

# **Experimental Evidence for Suppression of Vitrinite Reflectance by Liptinite During Hydrous Pyrolysis of Artificial Source Rock\***

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## **Abstract**

Mean random vitrinite reflectance of polished rock or kerogen samples under oil immersion ( $R_o$ ) is widely used to determine thermal maturity of coal and other sedimentary rocks. However,  $R_o$  values of liptinite-rich, oil-prone samples are commonly lower than those measured in samples from adjacent vitrinite-rich coals at the same level of thermal stress. So-called suppressed  $R_o$  values have also been observed in hydrous pyrolysis experiments performed on liptinite-rich compared to vitrinite-rich endmembers. Hypotheses to explain  $R_o$  suppression, such as sorption of products generated from liptinite during maturation, diagenetic formation of perhydrous vitrinite under anoxic conditions, and retardation by overpressure, remain controversial.

To experimentally test for  $R_o$  suppression caused by liptinite content, artificial rock was prepared using silica and a calcined blend of limestone and clay with various proportions of thermally immature vitrinite-rich Wyodak-Anderson coal and liptinite-rich kerogen isolated from the oil-prone Parachute Creek Member of the Green River Formation. Hydrous pyrolysis was performed on samples containing various proportions of the coal and liptinite-rich kerogen for 72 hours at isothermal temperatures of 300° C, 330° C, and 350° C to simulate burial maturation. The experimental results provide the first evidence that  $R_o$  suppression occurs in vitrinite mixed with liptinite-rich kerogen in a rock matrix without variations in redox conditions during diagenesis or overpressure during catagenesis. Compared to artificial rock that contains only coal, samples having

different proportions of oil-prone kerogen show suppressed  $R_o$  in the 300° C and 330° C experiments. For example, artificial rock containing only vitrinite-rich coal reaches  $R_o$  of  $0.97 \pm 0.07\%$ , while a 90:10 mixture of liptinite-rich kerogen and the same coal shows  $R_o$  suppression  $>0.2\%$  ( $0.75 \pm 0.05\%$  when heated under the same conditions). Solid bitumen generated during heating of the samples containing liptinite-rich kerogen shows distinctly lower reflectance than the associated vitrinite and does not interfere with  $R_o$  measurements. Although the precise mechanism for  $R_o$  suppression by liptinite remains unclear, free radicals generated during maturation of liptinite may contribute to termination reactions that slow aromatization of polyaromatic sheets in vitrinite, thus suppressing  $R_o$ . The experimental results do not preclude that  $R_o$  suppression in nature might also result from different redox conditions during diagenesis or overpressure during catagenesis.

### **Selected References**

Hutton A.C., and A.C. Cook, 1980, Influence of alginite on the reflectance of vitrinite from Joadja, NSW, and some other coals and oil shales containing alginate: *Fuel*, v. 59, p. 711-714.

Lewan M.D., 1993, Identifying and understanding suppressed vitrinite reflectance through hydrous pyrolysis experiments: 10th Annual Meeting of the Society of Organic Petrology, Abstract, v. 10, p. 1-3.

Peters K.E., P.C. Hackley, J.J. Thomas, and A.E. Pomerantz, 2018, Experimental evidence for suppression of vitrinite reflectance by liptinite during hydrous pyrolysis of artificial source rock: *Organic Geochemistry*, v. 125, p. 220-228.

Price L.C., and C.E. Barker, 1985, Suppression of vitrinite reflectance in amorphous rich kerogen - A major unrecognized problem: *Journal of Petroleum Geology*, v. 8, p. 59-84.

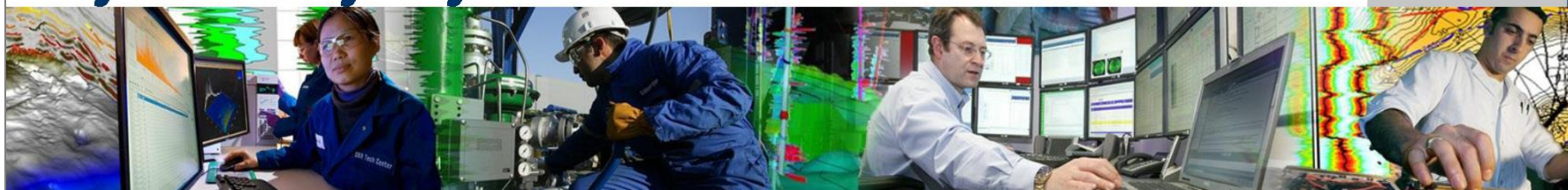


**Theme 3: Hydrocarbon Migration  
and Charge Risk Assessment**



# ***Experimental Evidence for Suppression of Vitrinite Reflectance by Liptinite During Hydrous Pyrolysis of Artificial Source Rock***

**MAY 19-22, 2019**  
**SAN ANTONIO, TEXAS**



**K.E. Peters<sup>1,2</sup>, P.C. Hackley<sup>3</sup>, J.J. Thomas<sup>4</sup>, and A.E. Pomerantz<sup>4</sup>**

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Presenter's notes: *Longstanding* controversy on the origin of  $R_o$  suppression in oil-prone source rocks.

# Vitrinite Reflectance ( $R_o$ ) is a Key Maturity Indicator

**Purpose - test the effect on  $R_o$  caused by dilution of vitrinite in coal by liptinite-rich, oil-prone kerogen.**



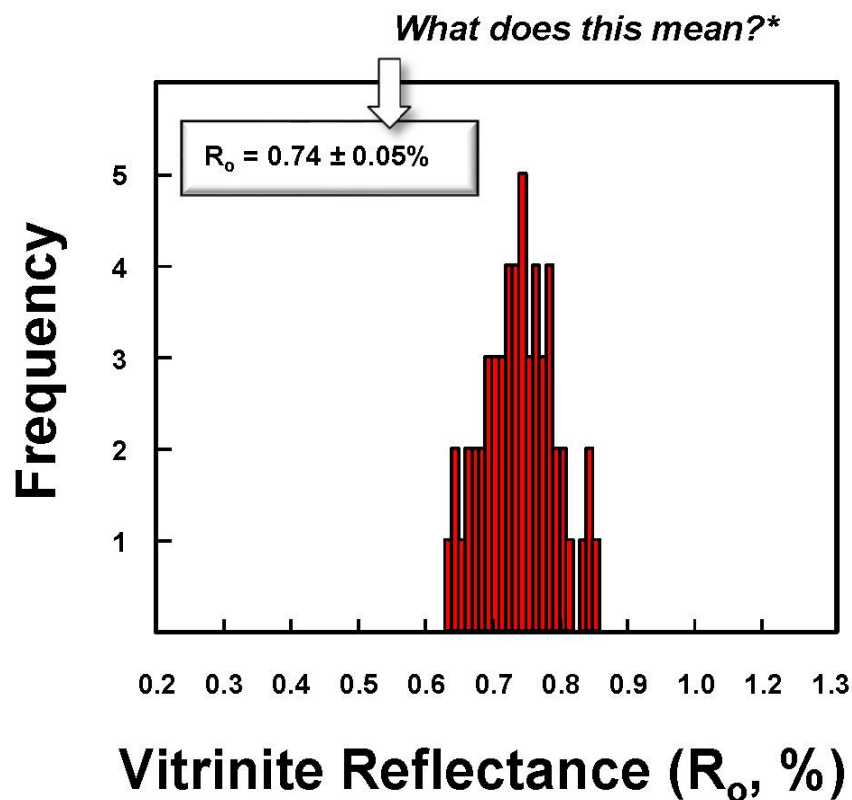
- **Kerogen** – insoluble particulate organic matter that consists of macerals from different organisms.
- **Vitrinite** – woody macerals from vascular plants.
- **Liptinite** – oil-prone macerals from spores, pollen, dinoflagellate cysts, leaf cuticles, plant resins, waxes

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Presenter's notes: Also used to calibrate basin and petroleum system models. Liptinite replaces exinite as one of the four maceral groups in kerogen.

# R<sub>o</sub> Histograms are Based on 20-100 Measurements



## Ordered $R_o$ Values for *One* Rock Sample

|      |      |      |      |      |      |
|------|------|------|------|------|------|
| 0.63 | 0.64 | 0.64 | 0.65 | 0.66 | 0.66 |
| 0.67 | 0.67 | 0.68 | 0.68 | 0.69 | 0.69 |
| 0.69 | 0.70 | 0.70 | 0.70 | 0.71 | 0.71 |
| 0.71 | 0.72 | 0.72 | 0.72 | 0.72 | 0.73 |
| 0.73 | 0.73 | 0.73 | 0.74 | 0.74 | 0.74 |
| 0.74 | 0.74 | 0.75 | 0.75 | 0.75 | 0.76 |
| 0.76 | 0.76 | 0.76 | 0.77 | 0.77 | 0.77 |
| 0.78 | 0.78 | 0.78 | 0.78 | 0.79 | 0.79 |
| 0.80 | 0.80 | 0.81 | 0.83 | 0.84 | 0.84 |
| 0.85 |      |      |      |      |      |

Number of Measurements = 55

Average Reflectance = 0.74%

Standard Deviation = 0.05%

Biomarker Guide, p. 90

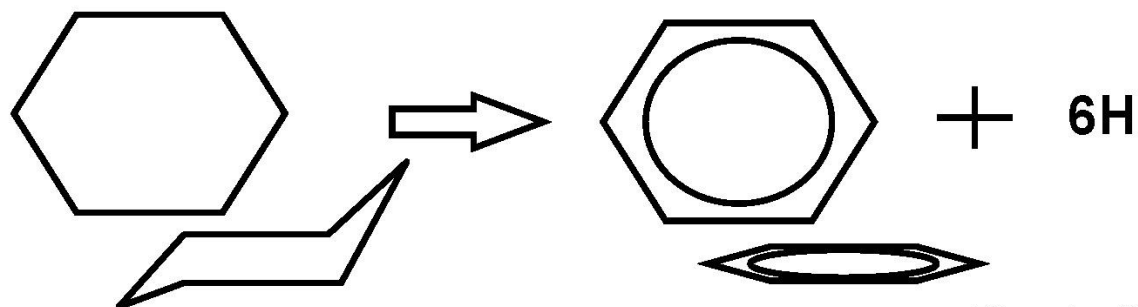
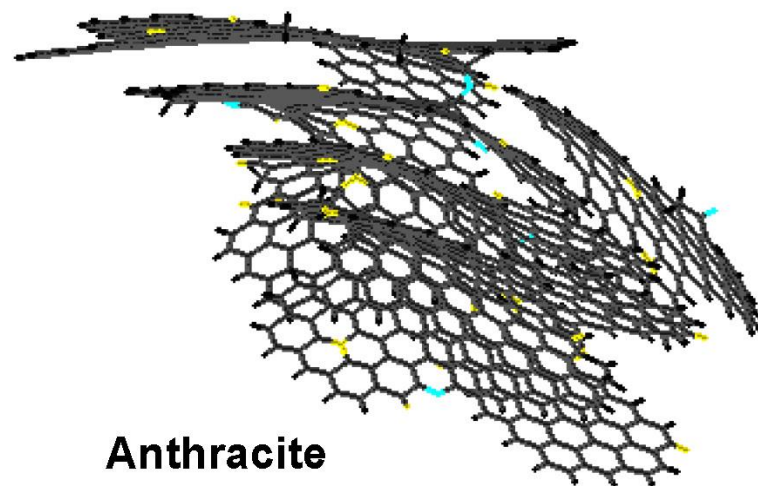
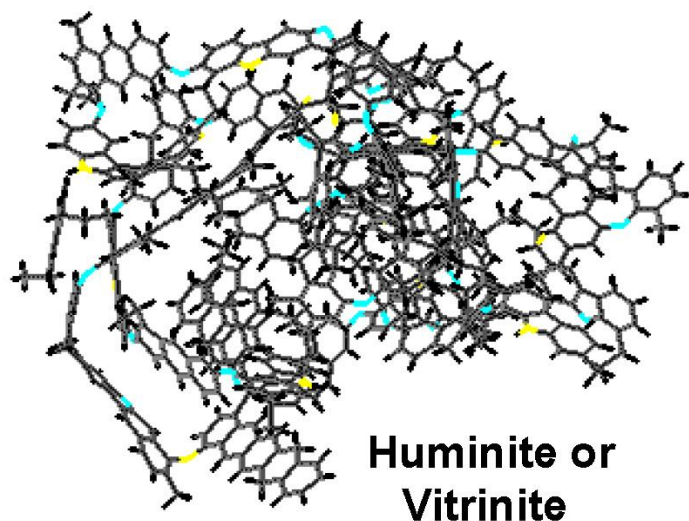
*\* A measure of the ability of the microscopist to select what he or she considers to be vitrinite.*

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Presenter's notes:  $R_o$  = Percentage of incident light (546 nm) reflected from polished vitrinite phytoclasts under oil immersion.

# Aromatization Liberates Hydrogen and Increases $R_o$



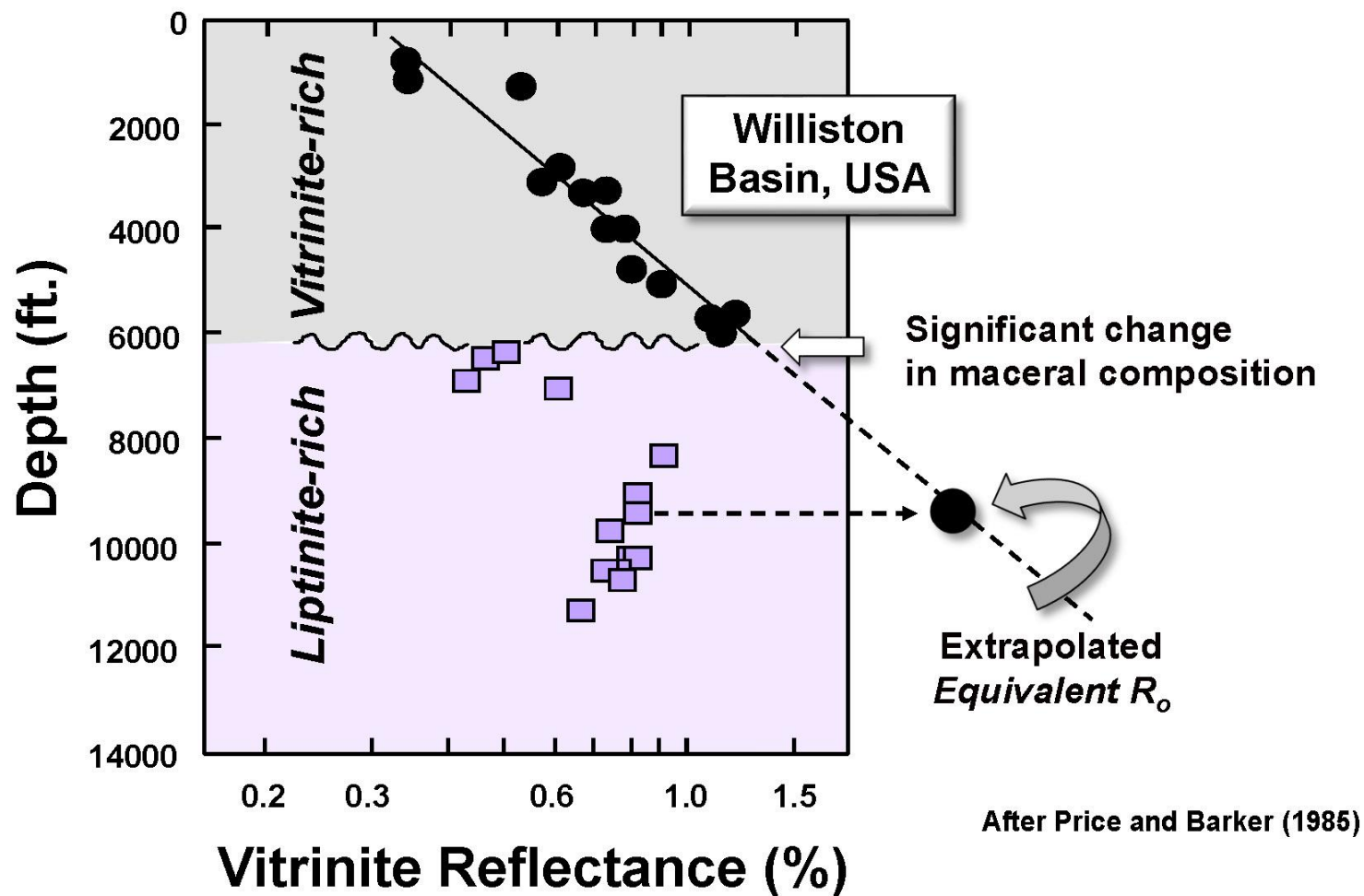
Biomarker Guide, p. 91

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Presenter's notes: Simple aromatization reaction from cyclohexane to benzene with loss of hydrogen (a). In "side" view, the aromatization converts a puckered ring to a flat ring (b) with  $sp^3$  and  $sp^2$  hybridized carbon atoms, respectively.

# Liptinite-Rich Rock Units Show “Suppressed” $R_o$

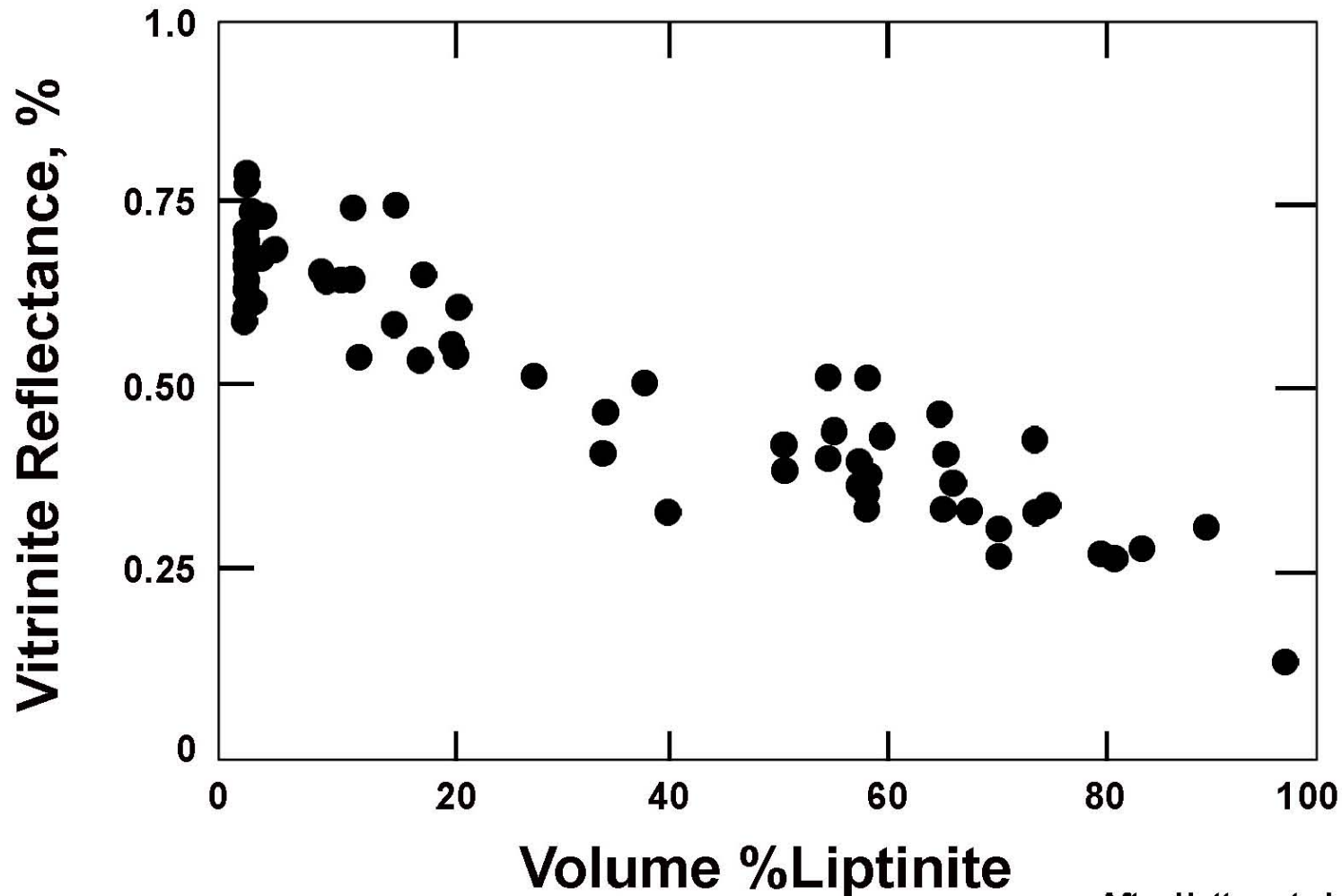


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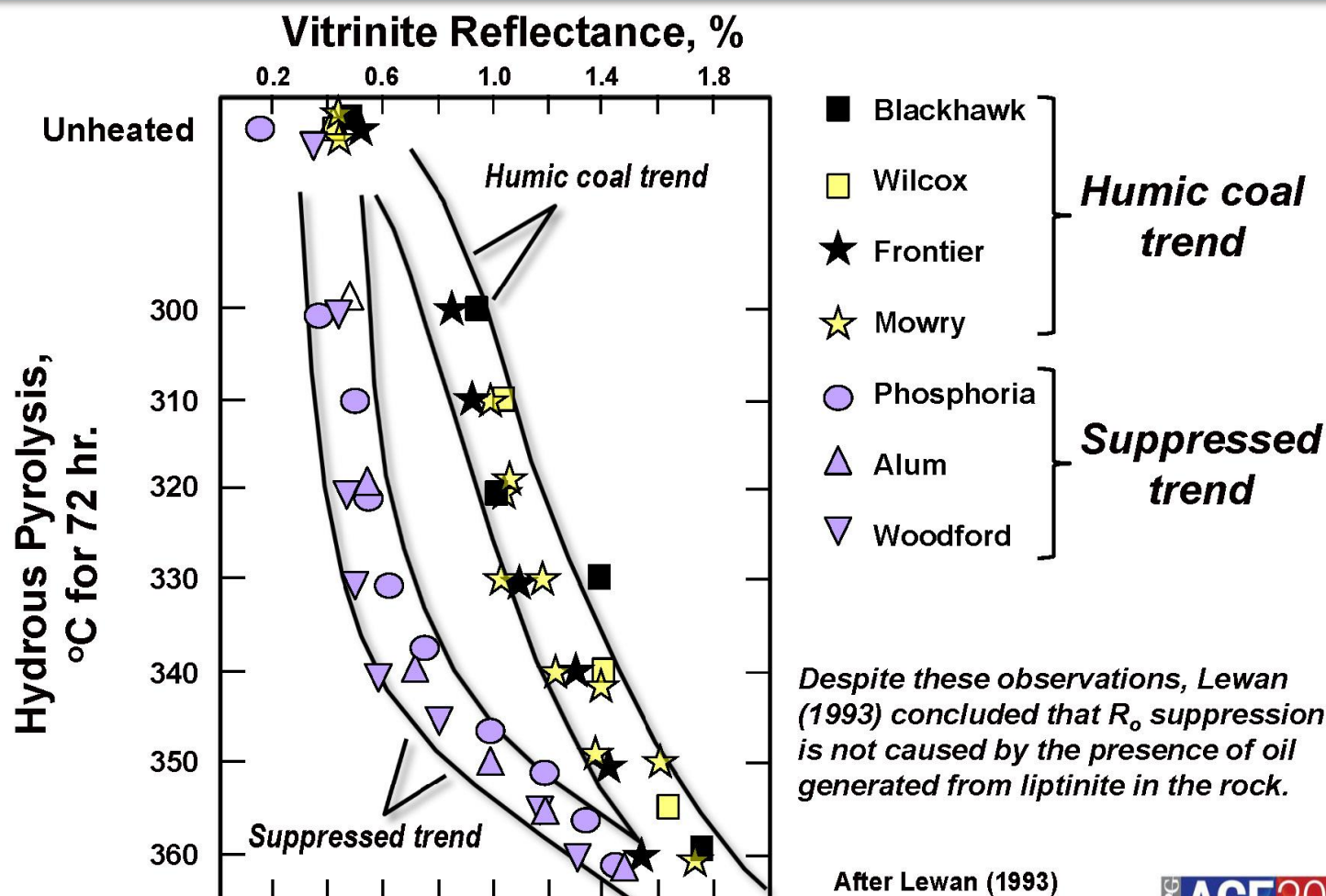
Presenter's notes: Otter-Bakken formations.

# $R_o$ Decreases with Liptinite Content in Oil Shales



After Hutton et al. (1980)

# Liptinite-Rich Samples Show Suppressed $R_o$ in the Lab

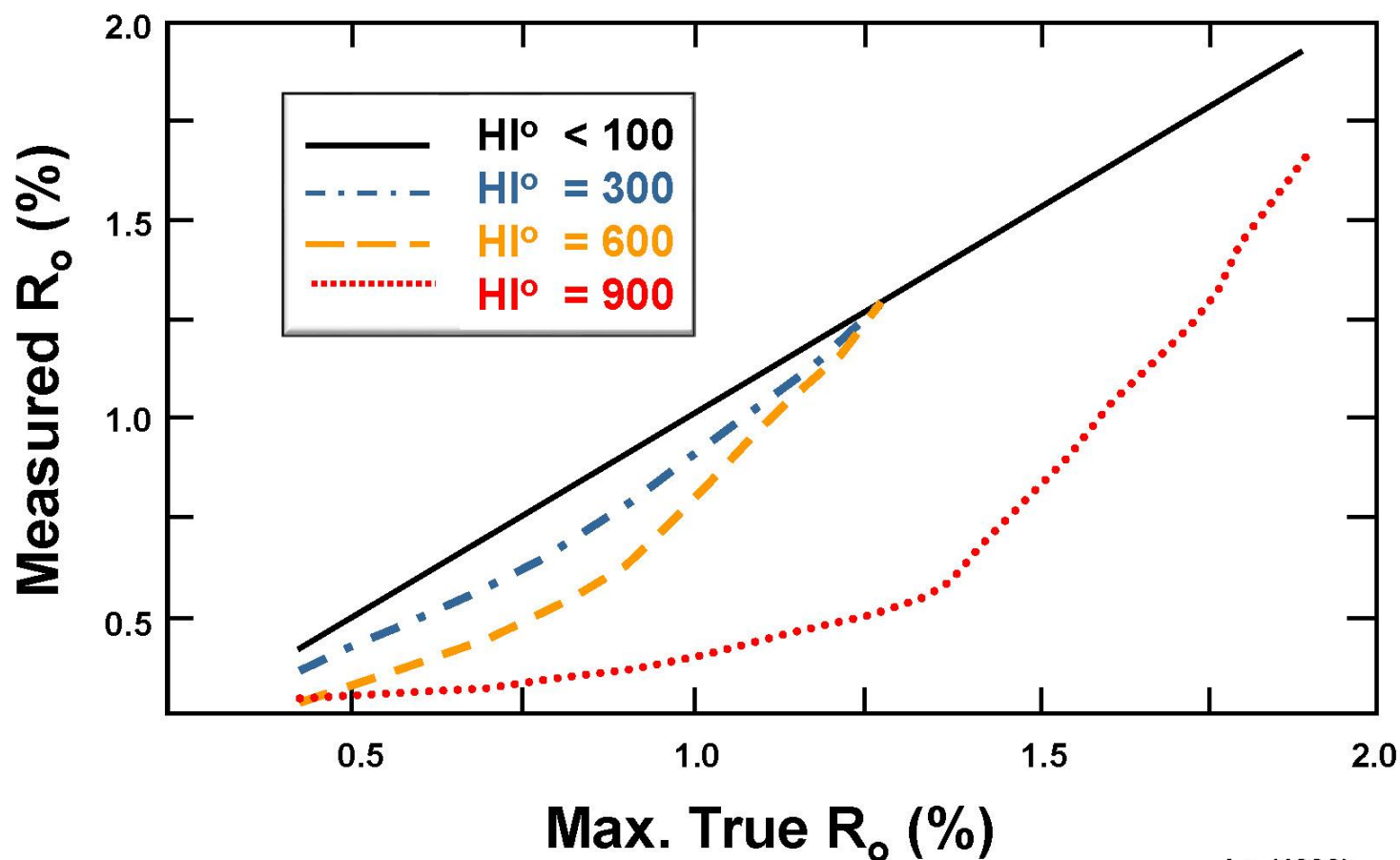


Presenter's notes: Mean random  $R_o$  of vitrinite from humic coals: Blackhawk, Frontier, Wilcox.

Suppressed trend: Phosphoria, Woodford, Alum, Mowry.

Remarkably, Lewan (1993) discounts liptinite as a factor in suppression. He believes that suppression results from anoxic conditions during diagenesis that form perhydrous (hydrogen-rich) vitrinite, which follows the suppressed trend.

# Correct Suppressed $R_o$ Using Original Hydrogen Index?



Lo (1993)

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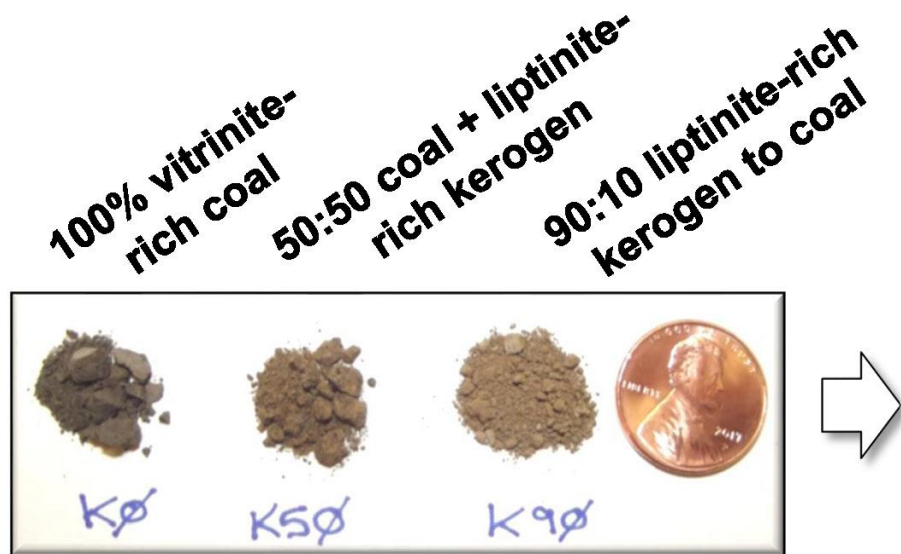
# Explanations for $R_o$ Suppression are Controversial

- **Liptinite generates oil that impregnates/coats vitrinite**  
e.g., Ting (1977), Jones & Edison (1978), Kalkreuth (1982), Stach et al. (1982)
- **Perhydrous vitrinite forms during diagenesis**  
e.g., Newman & Newman (1982), Toxopeous (1982), Price & Barker (1985), Lewan (1993)
- **Overpressure retards  $R_o$  trend**  
e.g., Hao et al. (1995, 2007), McTavish (1998), Carr (2000), Li et al. (2004)

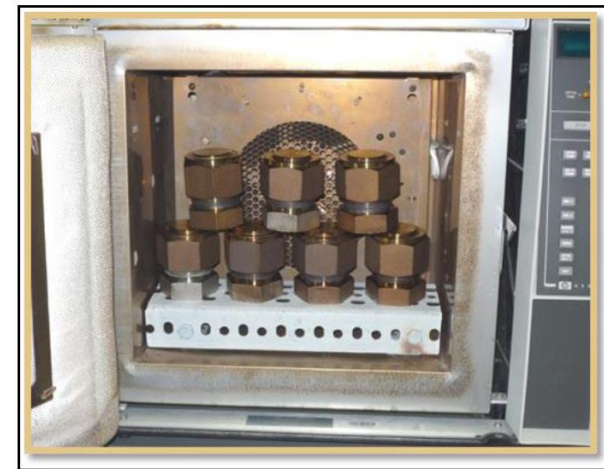
*Previous field and lab studies compared coaly versus oil-prone endmembers. Our study mixed vitrinite-rich coal with different proportions of liptinite-rich kerogen. Because one coal was used, diagenetic conditions affecting the vitrinite were identical. Since hydrous pyrolysis was repeated at the same temperatures for each artificial rock mixture, overpressure cannot explain the differences in  $R_o$  at each temperature.*

# Experiments Were Designed to Resolve the Controversy

This study used hydrous pyrolysis to simulate burial maturation of artificial rock\* containing vitrinite-rich humic coal and various proportions of liptinite.



\* Artificial rock was prepared using silica and a calcined blend of limestone and clay.



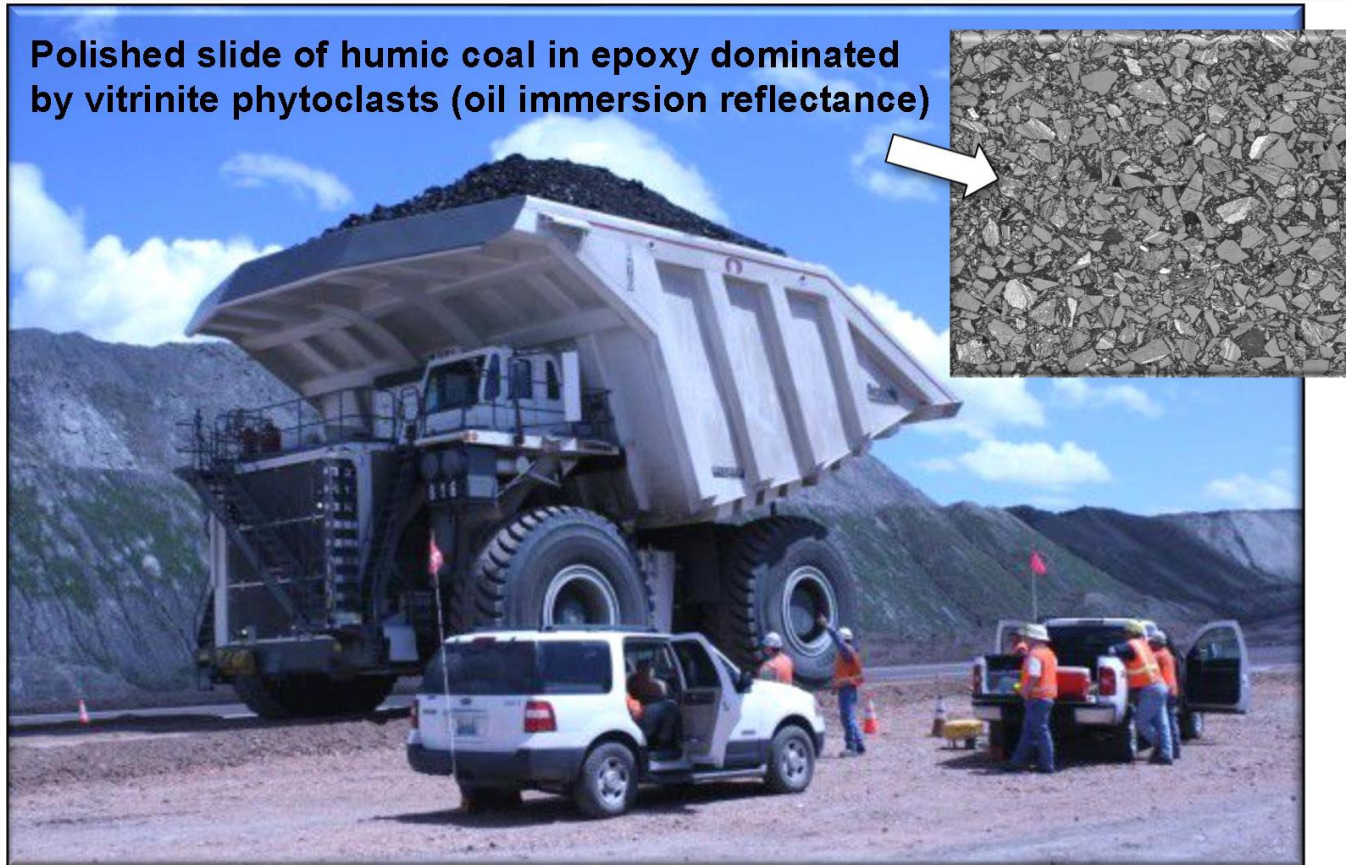
Unheated; 300, 330, and 350°C for 72 hr.

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Presenter's notes: Components and mix proportions for the artificial rock cement plugs. Coal = Paleocene Wyodak-Anderson seam, Wyoming; Kerogen = Parachute Creek Member, Eocene Green River Formation, Colorado. SwageLok hydrous pyrolysis vessels.

# Wyodak-Anderson Seam Coal, Campbell Co., Wyoming



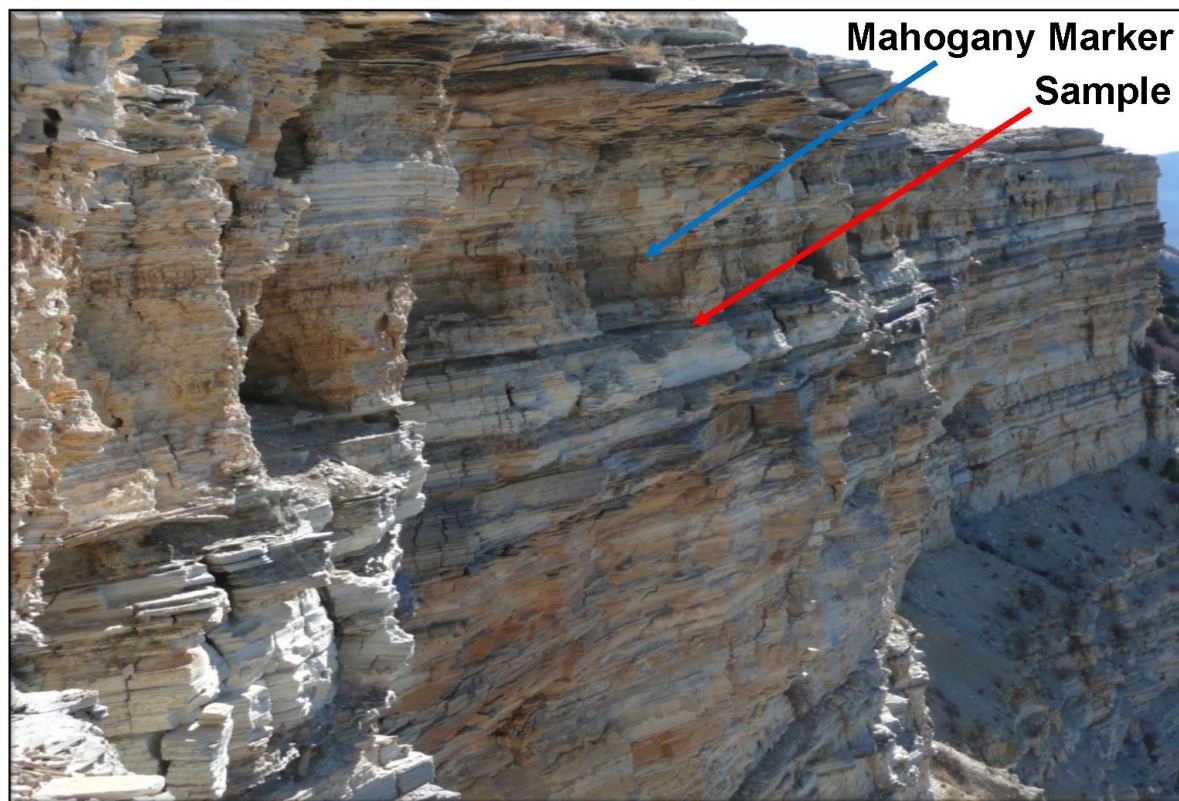
**Atomic H/C = 0.86; 89% vitrinite phytoclasts;  $R_o$  = 0.32%**

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Presenter's notes: Subbituminous Paleocene coal from the Wyodak-Anderson seam in Wyoming (Argonne Premium Coal Sample Bank; APCS-2) contains 9 wt.% dry ash, 0.6 wt.% sulfur, and carbon, hydrogen, and volatile matter (dry ash free) of 75%, 5.4%, and 49%. This low-hydrogen humic coal (atomic H/C = 0.86) is dominated by 89% vitrinite phytoclasts showing 0.32%  $R_o$ .

# Green River Formation, Parachute Creek Member



**Atomic H/C = 1.35; no vitrinite; Fisher Assay 57.9 gallons/ton**

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Presenter's notes: "Main" cliff = Mahogany Ledge Zone ~30 m in Cathedral Creek outcrop, ~0.3 m below Mahogany Marker (volcanic ash layer). Mahogany Ledge location (Cathedral Creek) near the western edge of the Piceance Basin, Rio Blanco County, Colorado. Thermally immature (Nuccio and Roberts, 2003) lacustrine oil shale was collected from a fresh outcrop of Eocene Green River Formation at the Mahogany Ledge location (Cathedral Creek) near the western edge of the Piceance Basin, Rio Blanco County, Colorado. This hydrogen-rich kerogen (atomic H/C = 1.35) yields 57.9 gallons/ton by Fisher Assay and lacks significant amounts of vitrinite phytoclasts. Solid bitumen in the sample showed 0.35% reflectance.

# $R_o$ Values: Hilgers FOSSIL System, Leica Microscope

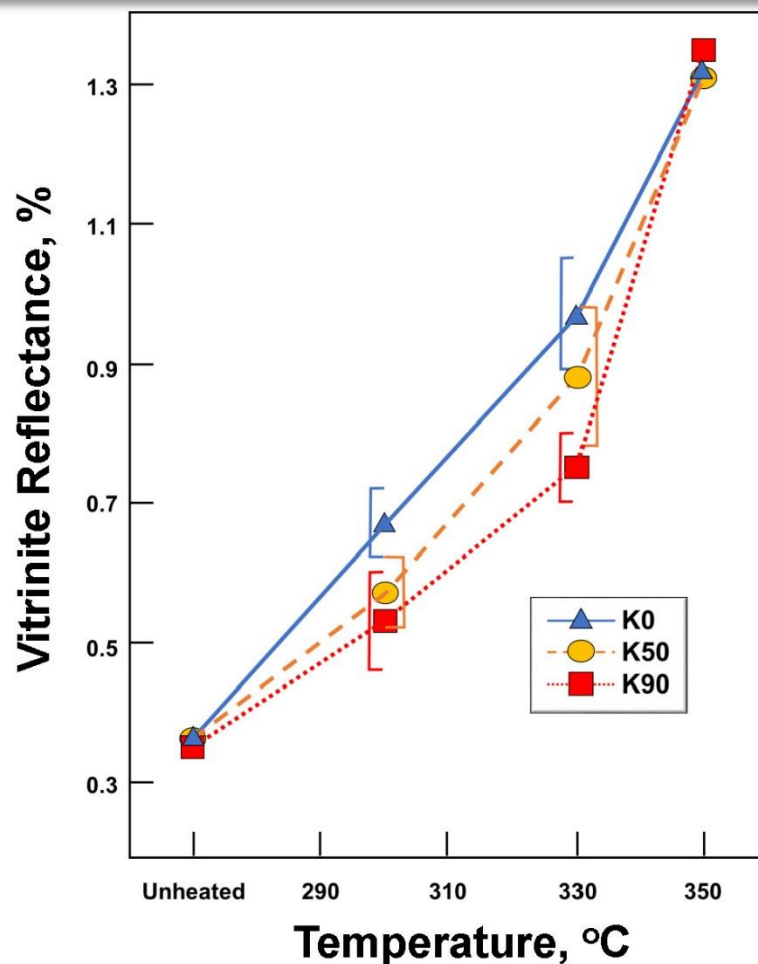


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Presenter's notes: A Leica DM4000 microscope equipped with LED illumination and monochrome camera detection (USGS Quality Management System identity Hilgers1) was used for reflectance analysis with the computer program DISKUS-FOSSIL by Hilgers Technisches Buero. Glass and yttrium-aluminum-garnet standards (1.312% and 0.908%  $R_o$ , respectively) from Klein and Becker were used for reflectance calibration.

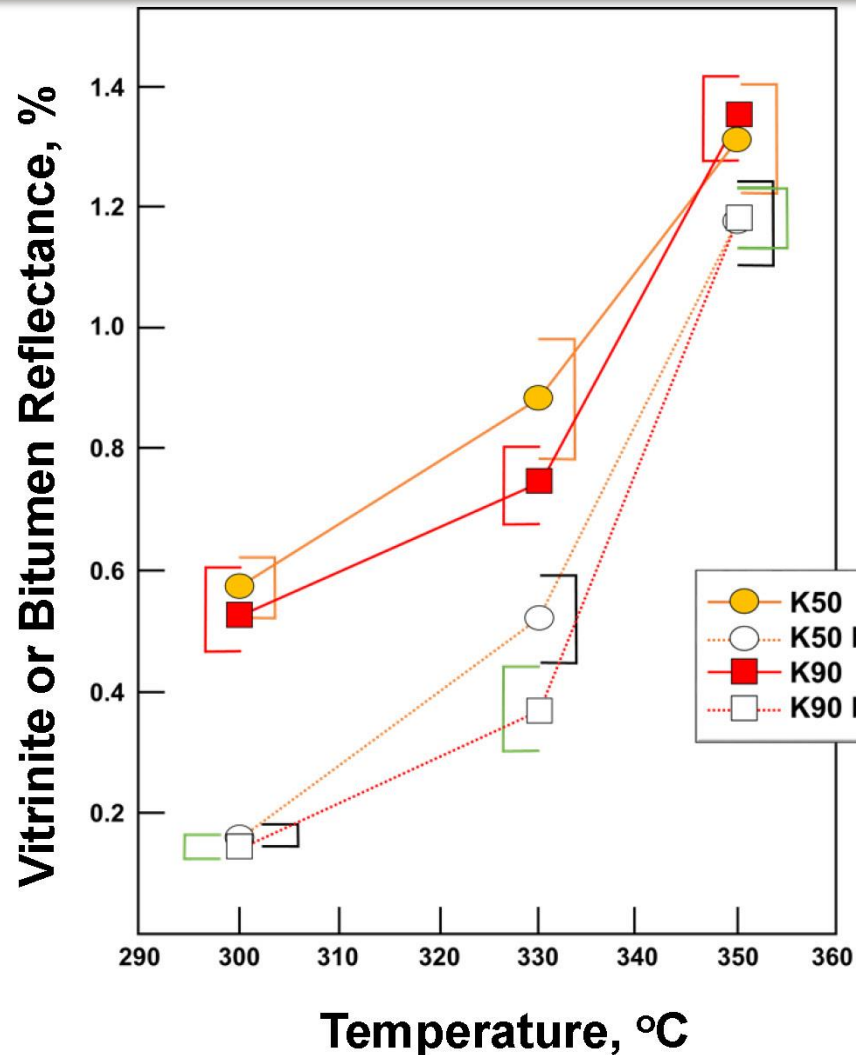
# $R_o$ Suppression Systematically Increases with Liptinite



- K0, K50, K90 contain 0:100, 50:50, and 90:10 liptinite-rich kerogen to coal.
- $R_o$  identical for K0, K50, K90 unheated.
- $R_o$  identical for K0\_350, K50\_350, K90\_350.
- Six samples at 300 and 330°C show significant  $R_o$  suppression with increased liptinite content.
- For example,  $R_o$  for K90\_300 is suppressed ( $0.53 \pm 0.07\%$ ) and distinct from K0\_350 ( $0.67 \pm 0.05\%$ ).

Presenter's notes: Systematic differences in mean random vitrinite reflectance ( $R_o$ ) versus hydrous pyrolysis temperature are related to the content of oil-prone kerogen in artificial rock samples with the following ratios of Green River kerogen to Wyodak-Anderson coal (K0 = 0:100, K50 = 50:50, K90 = 90:10). Brackets show one standard deviation in reflectance due to natural variation in the vitrinite phytoclast population for samples heated at 300°C and 330°C.  $R_o$  for K90\_300 is statistically lower (suppressed) compared to that for K0\_300, and K50\_300 shows intermediate  $R_o$  values. Likewise,  $R_o$  for K90\_330 is statistically lower (suppressed) compared to that for K0\_330, and K50\_330 shows intermediate  $R_o$  values.

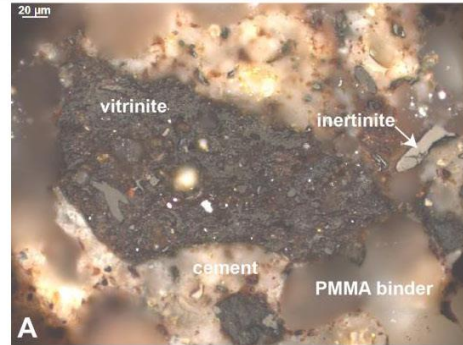
# Solid Bitumen Reflectance (Bit $R_o$ ) was Not Confused with $R_o$



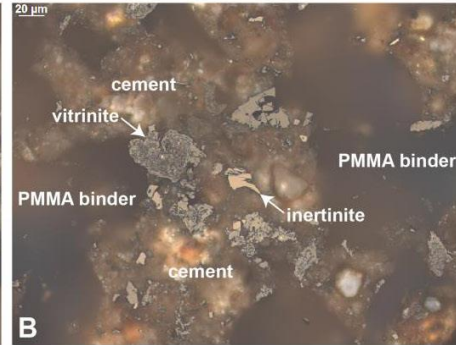
- K0 lacks liptinite-rich kerogen and solid bitumen at any temperature.
- Bit  $R_o$  is significantly lower than  $R_o$  for K50 and K90 at 300 and 330°C, but approaches  $R_o$  in the 350°C residue.
- Bit  $R_o$  for K50 and K90 is identical in 300 and 350°C residues; Bit  $R_o$  for K50 residue at 330°C is only slightly higher than that for K90.

# Microscopy Shows Bitumen Generated at 350°C, 72 hr.

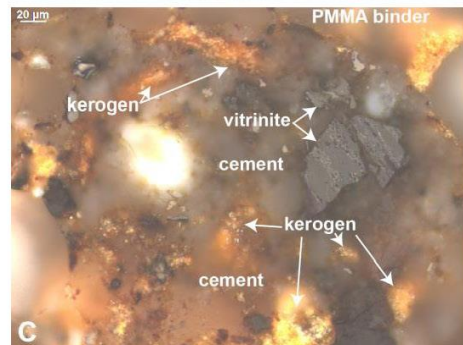
**K0 unheated**



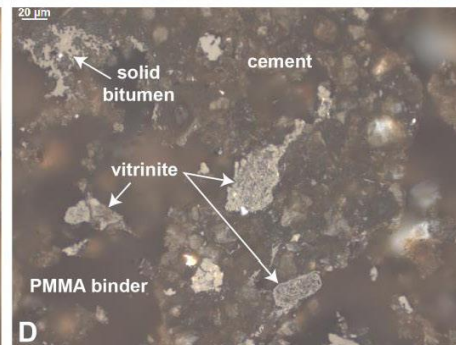
**K0 350°C**  
No solid bitumen



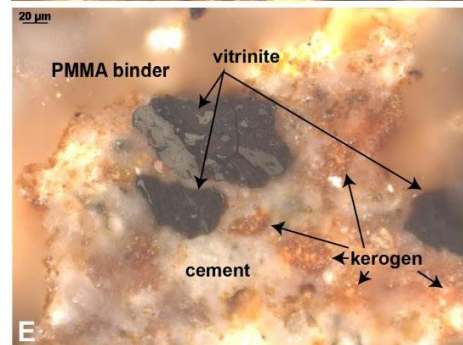
**K50 unheated**



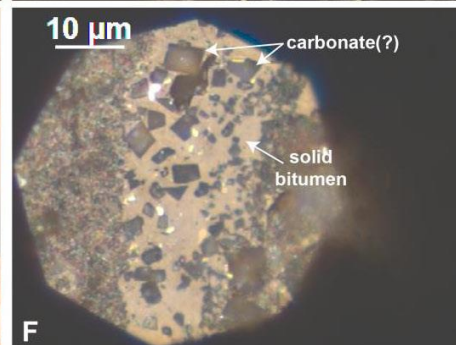
**K50 350°C**  
Solid bitumen



**K90 unheated**



**K90 350°C**  
Solid bitumen

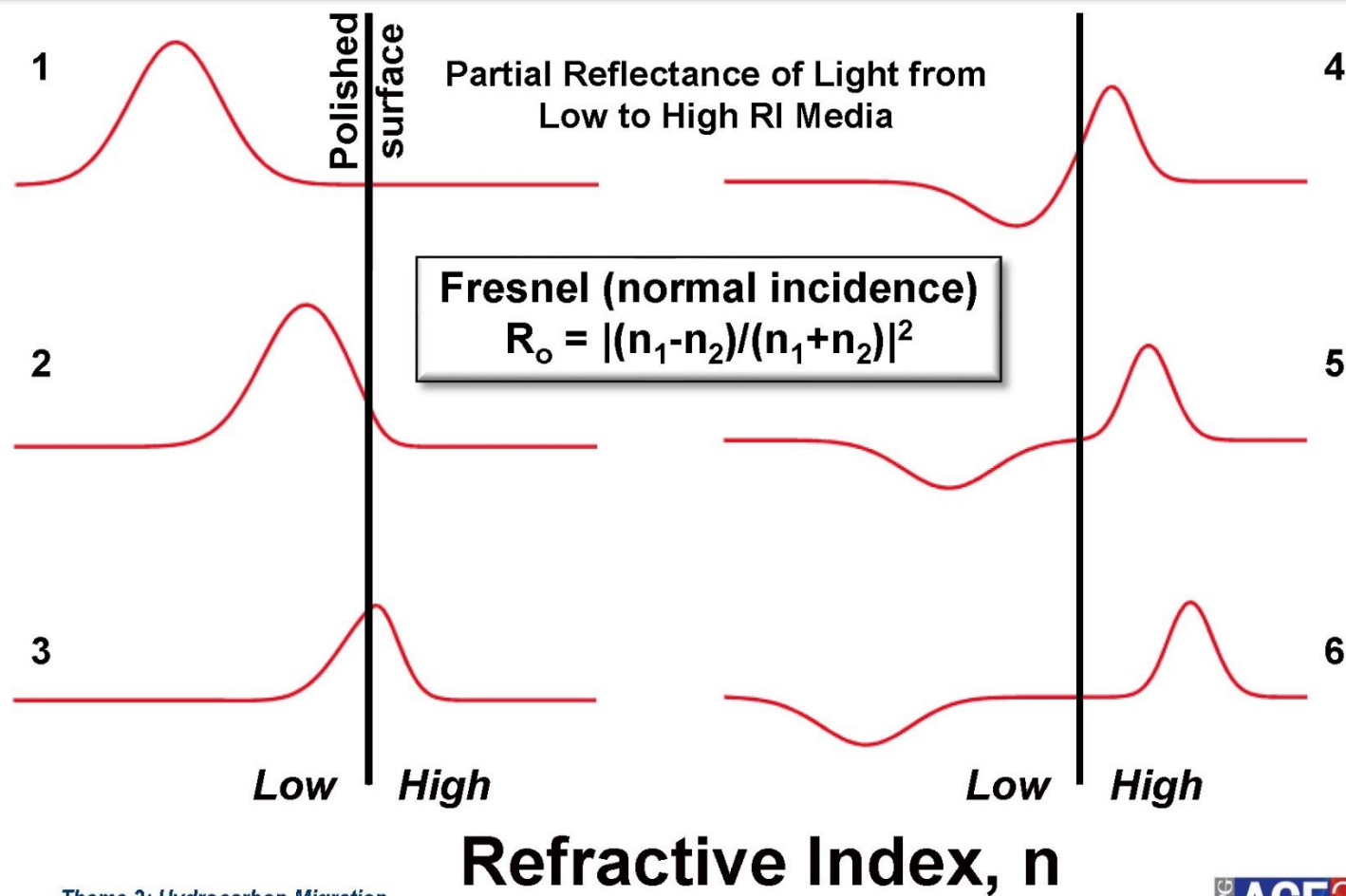


Presenter's notes: (A) Vitrinite and inertinite in artificial rock K0 (coal with no liptinite-rich kerogen; unheated). (B) Vitrinite and inertinite in K0\_350 (coal with no kerogen at 350°C for 72 hr.). (C) Vitrinite and liptinite-rich kerogen in K50 (50:50 coal and kerogen; unheated); slide also contains a high reflecting pyrite framboid. (Presenter's notes continued on next slide.)

*(Presenter's notes continued from previous slide.)*

(D) Vitrinite and solid bitumen in K50\_350 (50:50 coal and kerogen at 350° C for 72 hr.). (E) Vitrinite and liptinite-rich kerogen in K90 (90:10 kerogen and coal; unheated). (F) Solid bitumen and carbonate(?) in K90\_350 (90:10 kerogen and coal; 350° C for 72 hr.). Octagonal image is closed aperture of the field diaphragm to limit stray light using a 100X objective. All images in white incident light under oil immersion. PMMA binder is a thermoplastic compression mounting compound [TransOptic™ poly(methyl methacrylate); Buehler, Inc.] prepared at 180°C (360° F) and 4,000 psi for 10 min.

# $R_o$ Depends on $\Delta RI$ Between Vitrinite and Immersion Oil



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Presenter's notes:

## Smaller Difference in RI Gives Less Partial Reflectance

RI is a unitless value that describes how light is affected as it passes through various media. It is calculated by comparing the speed of light in a vacuum to its velocity in the medium. A **higher refractive index** indicates light moving *more slowly* through the medium.

(Presenter's notes continued on next slide.)

*(Presenter's notes continued from previous slide.)*

The Fresnel equations describe the reflection and transmission of light when incident on an interface between media having different refractive indices.

We use Cargille A at RI = 1.518. Vitrinite at 0.6% will have RI of about 1.77; i.e.  $[(1.77-1.518)/3.288] = 0.006$  or 0.6%  $R_o$ ;  $T = 4n_1n_2/(n_1+n_2)^2 = 99\%$

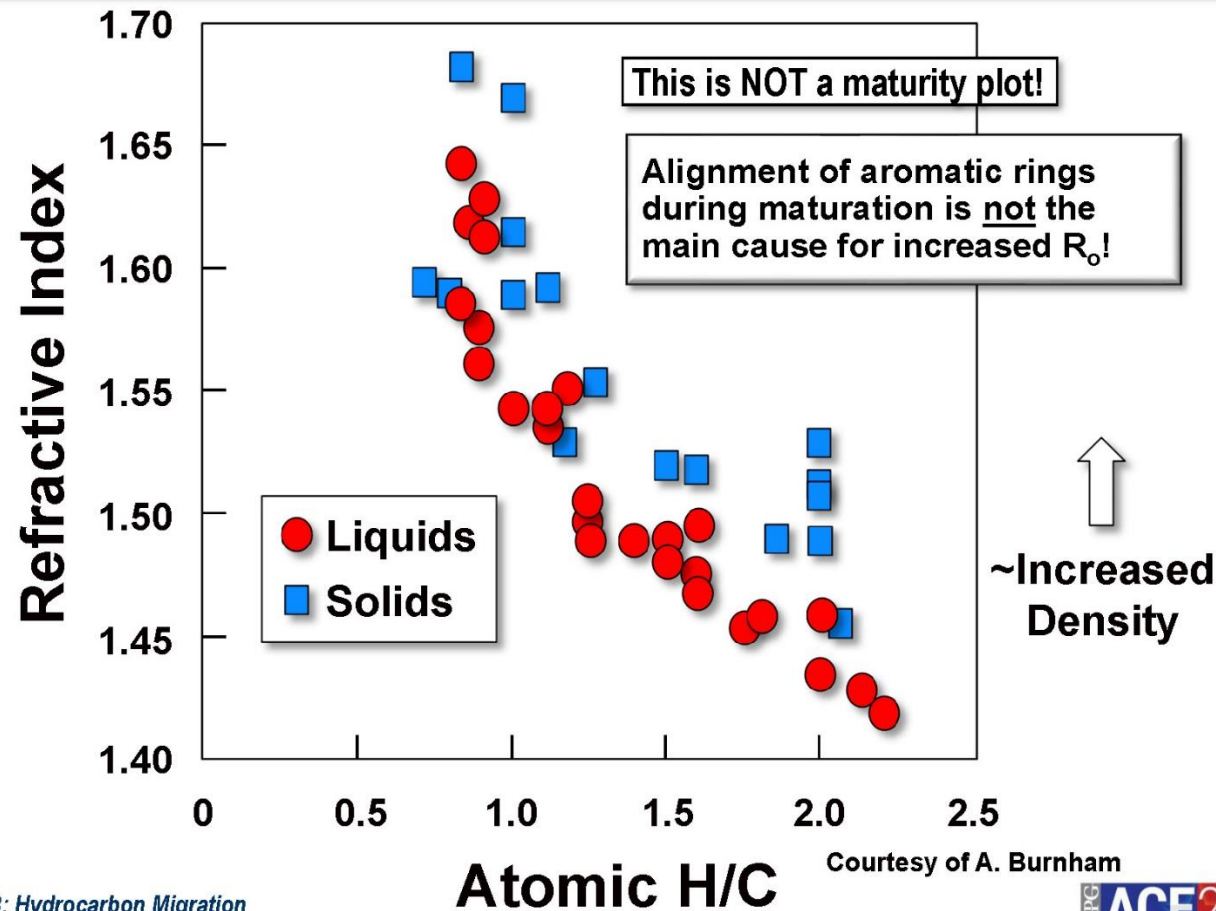
For normal incidence:  $R_o = |(n_1-n_2)/(n_1+n_2)|^2$ , i.e., greater difference between the two refractive indices ( $n_1$  vs.  $n_2$ ) gives greater reflectance. Lower atomic H/C gives higher refractive index and higher  $R_o$ .

Higher refractive indices for vitrinite relative to the immersion oil result in stronger partial reflectance from the low to high refractive index (i.e., from immersion oil to vitrinite) according to Fresnel. For normal (e.g. vertical) incidence on a planar surface:

$R_o = |(n_1-n_2)/(n_1+n_2)|^2$ , i.e. greater difference between the two refractive indices ( $n_1$  vs.  $n_2$ ) gives greater reflectance. Lower atomic H/C gives higher refractive index and higher  $R_o$ .

Suppression results from 'cross reaction of mobile species that alkylate structures in the vitrinite and increase the H/C ratio over what it would be without that alkylation'. I like that better than the free radical quenching speculation, which relies on aromatic structures as the principal control on  $R_o$ .

# RI Increases with Decreasing H/C for Hydrocarbons



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Presenter's notes: Refractive index depends on atomic H/C ratio even for non-aromatics and unaligned aromatic rings, which is the case in liquids. Therefore, alignment of aromatic rings is not the primary cause of the change in the mean reflectance to increased RI. Also note that at a given atomic H/C, the higher density solids have higher RI than the liquids, i.e. the conversion of mostly  $sp^3$  to  $sp^2$  hybridized vitrinite during maturation results in increased density and a relative increase in RI and reflectance.

The above alignment statement is true given the qualification of "main". Alignment is mostly responsible for the anisotropy, which becomes more important above the oil window when the kerogen is mostly aromatic and the alignment can actually happen.

# Conclusions: Liptinite Suppresses $R_o$ Maturation

- $R_o$  is commonly suppressed in oil-prone source rock.
- Interpolate *equivalent*  $R_o$  using trends above/below the source rock.
- Hydrous pyrolysis of artificial rock with mixed coal and liptinite-rich kerogen excludes diagenetic or overpressure mechanisms for suppression.
- Results prove that liptinite suppresses  $R_o$ , but they do not exclude diagenetic or overpressure mechanisms.
- Suppression occurs when liptinite products alkylate vitrinite, thus retarding the decrease in atomic H/C and the corresponding increase in refractive index.