# STANDARDIZATION OF VITRINITE REFLECTANCE MEASUREMENTS IN SHALE PETROLEUM SYSTEMS: HOW ACCURATE ARE MY $R_o$ DATA?

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***Presented for AAPG, April 7, 2014***

# Acknowledgments


- 2009 survey participants
- Writing committee for ASTM D7708
- 2012-2013 ASTM D7708 ILS participants
- USGS Energy Resources Program
- Alan C. Cook

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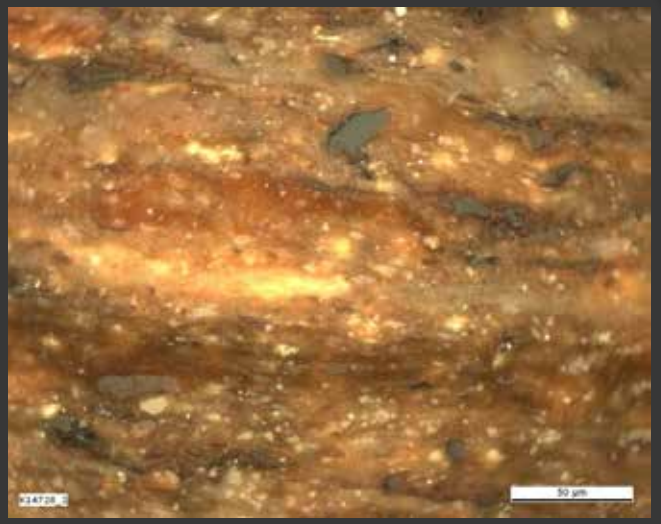
**Twenty-eight participants, 22 laboratories, 14 countries**

# Outline of this presentation

- What is vitrinite?
- What is the problem? Mean reproducibility limit of 0.4%
- History of this work
- 2012-2013 interlaboratory study
- Discussion and future directions

# Vitrinite

-Vitrinite is the remains of coalified material from vascular land plants in Upper Silurian and younger age sedimentary rocks.

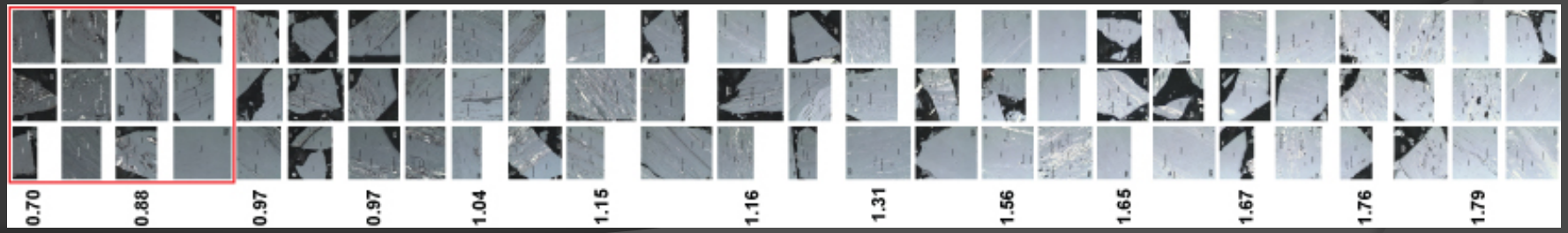


*Eocene shale*

# Vitrinite Reflectance is…

**Proportion of incident light reflected**

$R_o$ = 0.70% Same camera exposure throughout $R_o$ = 1.79%



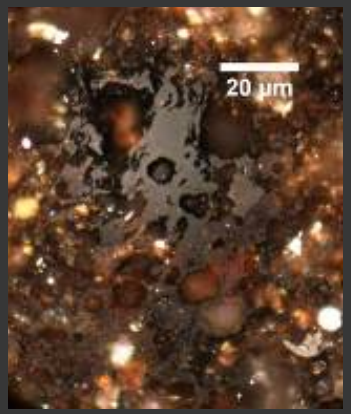

*Gesserman et al., 2009, GSA Abstracts*

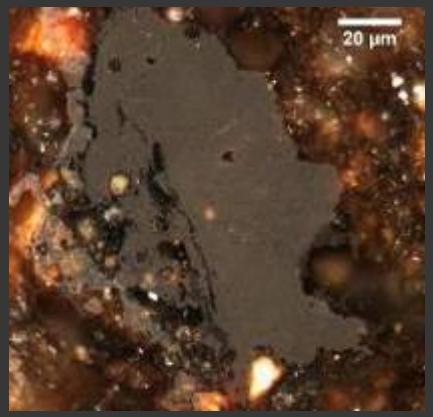
# WHAT ARE THE BIGGEST PROBLEMS WITH IDENTIFICATION OF PRIMARY VITRINITE?

- Recognition of primary vitrinite and distinguishing it from similar macerals in shale
- Lack of supporting documentation and data
- Lack of experience – or a particular experience guides interpretation
- Pressure to determine thermal maturity of vitrinite when vitrinite may or may not be present
- Preparation: whole rock vs. kerogen concentrate
- Poor polish

# RECOGNITION OF PRIMARY VITRINITE

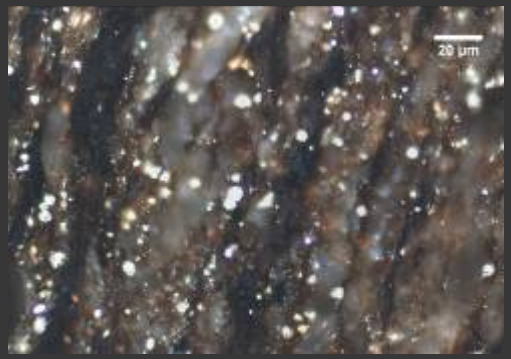
## Distinction from bitumens

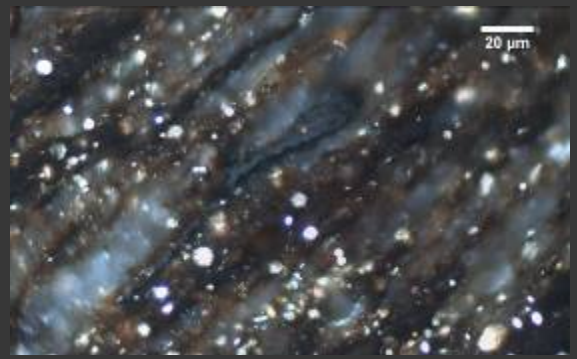



Vitrinite is not pore-filling or anastamosing, is not embayed by authigenic minerals, often is brighter, thicker, boundaries are more distinct, does not have mosaic anisotropy, may occur with other macerals; whereas bitumens cross bedding, can occur as droplets, dissolve in solvents, and may have mosaic anisotropy – rock type, rank, and geologic occurrence may influence expectations

## Distinction from bituminite

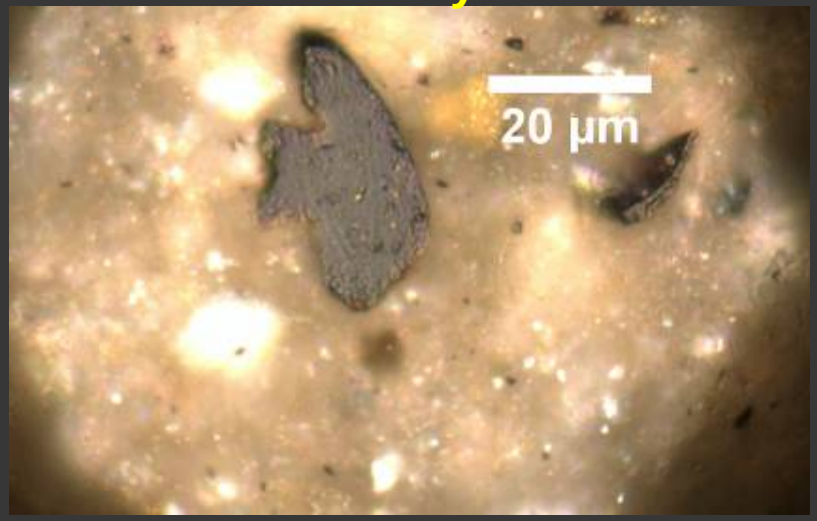



Vitrinite has brighter reflectance, lower fluorescence, more distinct boundaries, is more blocky and evenly colored; whereas bituminite often is observed in association with lamalginite and micrinite, is indistinct and wispy, and is speckled or unevenly colored

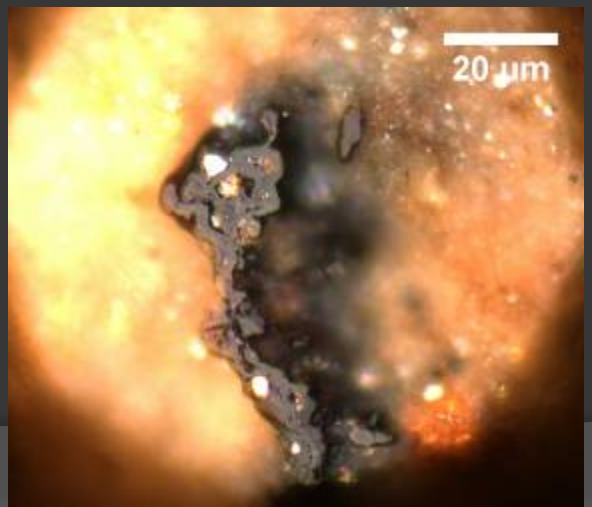
# RECOGNITION OF PRIMARY VITRINITE

## Distinction from recycled/oxidized vitrinite




Primary vitrinite is not as bright, more angular, recycled vitrinite may have bright or dark halos, recycling may be anticipated from geologic context, e.g., orogeny, recycled vitrinite has higher spread of reflectance values

## Distinction from low-reflecting semifusinite




Vitrinite is not as bright, has lower relief, is not usually as arcuate, does not have well-preserved cellular structure-lumens, has less distinct grain margins, has a more porous and textured surface; semifusinite may have irregular anisotropy regions

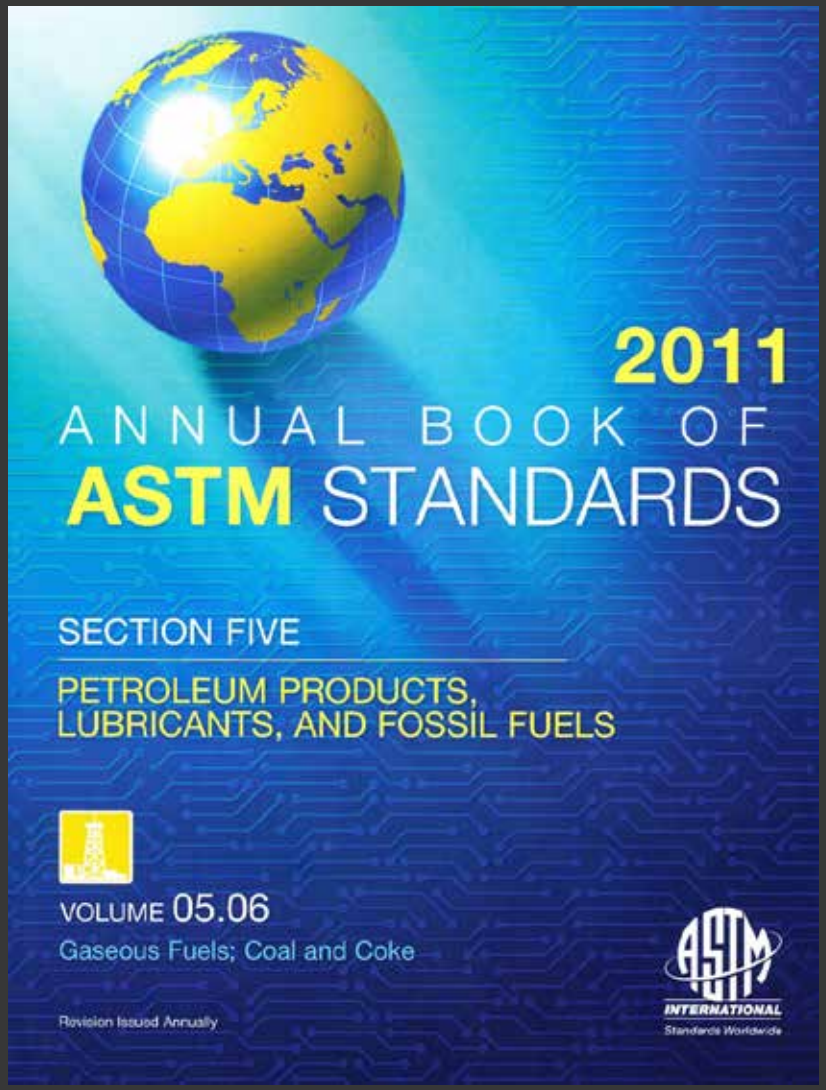
# Identification of primary vitrinite: history of ICCP working group

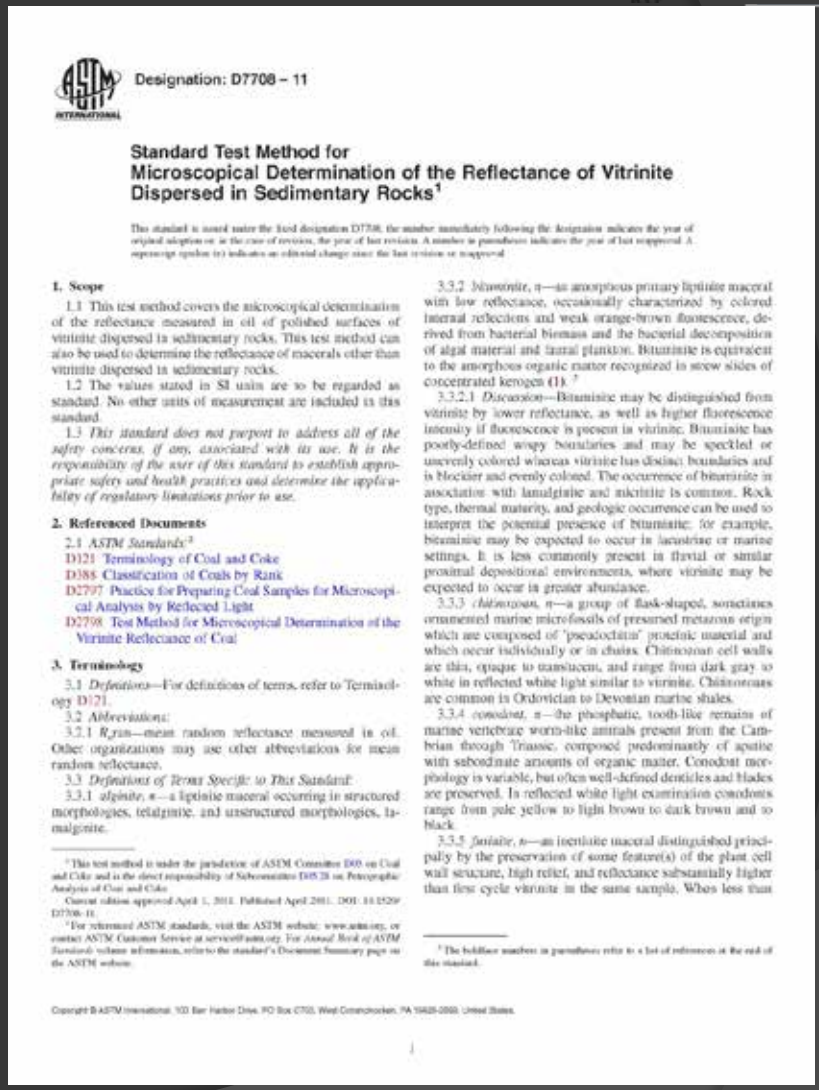
- Working group proposed by Angeles Borrego at September 2008 Oviedo ICCP meeting
- Survey about dispersed vitrinite reflectance analysis completed April 2009
- Results of survey presented 2009 Gramado meeting, published ICCP News 48, Nov. 2009
- Proposal to create new ASTM standard for dispersed vitrinite reflectance analysis, 2009 Gramado ICCP meeting
- D7708-11 first published in 2011 Annual Book of ASTM Standards September 2011
- Proposal for ILS to provide R&r for D7708-11 presented 2011 Porto ICCP meeting

# Identification of primary vitrinite: history of ICCP working group cont.

- Selection, collection and characterization of samples (~25) from 2011 Porto ICCP meeting to 2012 Beijing meeting
- 2012 Beijing meeting: proposal for six samples including type I (lacustrine), type II (marine), and type III (terrestrial, coal measures), immature, mature, and overmature, Devonian to Tertiary, to be analyzed in duplicate
- October-November 2012, samples distributed
- February-June 2013, results received, QA/QC with each petrographer; results passed to ASTM ILS program staff
- Sosnowiec 2013 ICCP meeting, first presentation of results
- Houston 2014 AAPG, presentation to O&G community
- ILS results published in ASTM D7708 and draft manuscript 2014

# Design of the 2012-2013 interlaboratory study



Designation: D7708 – 11

## Standard Test Method for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks[1]

This standard is issued under the fixed designation D7708; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

**1. Scope**

1.1 This test method covers the microscopical determination of the reflectance measured in oil of polished surfaces of vitrinite dispersed in sedimentary rocks. This test method can also be used to determine the reflectance of macerals other than vitrinite dispersed in sedimentary rocks.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

**2. Referenced Documents**

2.1 *ASTM Standards*[2]

D121 Terminology of Coal and Coke

D388 Classification of Coals by Rank

D2797 Practice for Preparing Coal Samples for Microscopical Analysis by Reflected Light

D2798 Test Method for Microscopical Determination of the Vitrinite Reflectance of Coal

**3. Terminology**

3.1 *Definitions*—For definitions of terms, refer to Terminology D121.

3.2 *Abbreviations:*

3.2.1 *R*$_r$*in*—mean random reflectance measured in oil. Other organizations may use other abbreviations for mean random reflectance.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *alginite, n*—a liptinite maceral occurring in structured morphologies, telalginite, and unstructured morphologies, lamalginite.

3.3.2 *bituminite, n*—an amorphous primary liptinite maceral with low reflectance, occasionally characterized by colored internal reflections and weak orange-brown fluorescence, derived from bacterial biomass and the bacterial decomposition of algal material and faunal plankton. Bituminite is equivalent to the amorphous organic matter recognized in straw slides of concentrated kerogen (1).[3]

3.3.2.1 *Discussion*—Bituminite may be distinguished from vitrinite by lower reflectance, as well as higher fluorescence intensity if fluorescence is present in vitrinite. Bituminite has poorly-defined wispy boundaries and may be speckled or unevenly colored whereas vitrinite has distinct boundaries and is blockier and evenly colored. The occurrence of bituminite in association with lamalginite and micrinite is common. Rock type, thermal maturity, and geologic occurrence can be used to interpret the potential presence of bituminite; for example, bituminite may be expected to occur in lacustrine or marine settings. It is less commonly present in fluvial or similar proximal depositional environments, where vitrinite may be expected to occur in greater abundance.

3.3.3 *chitinozoan, n*—a group of flask-shaped, sometimes ornamented marine microfossils of presumed metazoan origin which are composed of 'pseudochitin' proteinic material and which occur individually or in chains. Chitinozoan cell walls are thin, opaque to translucent, and range from dark gray to white in reflected white light similar to vitrinite. Chitinozoans are common in Ordovician to Devonian marine shales.

3.3.4 *conodont, n*—the phosphatic, tooth-like remains of marine vertebrate worm-like animals present from the Cambrian through Triassic, composed predominantly of apatite with subordinate amounts of organic matter. Conodont morphology is variable, but often well-defined denticles and blades are preserved. In reflected white light examination conodonts range from pale yellow to light brown to dark brown and to black.

3.3.5 *fusinite, n*—an inertinite maceral distinguished principally by the preservation of some feature(s) of the plant cell wall structure, high relief, and reflectance substantially higher than first cycle vitrinite in the same sample. When less than

[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.28 on Petrographic Analysis of Coal and Coke.

Current edition approved April 1, 2011. Published April 2011. DOI: 10.1520/D7708-11.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.



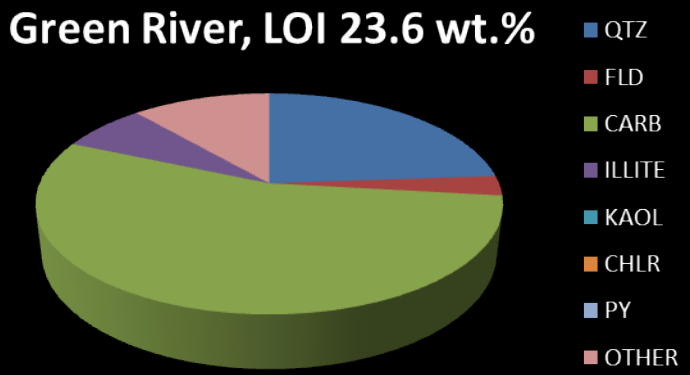


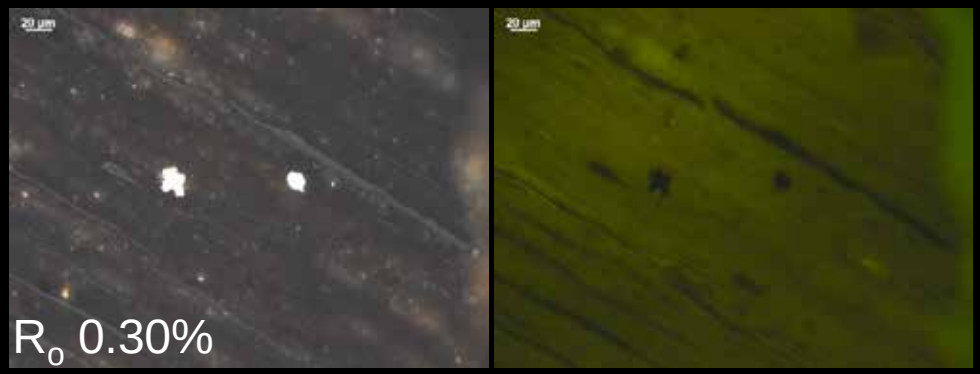
**Use D7708, follow reporting requirements**

# Instructions distributed with samples

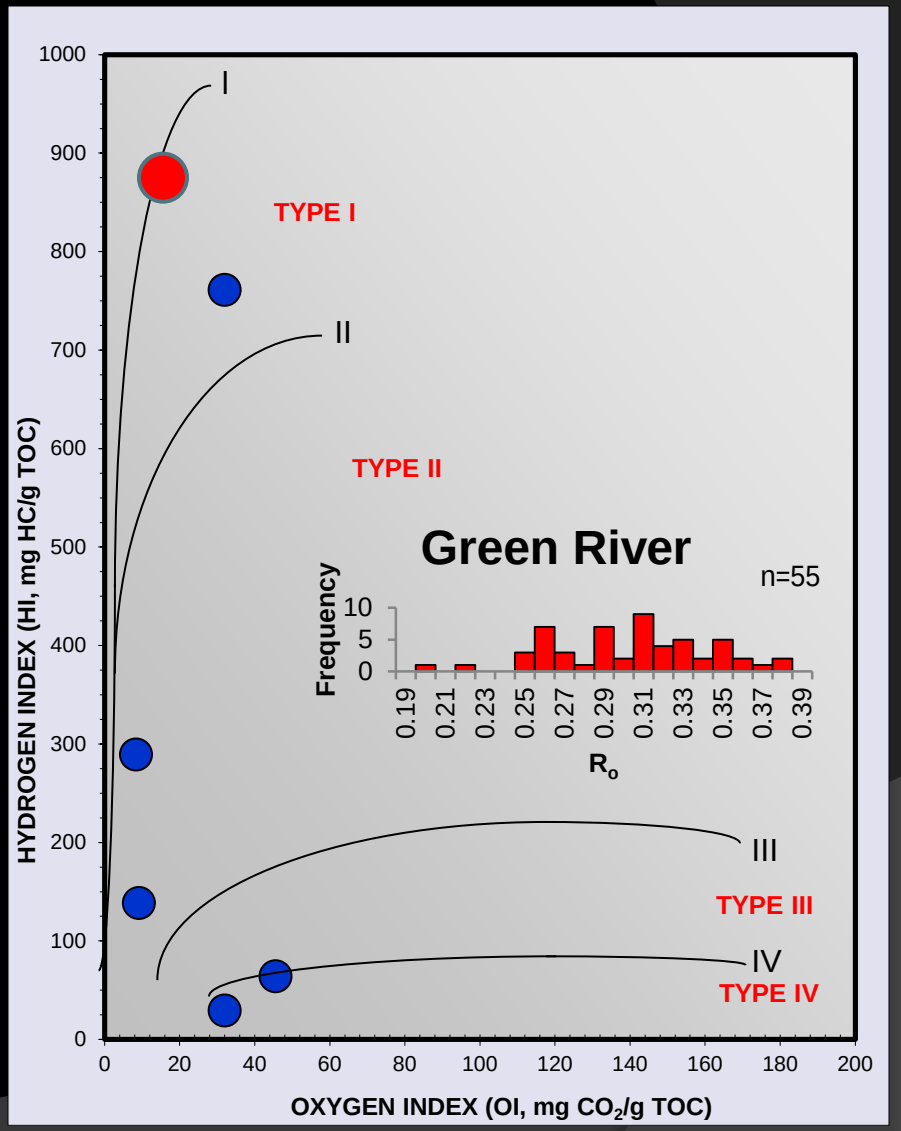
- Please read and follow ASTM D7708 carefully!
- Please follow reporting instructions!
- Please provide any commentary on samples and on ASTM D7708!
- Please contact convener with any questions about samples!

# Sample 1 – Green River Shale, Eocene

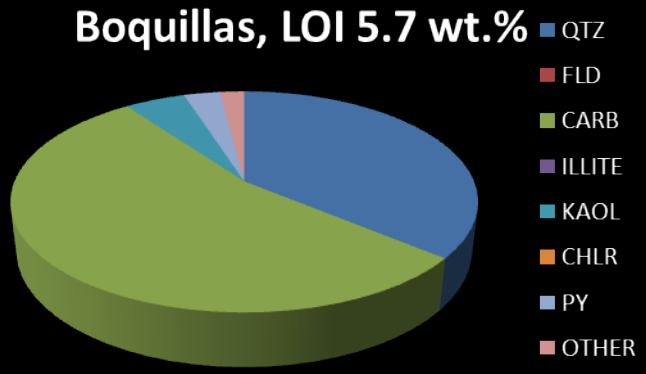


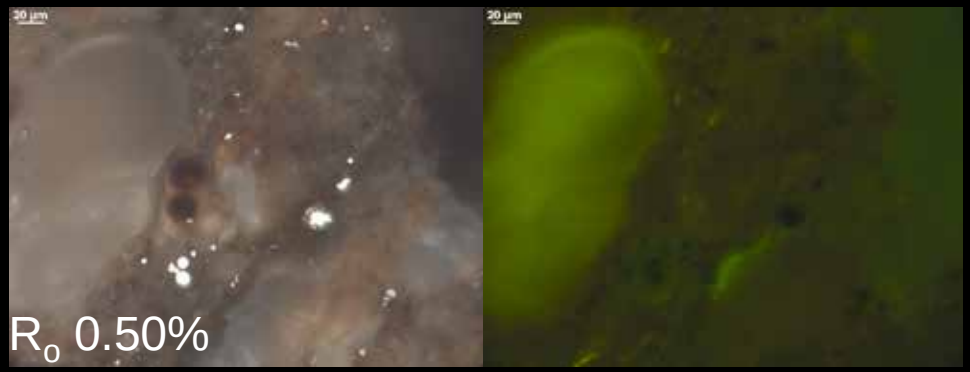




Material is bitumen per 3 petrographers (but Jacob's equation gives unrealistic conversion of >0.6%). Cellular structure is rare but present in some samples. AOM is abundant, fluorescence is very strong.

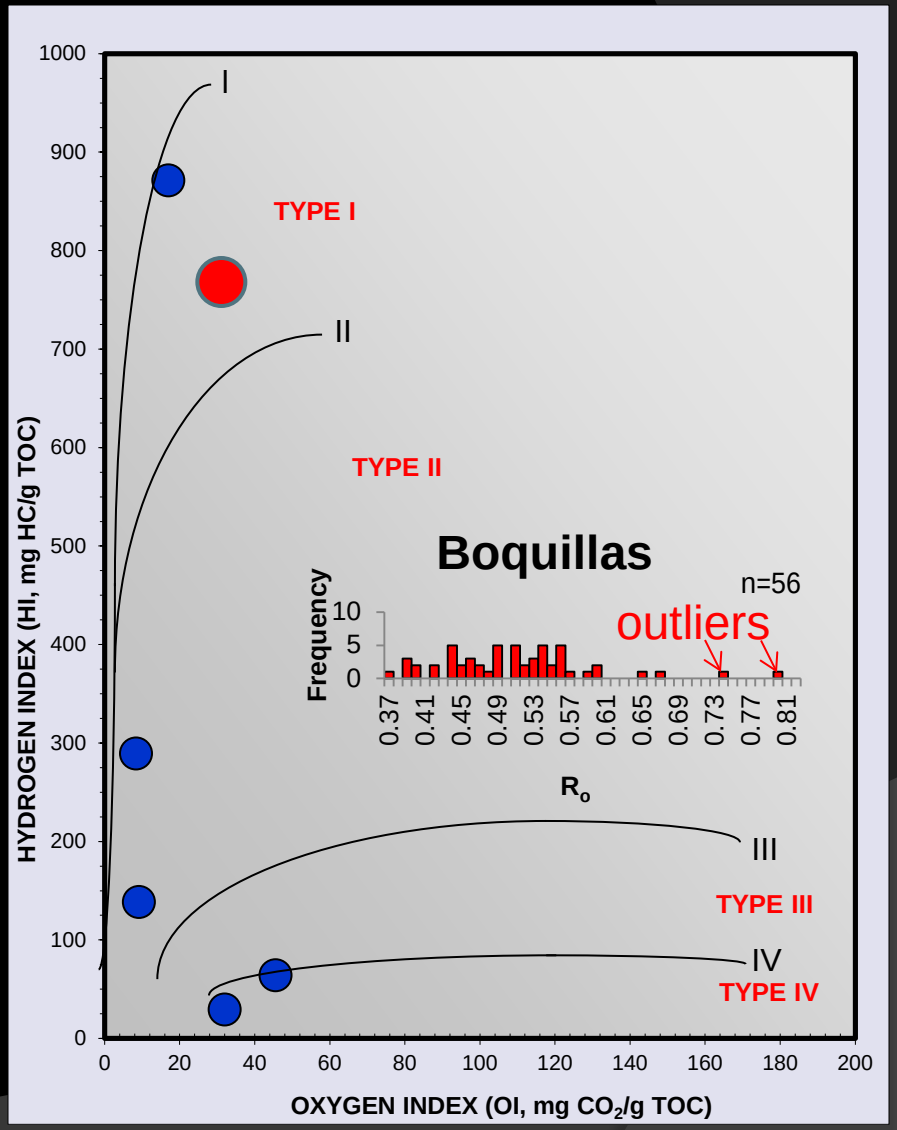


# Sample 2 – Boquillas Shale, Upper Cretaceous

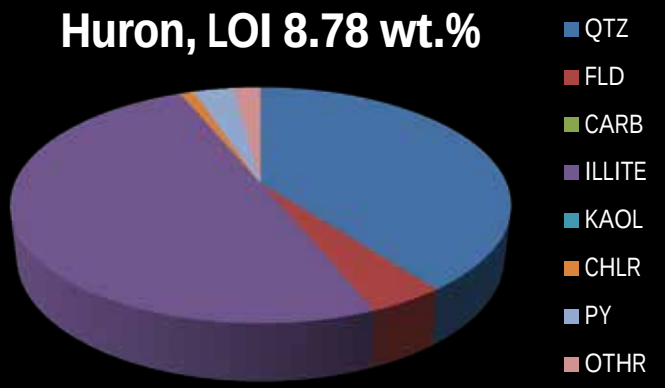


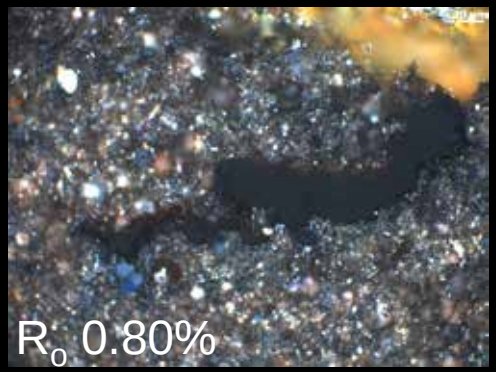




In addition to vitrinite, contains lower reflectance bitumen ($R_o$ 0.25%) which was noted by several, but not measured. Foraminifera are abundant, AOM is relatively abundant, fluorescence is strong.

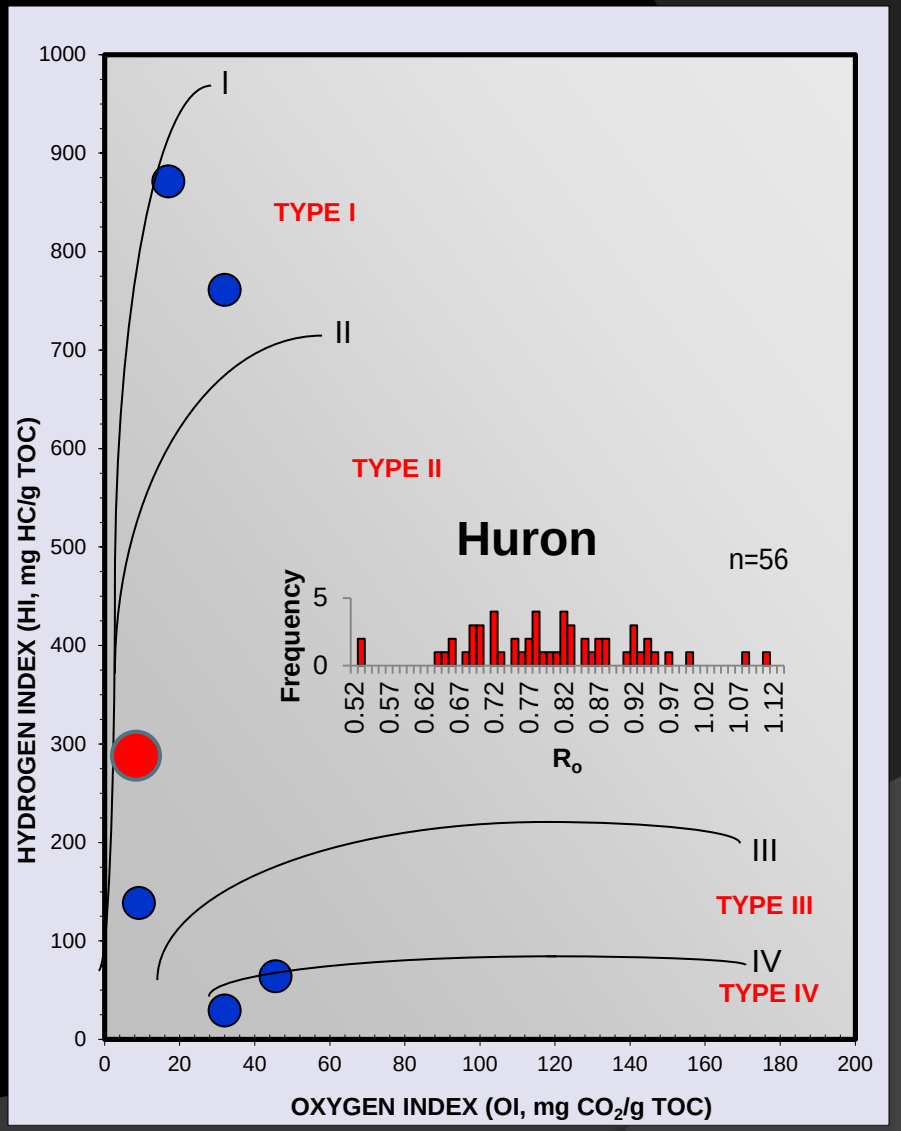


# Sample 3 – Huron Shale, Devonian

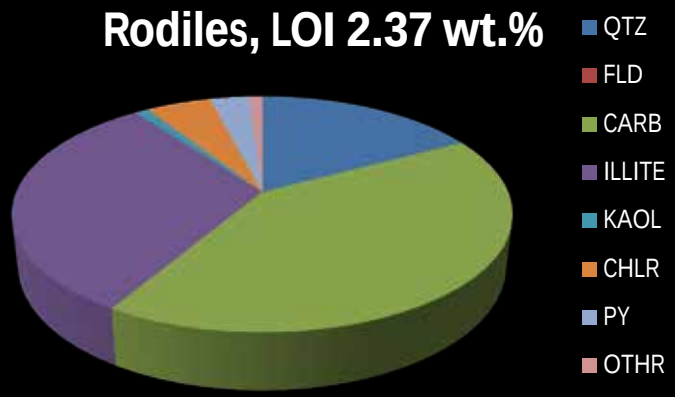


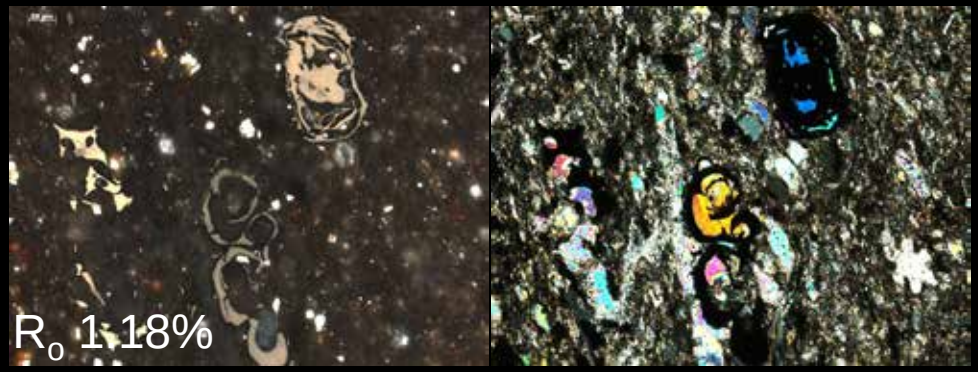




Vitrinite is rare or absent; four petrographers reported bitumen reflectance. Tasmanites is abundant (some misidentified for vitrinite or mega-spores) with strongly red-shifted fluorescence. Weathering (sulfates, oxides) prevalent.

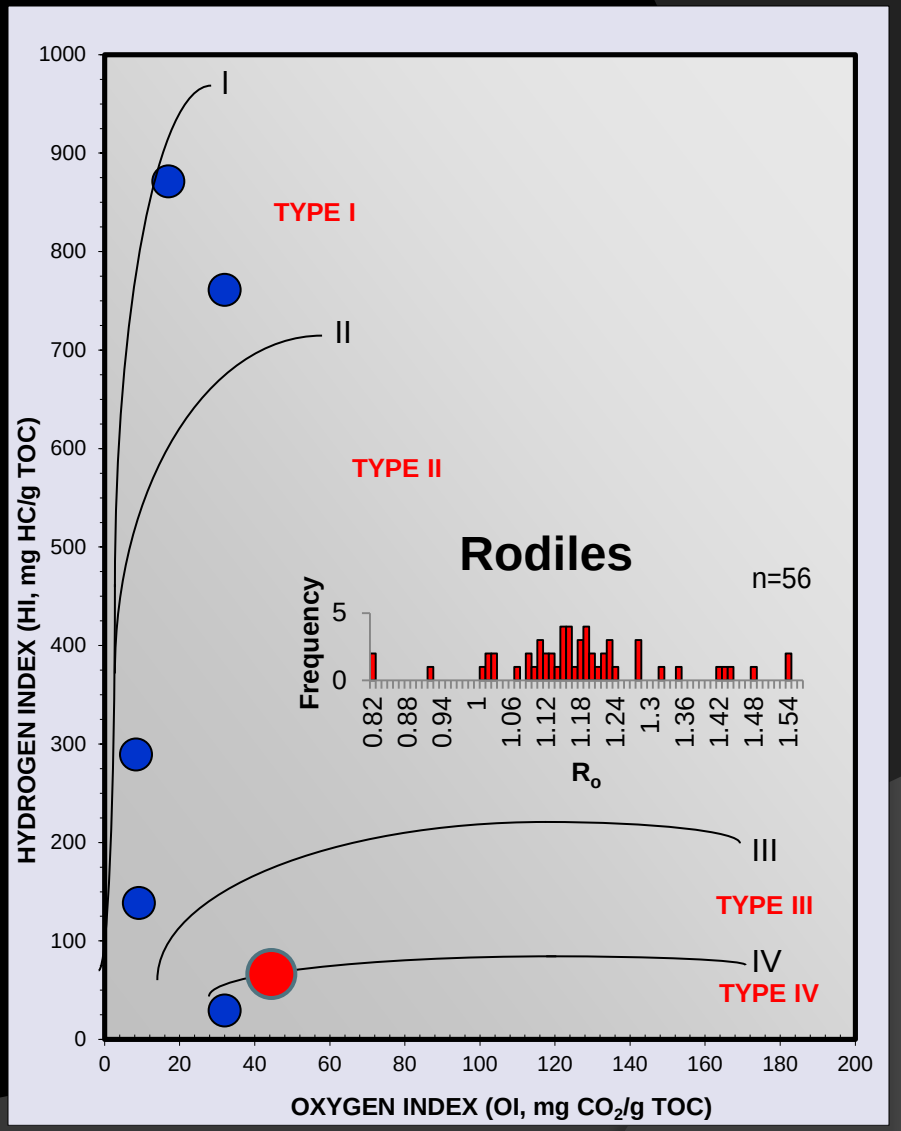


# Sample 4 – Rodiles Shale, Jurassic

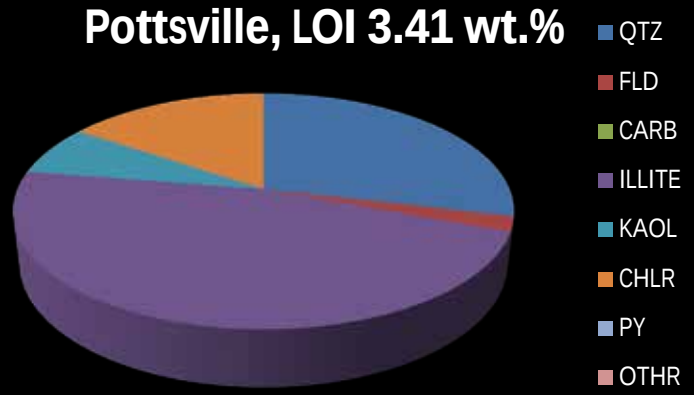



Sample contains multiple populations of recycled vitrinite/semifusinite. Contains bitumen with same reflectance as the indigenous vitrinite. Char particles abundant; six and eight spindle calcareous fossils

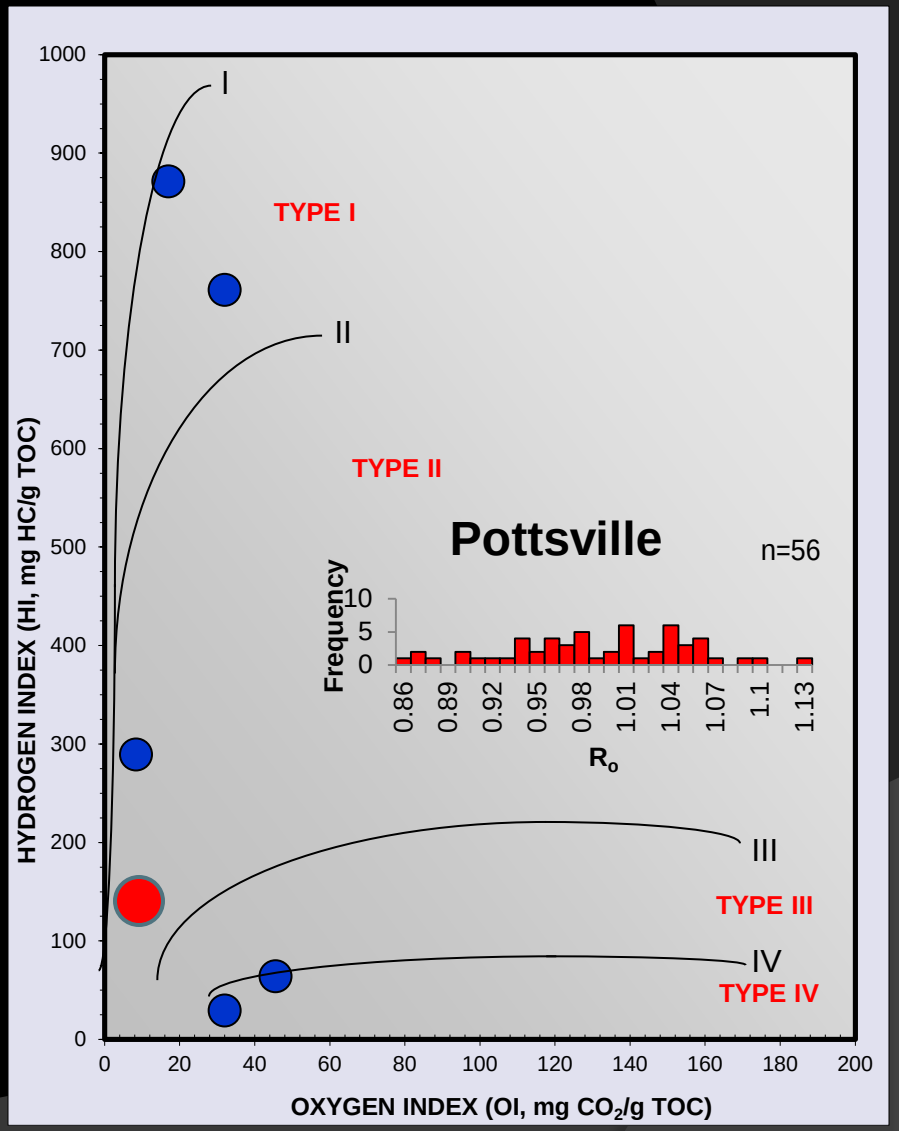


# Sample 5 – Pottsville Shale, Carboniferous

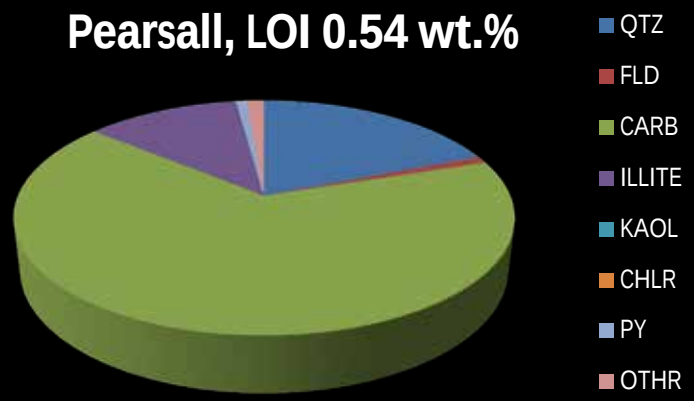


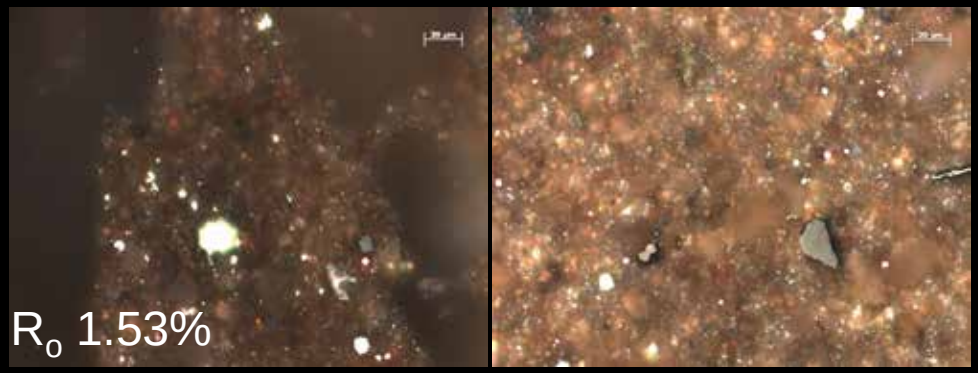


Sample is from coal measures, very organic rich; organic fluorescence is present but dim. High level of agreement in measurements (0.06 GSD). Some petrographers confused highly structured semifusinite for vitrinite.

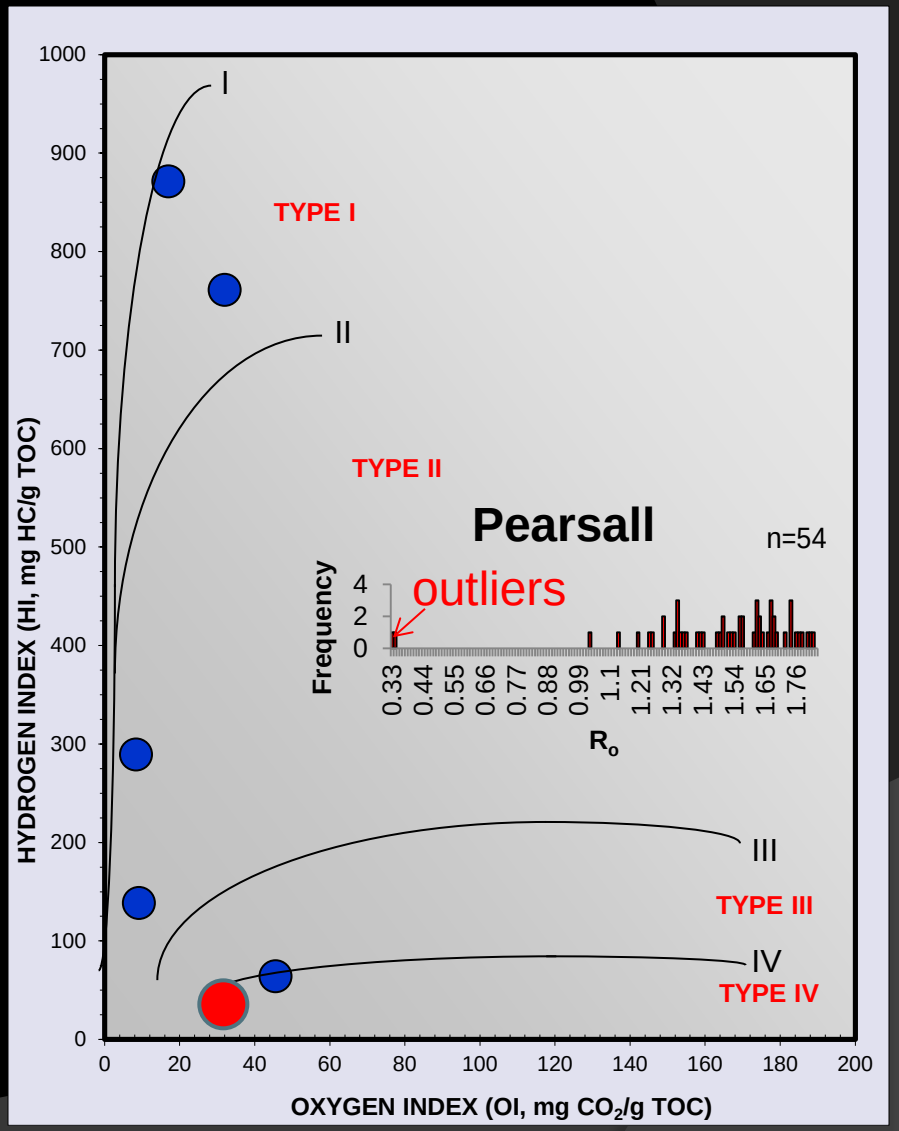


# Sample 6 – Pearsall Shale, Lower Cretaceous




Very organic-lean, most difficult sample. Vitrinite(?) grades into semifusinite. Euhedral authigenic carbonate (dolomite?) abundant. Contains textural bitumen with same reflectance as vitrinite.



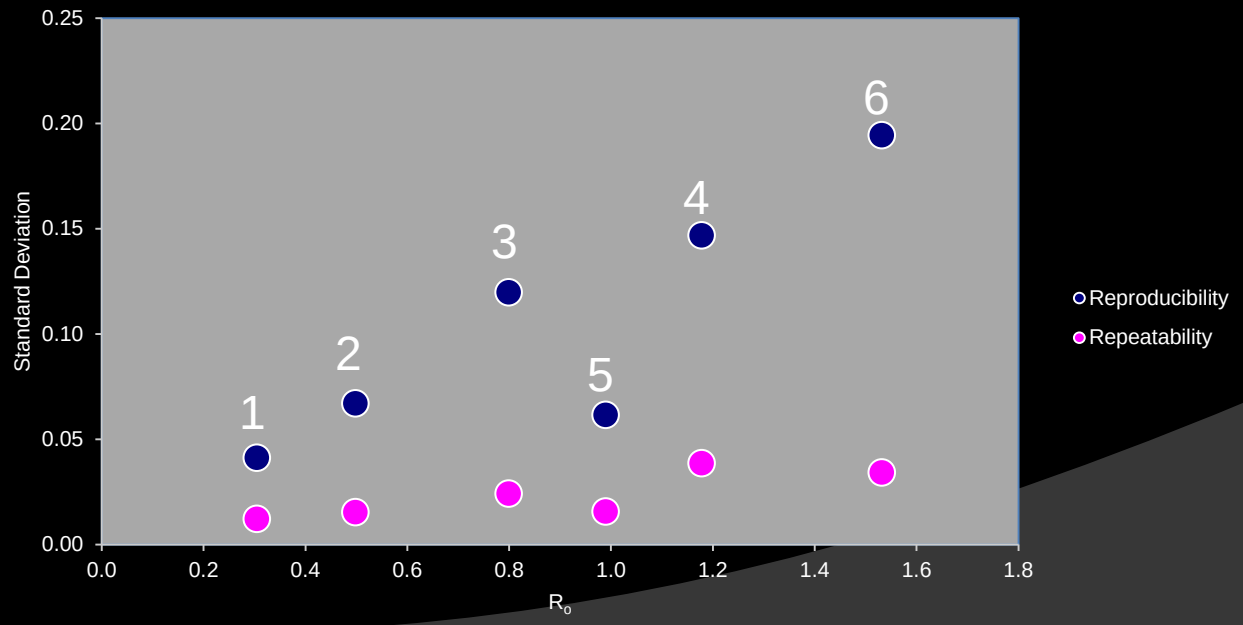
# Results – Precision Statistics

| | Material | Average | Repeatability Standard Deviation | Reproducibility Standard Deviation | Repeatability Limit | Reproducibility Limit |
|---|---|---|---|---|---|---|
| | | | $s_r$ | $s_R$ | r | R |
| 6 | Lower Cretaceous shale | 1.532 | 0.034 | 0.194 | 0.095 | 0.544 |
| 1 | Eocene shale | 0.305 | 0.012 | 0.041 | 0.034 | 0.115 |
| 3 | Devonian shale | 0.800 | 0.024 | 0.120 | 0.067 | 0.335 |
| 4 | Jurassic shale | 1.178 | 0.038 | 0.147 | 0.108 | 0.411 |
| 5 | Carboniferous shale | 0.990 | 0.015 | 0.061 | 0.043 | 0.172 |
| 2 | Upper Cretaceous shale | 0.498 | 0.015 | 0.067 | 0.043 | 0.187 |

$r=2.8*s_r$

$R=2.8*s_R$

Standard Deviations of Reproducibility and Repeatability Versus $R_o$




**Precision and Bias Statement, ASTM ballot closes April 7**

# DISCUSSION

- Use caution in converting bitumen reflectance to vitrinite reflectance equivalent!
- Difficulty in obtaining minimum of 20 measurements for compliance with ASTM. Added statement to reporting requirements that non-compliant values can be used as a *qualitative* thermal maturity indicator
- Additional ILS exercises are needed:
  - Similar samples – one with supporting information and one without, to test the hypothesis that supporting information will improve accuracy of test
  - High maturity samples with high TOC
- Development of online photomicrograph atlases

# DISCUSSION

- Many petrographers attempted to follow the ASTM reporting requirements but some disregarded the instructions completely. Therefore, a template clearly is needed in the standard to help petrographers conform to reporting requirements

DISPERSED VITRINITE REFLECTANCE REPORT

SAMPLE INFORMATION

Submitted by: P. Warwick
Date Submitted: 4.25.11
Project: Gulf Coast

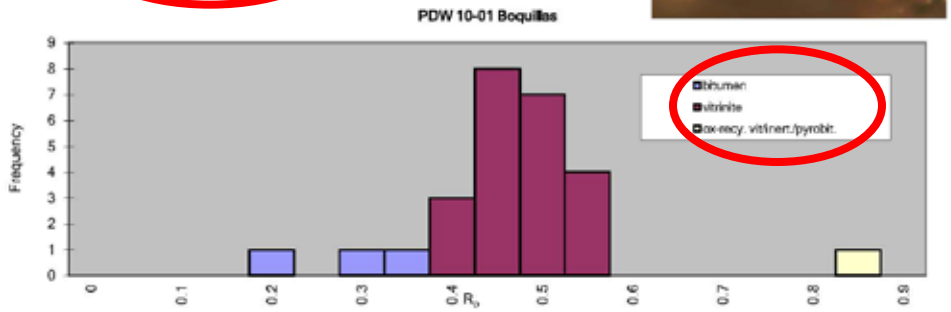
Sample ID: PDW 10-01 Boquillas
Lab ID: 1743
Sample Type: outcrop
Date Analyzed: 8.25.11
Operator: P. Hackley

Standard: ASTM D7708-11

RESULTS

No. measurements: 22
macerals type: vitrinite
s.d.: 0.05

Example Photograph:


DATA

| | | |
|---|---|---|
| 0.160 | 0.421 | 0.486 |
| 0.270 | 0.426 | 0.505 |
| 0.333 | 0.445 | 0.515 |
| 0.355 | 0.446 | 0.542 |
| 0.361 | 0.453 | 0.548 |
| 0.382 | 0.456 | 0.829 |
| 0.408 | 0.460 | |
| 0.408 | 0.462 | |
| 0.414 | 0.476 | |
| 0.415 | 0.480 | |

All Data: min: 0.160 max: 0.829

Vitrinite Only: min: 0.355 max: 0.548 V-types: 3

COMMENT

Middle Boquillas Fm., Upper Cretaceous, outcrop sample from Big Bend Park, Texas, dark gray laminated siltstone. Forams abundant, wispy AOM abundant, bitumen and bituminite present, good preparation and polish (1A Excellent), strong fluorescence. Whole-sample preparation by ASTM D2797.

U.S. Department of the Interior
U.S. Geological Survey

ICCP/DOM/VR/068
expires 6/30/2011

Eastern Energy Resources Team
Organic Petrology Laboratory

# Reporting

- 11.1.1 Mean and standard deviation of the readings of random reflectance of vitrinite, as percent reflectance in immersion oil, ***shall be noted***.
- The number of measurements collected shall be noted.
- The identification of macerals other than vitrinite presented in the reflectance table or histogram shall be noted.
- 11.1.2 Sample preparations and measuring equipment, or indication of compliance with Test Method D7708 and Practice D2797 shall be noted.
- Any descriptive information....shall be noted.
- Fluorescence.....shall be noted.
- Report the quality of sample preparation

# DISCUSSION

- Most important – compared to historical results, use of D7708 improves reproducibility!
- Mean R of 0.29% compared to 0.41%
  - For Ro < 1.0%, mean R of 0.20% compared to 0.35%
  - For Ro > 1.0%, mean R of 0.48% compared to 0.68%
- Make sure your Ro data are by D7708!

# THANKS!