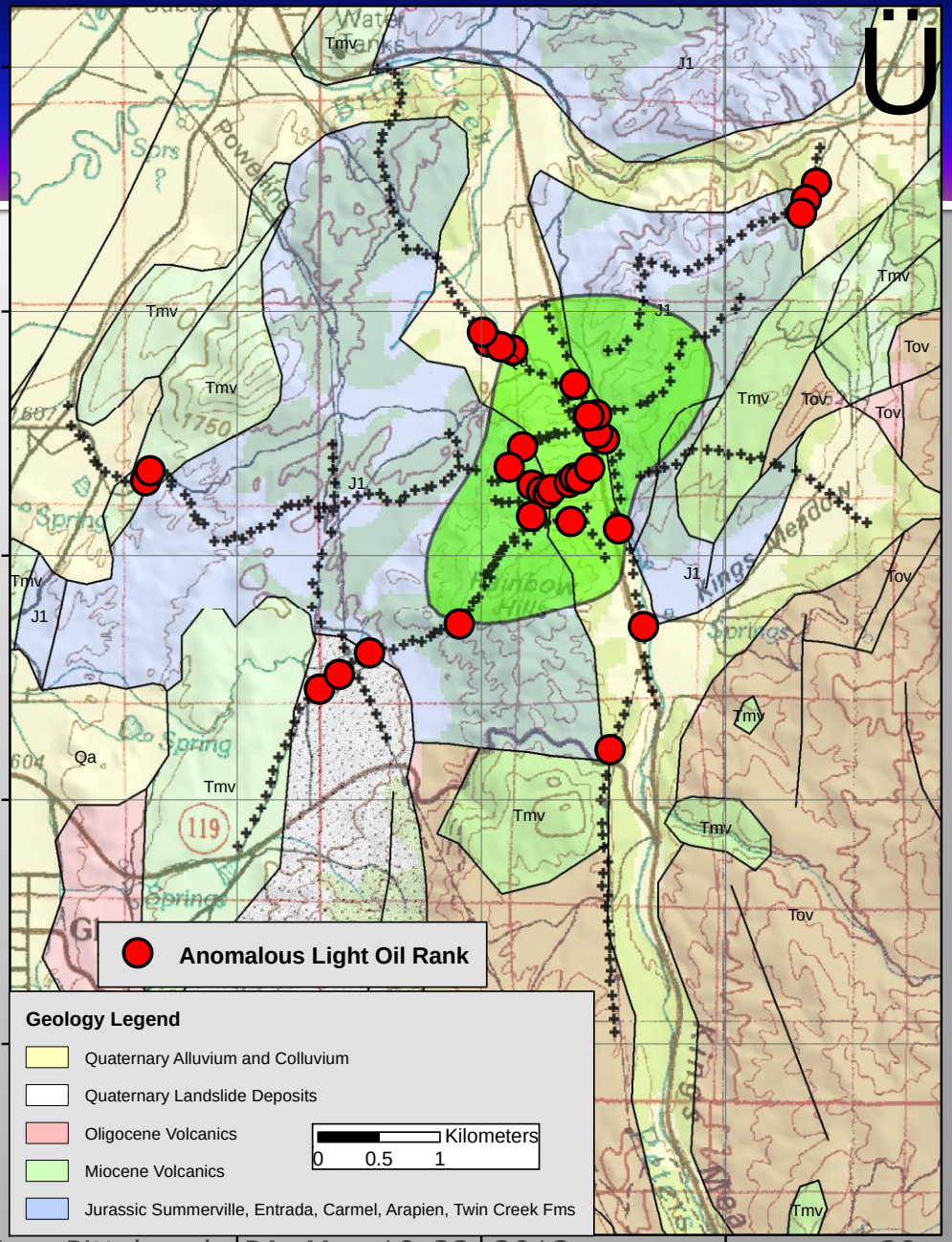
- Utah Overthrust
- HTTD Method
- Wet Gas Ratio in Desorbed Soil Gas
  - % nC_4/C_1
- Apical- & Fault-Related Anomalies



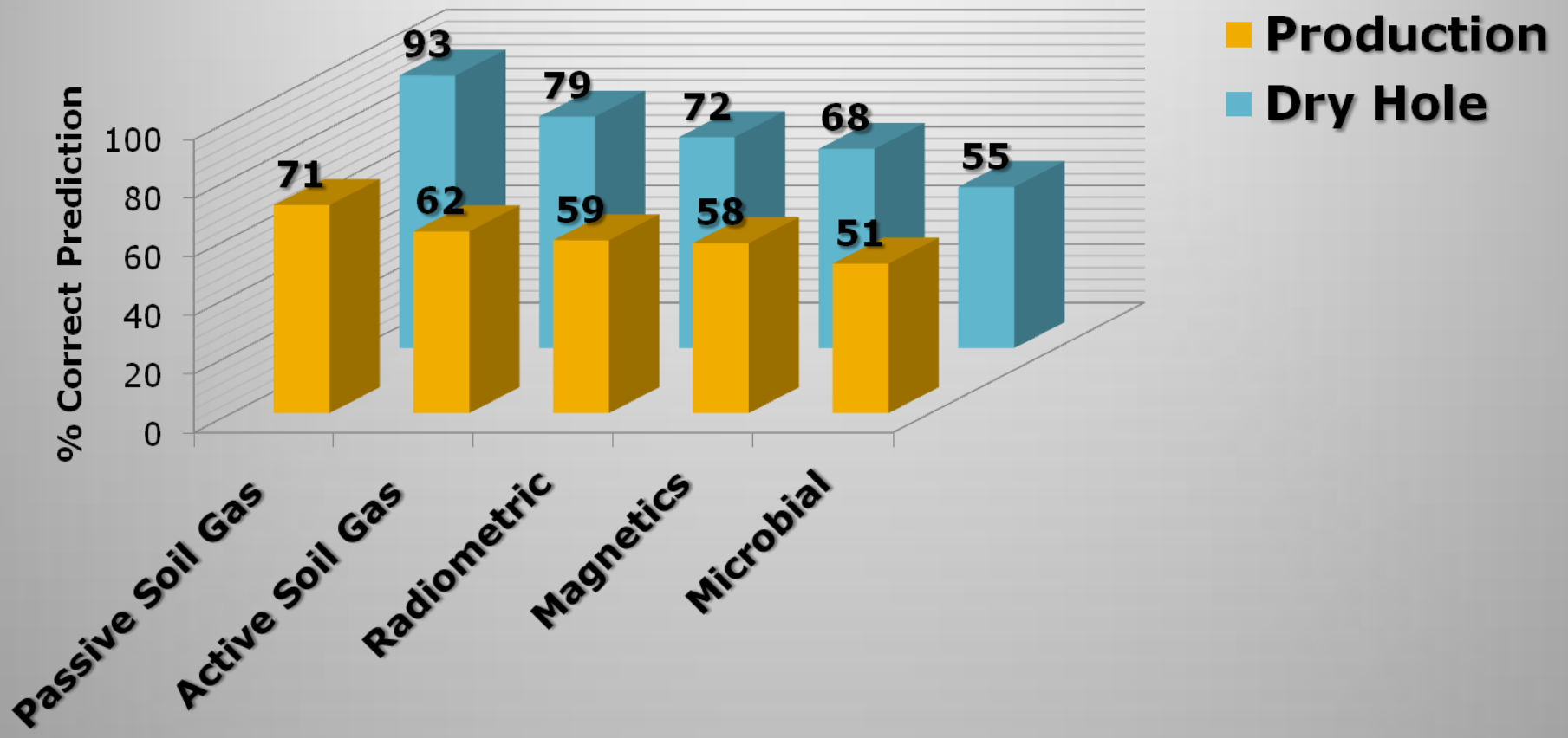
Covenant Field
Fluorescence

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

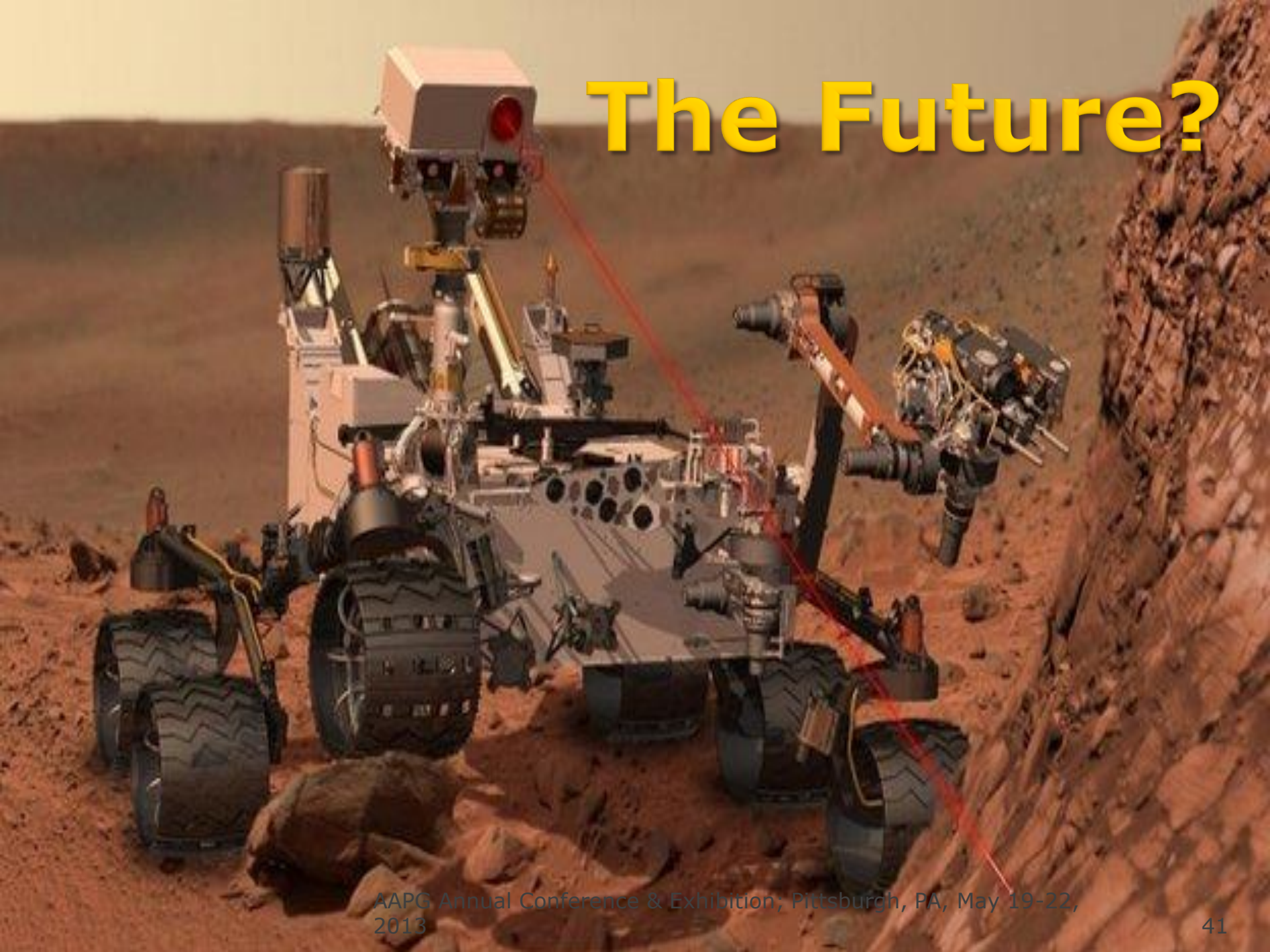




Success of Geochemical Exploration Methods



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 to 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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