Finding and Protecting Energy Resources with 21st Century Geochemical Tools

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Organic and inorganic geochemical analyses of various sample media are used to reduce risk in oil & gas exploration and development. More specifically, the methods help to focus land acquisition, seismic surveys and drill targets in petroleum exploration. Additionally the geochemical methods are used for documenting baseline environmental conditions before and after development of an energy resource to prevent potential litigation and complaints down the road.

The results of unique geochemical exploration surveys from the following areas will be presented:

(1) Albion-Scipio Oil Field (Michigan) – Crude oil microseeps, which are compositionally identical to produced oil, guided the drilling of commercial oil wells in the 4,000-foot deep, Ordovician Trenton hydrothermal dolomite reservoir.

(2) Devonian Carbonate Oil Field (Illinois) – Passive gas anomalies at surface are compositionally linked with a 2,000-foot deep oil reservoir.

(3) Grant Canyon Oil Field (Nevada) – Lithium and magnesium anomalies in soils are compositionally linked to water in the 5,000-foot deep carbonate oil reservoir.

Baseline environmental surveys are done before and after the development of an energy resource to document groundwater quality and natural hydrocarbon seeps. This documentation is important for avoiding future potential litigation and complaints from landowners and regulatory agencies. Groundwater from domestic and stock wells near proposed oil and/or gas wells are tested for dissolved C₁-C₇ hydrocarbons, carbon and deuterium isotopes of detected hydrocarbons, cations and anions, and pathogenic and non-pathogenic bacteria to document general water quality before and after stimulation of an oil and/or gas reservoir. Examples of baseline environmental surveys from the DJ and Ration Basins will be presented. Forensic isotopic evidence from shallow aquifers and produced water in the DJ Basin will be shown to emphasize the lack of fluid mixing between oil and gas reservoirs and shallow groundwater aquifers.
Finding and Protecting Energy Resources with 21st Century Geochemical Tools

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2013 AAPG-ACE (Pittsburgh)
Outline of Presentation

- Finding Energy Resources with Geochemical Tools
  - Sampling and Analytical Methods
  - Linking Reservoir Fluids with Surface Seeps Using Hydrocarbons and Major/Trace Elements

- Protecting Energy Resources with Geochemical Tools
  - Why Baseline Surveys?
  - Geochemical Tools Used in Baseline Surveys
    - Denver Basin Case Study
  - Summary
Sample Media Collected

Shallow Soils

Deep Soils & Soil Gas

Shot-Holes

Lake Sediments

Sediment or soil particle

HC Extraction Methods

- Heat
- Acid
- Organic Solvent

Occluded CH₄

acid extraction and analysis of headspace for C1-C20 hydrocarbons

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Passive Soil Gas

Active Soil Gas

VaporTec™
Chromatography of Oil Microseeps in Surface Soils

Productive

Non-Productive

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1 ring (270-275nm): Benzene, Xylenes
2 rings (300-305nm): Naphthalene, Methyl Naphthalene
3-4 rings (325-335nm): Phenanthrene, Anthracene, Benzo(a)anthracene, Chrysene, Pyrene
5+ rings (390-600nm): Anthanthrene, Dibenzo(a,h)anthracene, Coronene, Benzo(g,h,i)fluoranthene, Perylene

Fluorescence Spectra of High, Medium and Low Gravity Oils
Linking Oil Microseeps with an Albion-Scipio Oil Reservoir
Oil Microseeps in Michigan Basin, USA

Before Drilling

- 1,200 m deep Ordovician carbonate reservoir
- Oil seeps are compositionally identical to produced oil
- Seeps at 50 cm depth

Fluorescence spectral pattern for oil seep.

Fluorescence spectral pattern of reservoir oil
After Drilling

Oil Seeps and 3D Seismic Predict Commercial Oil Wells

Fluorescence spectral pattern for oil seep.

Fluorescence spectral pattern of reservoir oil

0 500 Meters

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Linking Gas Microseeps With Devonian Carbonate Oil Reservoir
Passive Gas Anomalies Over Oil-charged Carbonates

Oil Probability
- 0.00 - 0.70
- 0.71 - 0.90
- 0.91 - 1.00
+ Non-anomalous Samples

Heptane
Propane
Butene
Pentene
2-Methylpentane

-2.50 -1.50 -0.50 0.50 1.50
Linking Major/Trace Element Anomalies With Grant Canyon Oil Reservoir
Magnesium and Lithium Anomalies in Soils

Oligocene Felsic Ignimbrites
Eocene Sheep Pass Formation
Cretaceous Granitic Rocks
Pennsylvanian Ely Limestone
Mississippian Chainman Shale
Devonian Guilmette Formation and Simonson Dolostone
Cambrian - Ordovician Metasiliciclastic and Metacarbonate Rocks

Grant Canyon (21 MMBO)
Bacon Flat (0.9 MMBO)

Lithium Z-scores
-20.0 to -1.0
-1.0 to 0.0
0.0 to 0.5
0.5 to 1.0
1.0 to 1.5
1.5 to 2.0
2.0 to 20.0

Magnesium Z-scores

High-Angle Normal Fault
Oil-Water Contact

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## Grant Canyon Produced Water Composition

### Hulen et al (1994)

<table>
<thead>
<tr>
<th>Concentrations (mg/kg)</th>
<th>GC #3 Oil Well</th>
<th>WGC Dry Well 21-31</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>72</td>
<td>14.6</td>
</tr>
<tr>
<td>Ca</td>
<td>56.3</td>
<td>31.8</td>
</tr>
<tr>
<td>Mg</td>
<td>7.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Sr</td>
<td>1.07</td>
<td>0.93</td>
</tr>
<tr>
<td>Br</td>
<td>4.86</td>
<td>0.63</td>
</tr>
<tr>
<td>Li</td>
<td>1.8</td>
<td>0.21</td>
</tr>
<tr>
<td>Cs</td>
<td>0.058</td>
<td>0.025</td>
</tr>
<tr>
<td>Rb</td>
<td>0.31</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 2. Composition of reservoir water from oil and dry wells at Grant Canyon Field, Railroad Valley, Nevada (modified after Hulen et al., 1994).
Google Images (1st page)
Fracking, Water
Benefits of Baseline Surveys to the Oil & Gas Industry

- Document Environmental Conditions Before and After Oil & Gas Development
- Improve Community Relationships
Phases of a Baseline Environmental Survey

- Map Existing Oil, Gas and Water Wells
- Examine Air Photos, Geology Maps and Interview Residents
- Map Stressed Vegetation, Probable Faults and Gas Seeps Noted by Landowners
- Conduct Regional and Detailed Hydrocarbon Seep Survey (P&A wells, springs, water wells etc.)
- Sample and Analyze Soil Gas Seeps and Water Wells for Organics and Inorganics.
Real-time sub-ppm airborne $\text{CH}_4$, $\text{C}_2+$, $\text{CO}_2$

$<1$ppm sensitivity
Regional Hydrocarbon Seep Survey in Raton Coal Basin, Colorado, USA

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Locate Source of Seeps on Foot

- Flame Ionization (FID)
  - Sees all hydrocarbons
  - 1 ppm CH₄ sensitivity
- Photo Ionization (PID)
  - Aromatics, alkenes, heavies
- Modified for surface detection to replace probing & intrusive methods, avoiding utilities
- Continuous data transects
- Calibrated daily, multi-point
- LEL meters lack sensitivity
Leaking O&G Wells

- Well Casing Leaks
  - Historic, Old & New

Leakage Mechanisms:

- **Quaternary**
- **Tertiary**
- **Fruitland**
- **Pictured Cliffs**
- **Lewis Shale**
- **Mesaverde / Dakota**

Diagram showing geological layers and potential leak pathways.
Map Seep Features (Stressed Vegetation, Salt Crusts, etc.)
Collect Gas Samples

- If gas seeps are detected, samples are required for C$_1$-$C_6$, fixed gases (CO$_2$, O$_2$, He, H$_2$) and carbon and deuterium isotopes of CH$_4$. 
Collect Water Samples (wells, springs etc.)
<table>
<thead>
<tr>
<th>pH</th>
<th>Dissolved Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Conductance</td>
<td>Methane</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>Ethane</td>
</tr>
<tr>
<td>Alkalinity (total bicarbonate, and carbonate; as CaCO₃)</td>
<td>Propane</td>
</tr>
<tr>
<td>Major Anions</td>
<td>BTEX Compounds</td>
</tr>
<tr>
<td>Bromide</td>
<td>Benzene</td>
</tr>
<tr>
<td>Chloride</td>
<td>Toluene</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Nitrate and Nitrite as N</td>
<td>Xylenes (o-xylene, m-p-xylene, total xylene)</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>If dissolved CH₄ &gt; 1 mg/L</td>
</tr>
<tr>
<td>Major Cations (Dissolved)</td>
<td>Fixed gases and C1-C6 hydrocarbons</td>
</tr>
<tr>
<td>Boron</td>
<td>Stable isotopic concentration of the carbon (¹²C and ¹³C) and hydrogen (¹H and ²H) in the methane</td>
</tr>
<tr>
<td>Calcium</td>
<td>BART Bacteria Analysis</td>
</tr>
<tr>
<td>Iron</td>
<td>Sulfate-reducing bacteria (SRB)</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Iron-related Bacteria (IRB)</td>
</tr>
<tr>
<td>Manganese</td>
<td>Slime Forming Bacteria (SLYM)</td>
</tr>
<tr>
<td>Potassium</td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td>Strontium</td>
<td></td>
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</table>
Source of Anomalous Methane in Fox Hills Aquifer?
## Denver Basin Baseline Survey, Colorado, USA

### Generalized Time & Rock Stratigraphic Column

<table>
<thead>
<tr>
<th>Era/Period</th>
<th>Geologic Epoch/Age</th>
<th>Formation Name</th>
<th>Type Well</th>
<th>M. Segelke #1 NENE Sec. 27 T11N R53W API 05-075-09050</th>
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</thead>
<tbody>
<tr>
<td>Recent</td>
<td>Holocene Pleistocene</td>
<td>Alluvial &amp; Dune Sand</td>
<td>0 - 50 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pliocene</td>
<td>Ogallaha</td>
<td>0 - 180 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Miocene</td>
<td>Arikaree</td>
<td>0 - 80 ft</td>
<td>(Not present in area)</td>
</tr>
<tr>
<td></td>
<td>Lower Oligocene</td>
<td>White River</td>
<td>25 - 100 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Late Maestrichtian</td>
<td>Laramie Fox Hills</td>
<td>400 - 550 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cretaceous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maestrichtian Campanian</td>
<td>Pierre</td>
<td>3150 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Campanian Coniacian</td>
<td>Niobrara &amp; Fort Hays</td>
<td>350 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Turonian</td>
<td>Carlile</td>
<td>195 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cenomanian</td>
<td>Graneros Shale</td>
<td>250 ft (Storage Caprock)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Albion</td>
<td>Dakota &quot;D&quot;</td>
<td>50 ft (Storage Zone)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aptian</td>
<td>Huntsman</td>
<td>65 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dakota &quot;J&quot;</td>
<td>104 ft (Storage Zone)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jurassic</td>
<td>Morrison</td>
<td>420 ft</td>
<td></td>
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<tr>
<td></td>
<td>Guadalupian</td>
<td>Cedar Hills - Blaine</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Leonidarian</td>
<td>Stone Corral</td>
<td>104 ft</td>
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<td></td>
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<td>Lyons</td>
<td>46 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wellington - Lower Satanka</td>
<td>44 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wolfcampian</td>
<td>Wolfcamp</td>
<td>328 ft</td>
<td></td>
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<tr>
<td></td>
<td>Virgilian</td>
<td>Virgil</td>
<td>352 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Missourian</td>
<td>Missouri</td>
<td>135 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desmoinesian</td>
<td>Marmaton Cherokee</td>
<td>165 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atokan</td>
<td>Atoka</td>
<td>200 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Morrowan</td>
<td>Morrow</td>
<td>165 ft</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Precambrian</td>
<td>Precambrian</td>
<td>Unknown</td>
<td></td>
</tr>
</tbody>
</table>

### Aquifers
- **Ogallala Aquifer** (80 m)
- **Fox Hills Aquifer** (300 m)
- **O&G Reservoir** (2,100 m)

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Biogenic Methane in Aquifer is Not Produced Gas

- Water Well - Fox Hills Aquifer (300 m)
- Produced Gas (2,100 m)

δC\text{\textsuperscript{13}}_{\text{Methane}} (‰)

δD_{\text{Methane}} (‰)

Gas Wetness (% C\textsubscript{2+})
No Mixing of Groundwater and Produced Water

Ogalla Aquifer  
(CaMgHCO$_3$ Water)

Fox Hills Aquifer  
(NaHCO$_3$ Water)

Produced Water  
(NaCl Water)
SUMMARY

- Surface geochemical methods reduce exploration risk for energy resources.
- Important to link surface seeps with reservoir fluids.
- Baseline environmental surveys can help protect energy resources from potential complaints and litigation.