ICCP WORKING GROUP IDENTIFICATION OF PRIMARY VITRINITE IN SHALE 2013 REPORT

Paul C. Hackley - U.S. Geological Survey, Reston, Virginia, USA

Presented for ICCP Commission II, August 27, 2013

Outline of this presentation

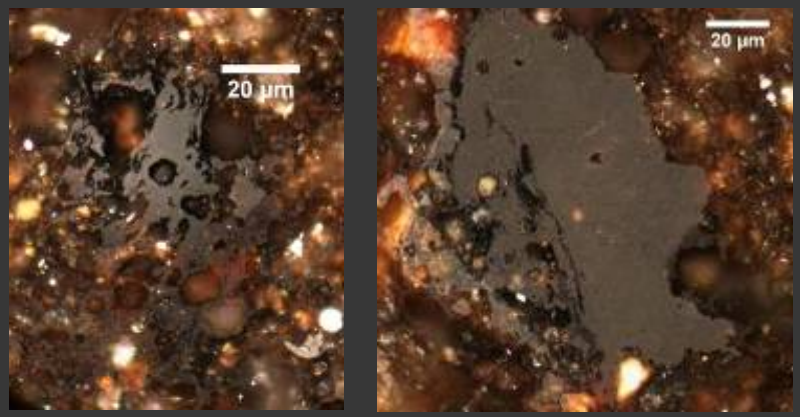
- Problem to be solved
- History of the working group
- 2012-2013 Shale Round Robin
- Discussion and Future Directions

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
- Poor polish
- Preparation: whole rock vs. kerogen concentrate

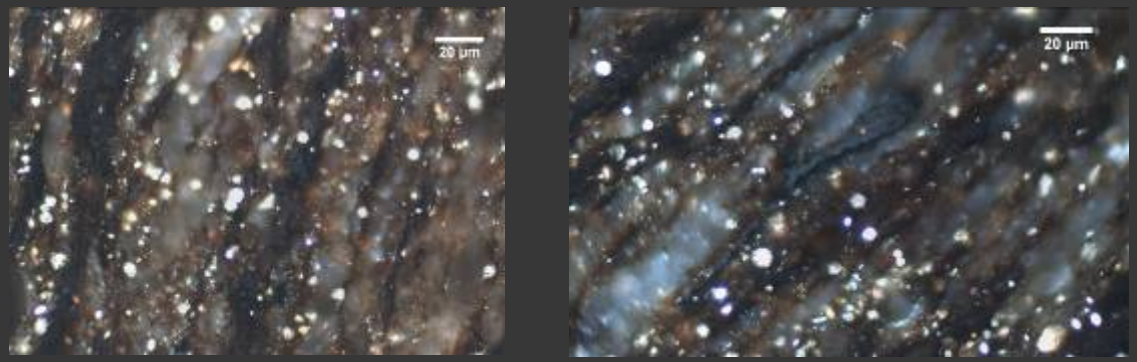
RECOGNITION OF PRIMARY VITRINITE

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

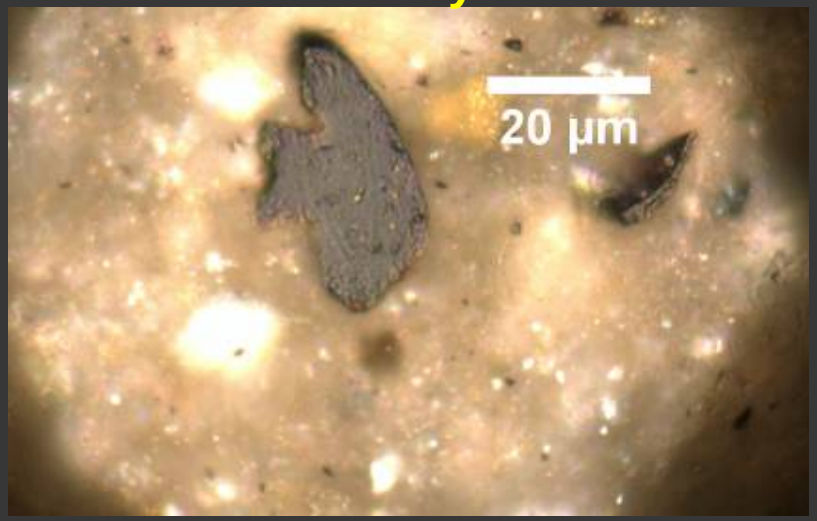
Distinction from bituminite



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

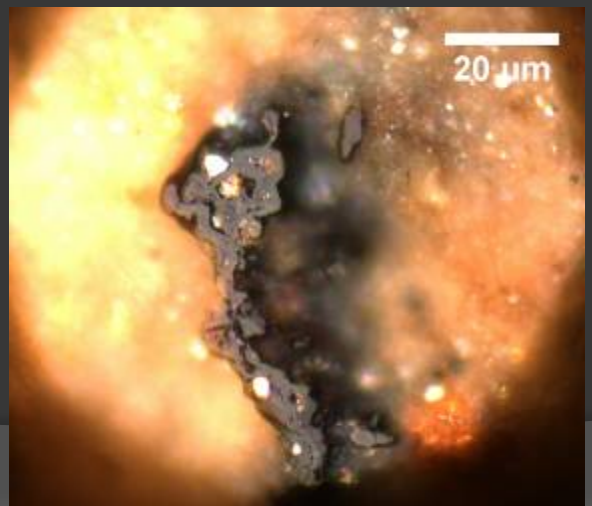
RECOGNITION OF PRIMARY VITRINITE

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 the working group

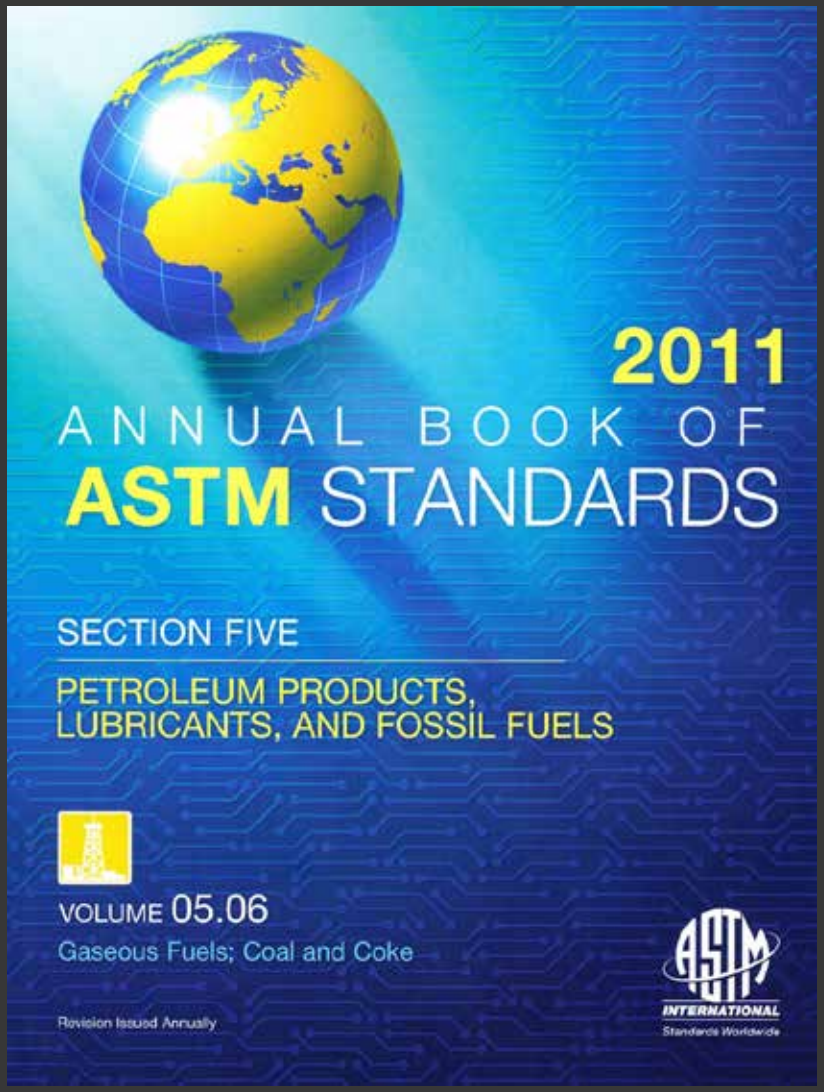
- Working group proposed by Angeles Borrego at September 2008 Oviedo ICCP meeting
- Questionnaire about DOMVR analysis and identification of primary vitrinite completed by April 2009
- Results of questionnaire presented at the 2009 Gramado meeting and published in ICCP News No. 48, Nov. 2009
- Proposal to create new ASTM standard for DOMVR presented and accepted during 2009 Gramado ICCP meeting
- D7708-11 published in 2011 Annual Book of ASTM Standards September 2011
- Proposal for round robin exercises to provide R&r for D7708-11 presented and accepted at 2011 Porto ICCP meeting

Oviedo 2008 ***Gramado 2009*** ***Belgrade 2010*** ***Porto 2011***

Identification of primary vitrinite: History of the 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, first presentation of results

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 lipinite 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.

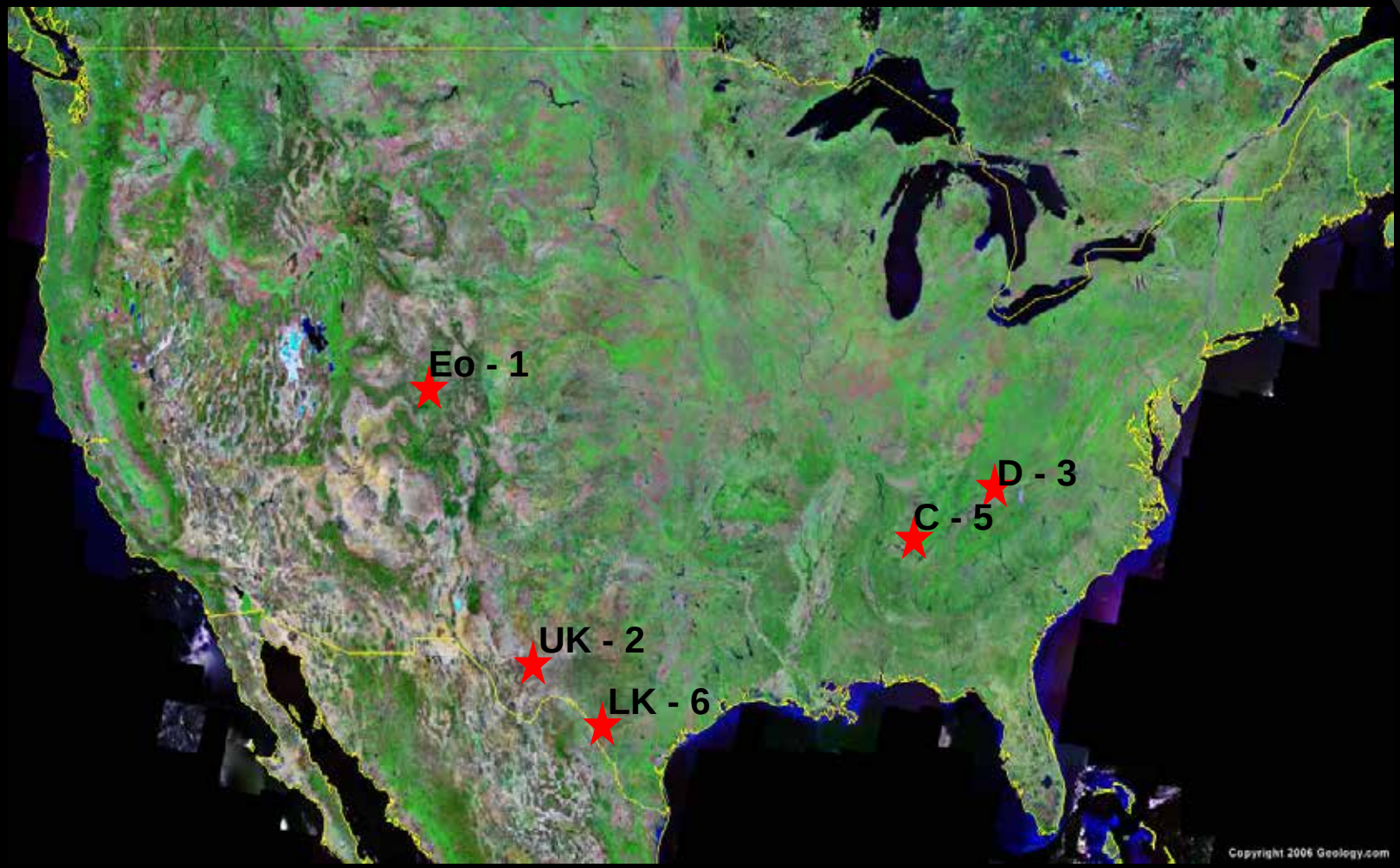
Use D7708, follow reporting requirements

Instructions distributed with samples

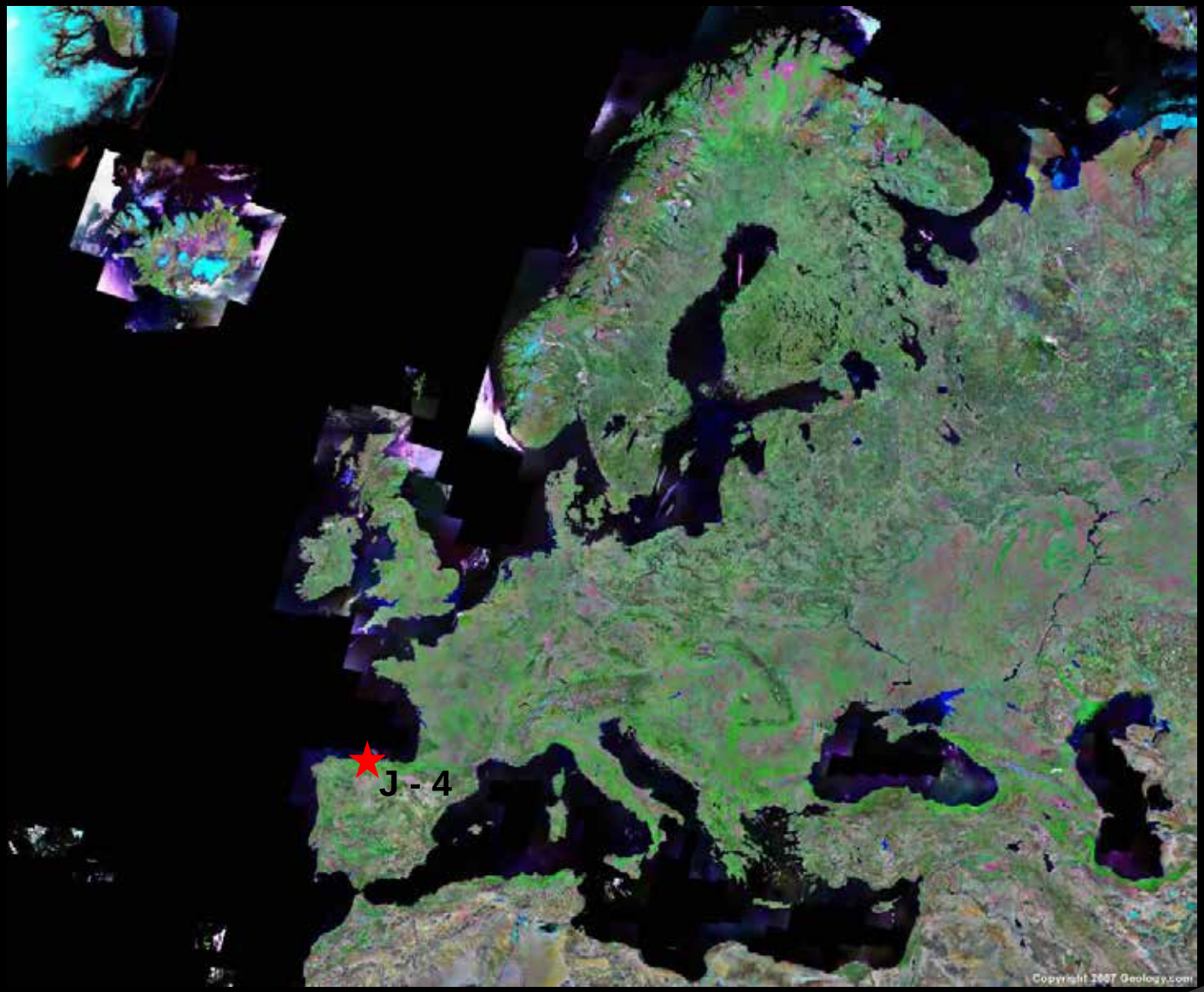
- Please read and follow ASTM D7708 carefully!
- Please follow reporting instructions!
- Please provide any commentary on samples and on ASTM D7708!
- Please contact convener with any questions about samples!

NAME	AFFILIATION	COUNTRY
Carla Viviane Araujo	Petrobras	Brazil
Angeles Borrego	INCAR	Spain
Antonis Bouzinos	Energy Resource Consulting	Australia
Brian Cardott	Oklahoma Geological Survey	USA
Cortland Eble	Kentucky Geological Survey	USA
Deolinda Flores	University of Porto	Potugal
Thomas Gentzis	Core Laboratories	USA
Paula Gonçalves	University of Porto	Portugal
João Graciano Mendonça	UFRJ	Brazil
Paul Hackley	U.S. Geological Survey	USA
Mária Hámor-Vidó	Geol. & Geophysical Inst.	Hungary
Iwona Jelonek	University of Silesia	Poland
Kees Kommeren	Shell (retired)	The Netherlands
Wayne Knowles	Weatherford	United Kingdom
Jolanta Kus	BGR	Germany
Maria Mastalerz	Indiana Geological Survey	USA
Taíssa Rêgo Menezes	Petrobras	Brazil
Jane Newman	Newman Energy Research	New Zealand
Mark Pawlewicz	U.S. Geological Survey	USA
Walter Pickel	Coal & Org. Pet. Services	Australia
Paddy Ranasinghe	GeoGAS	Australia
Harold Read	Coal & Org. Pet. Services	Australia
Julito Reyes	Geological Survey of Canada	Canada
Genaro Rodriguez	Servicio Geologico Mexicano	Mexico
Igor Viegas	Petrobras	Brazil
Isabel Suarez-Ruiz	INCAR	Spain
Ivana Sýkorová	Inst. Rock Structure and Mech.	Czech Republic
Brett Valentine	U.S. Geological Survey	USA

Twenty-eight participants, 22 laboratories, 14 countries

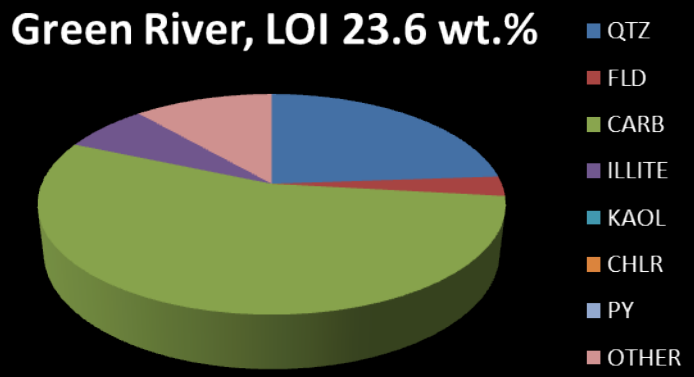


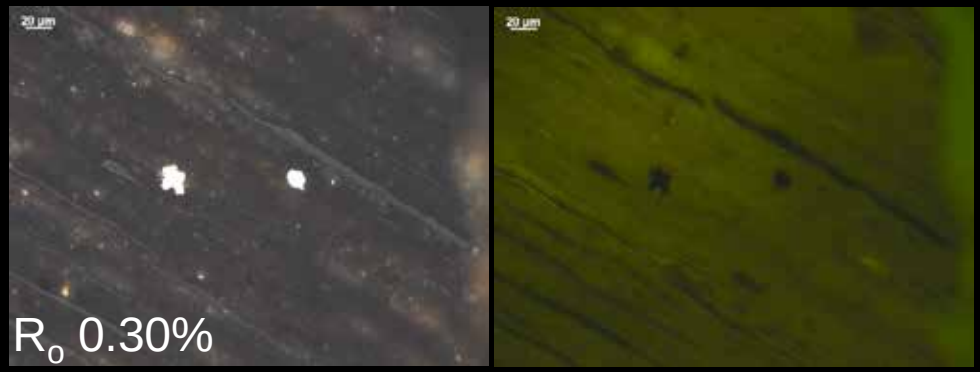
Sample Distribution – most are from USA



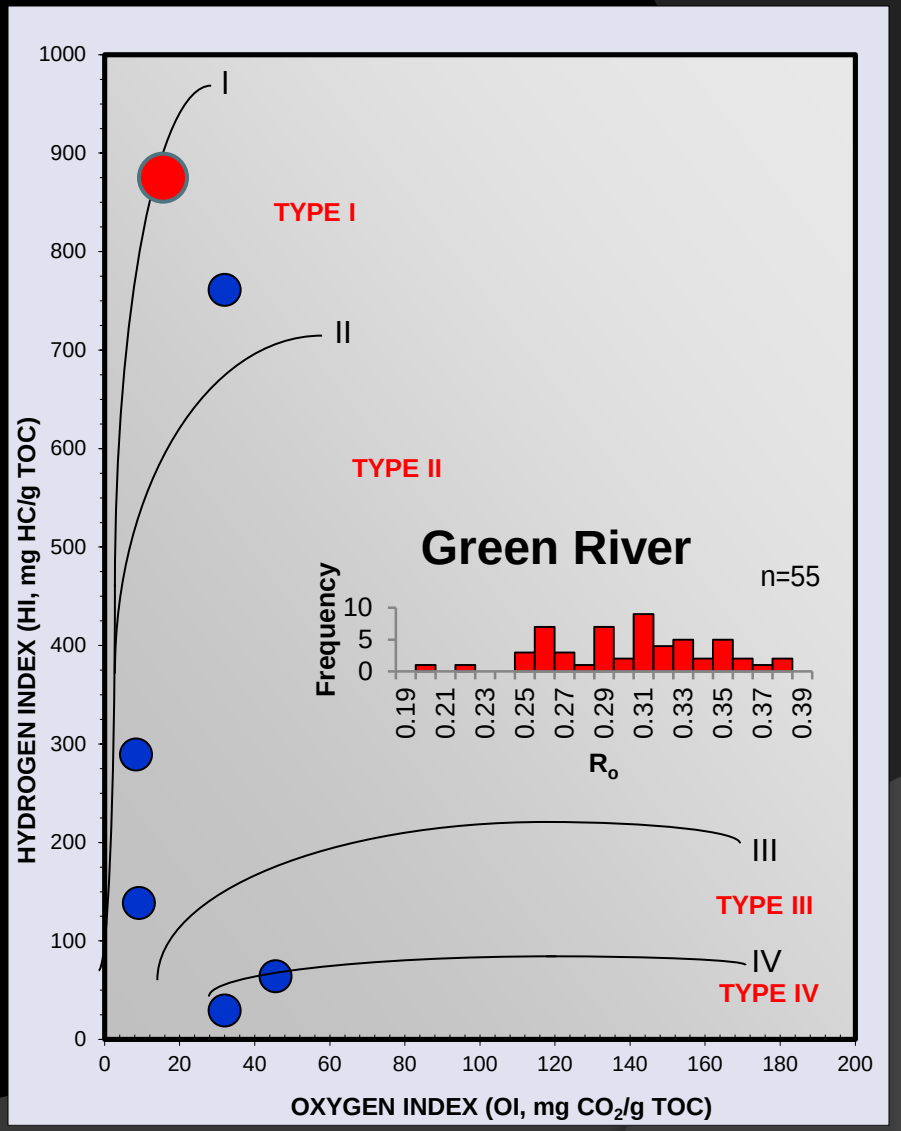
USGS

Sample 1 – Green River Shale, Eocene

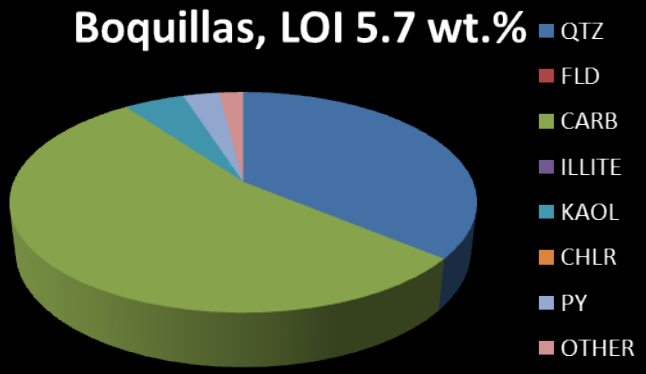


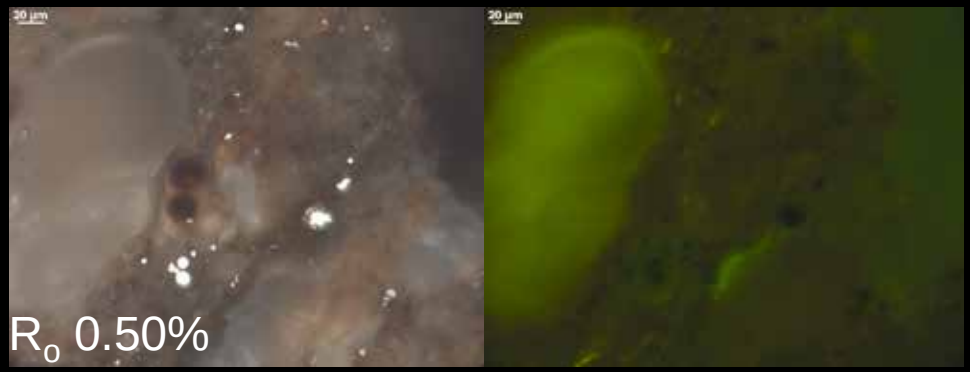


Material is bitumen per 3 petrographers (but Jacob's equation gives unrealistic conversion of >0.6%). Cellular structure is rare but present in some samples. AOM is abundant, fluorescence is very strong.

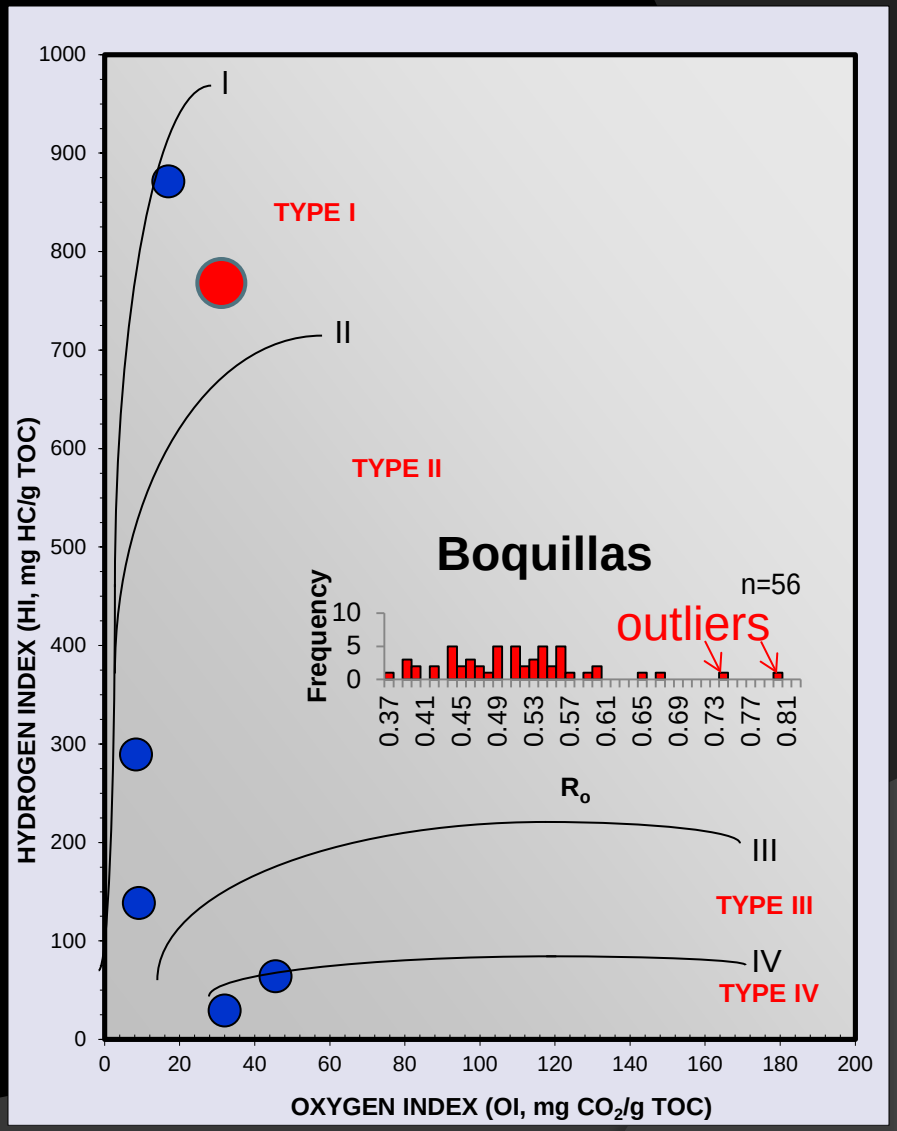


Sample 2 – Boquillas Shale, Upper Cretaceous

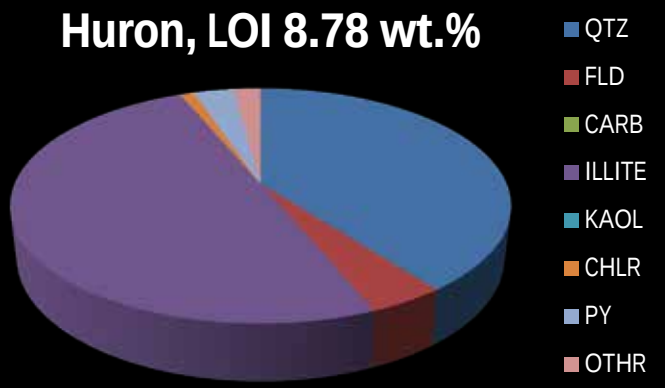


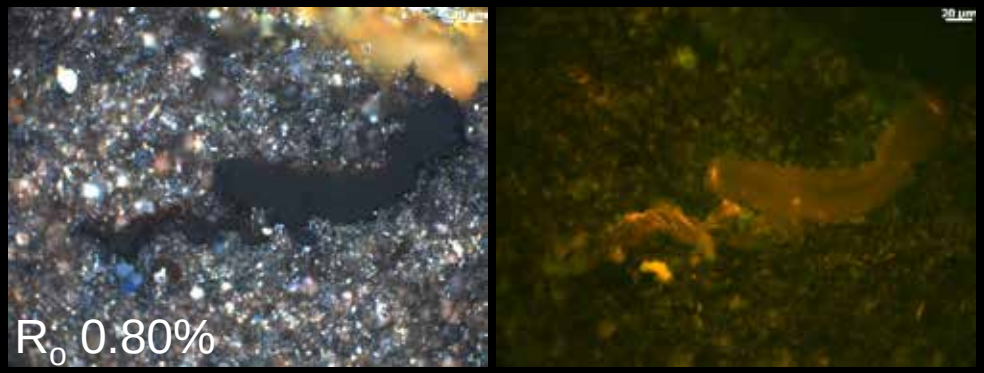


In addition to vitrinite, contains lower reflectance bitumen (R_o 0.25%) which was noted by several, but not measured. Foraminifera are abundant, AOM is relatively abundant, fluorescence is strong.

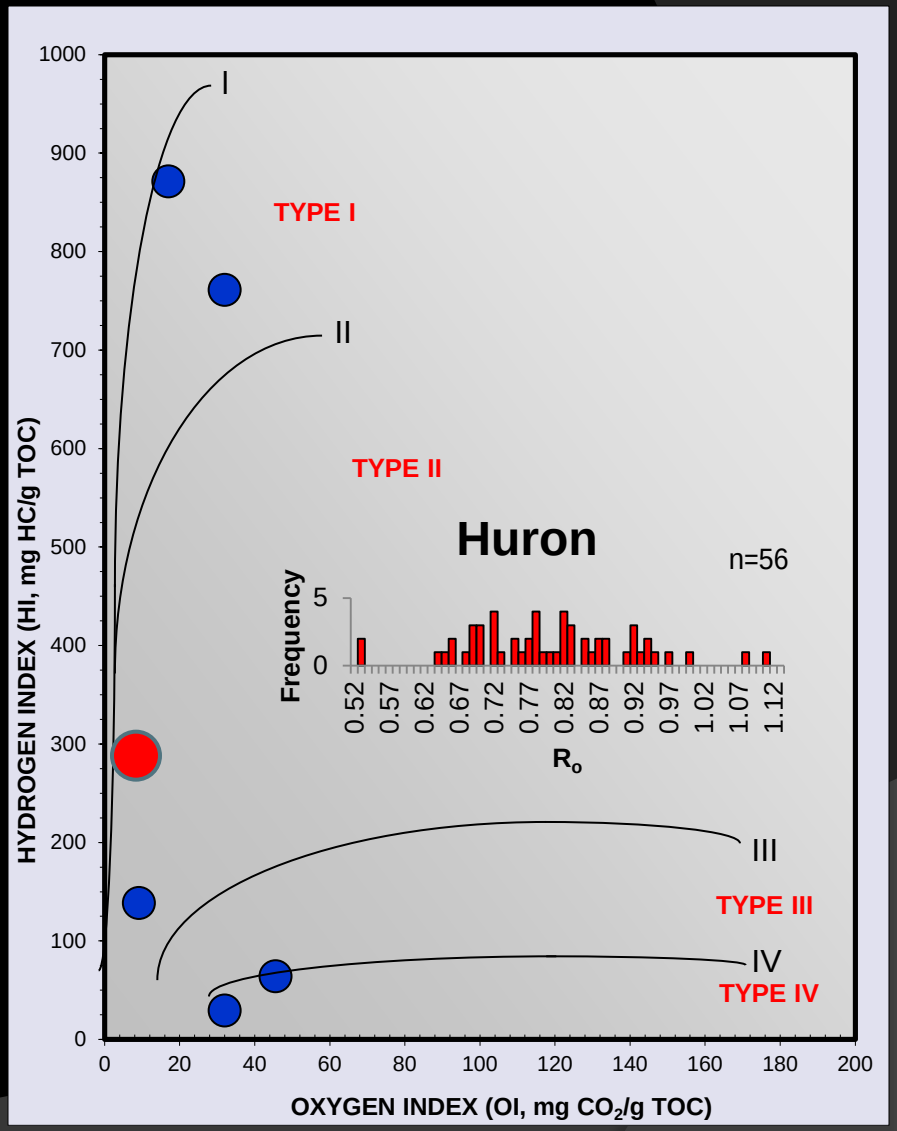


Sample 3 – Huron Shale, Devonian

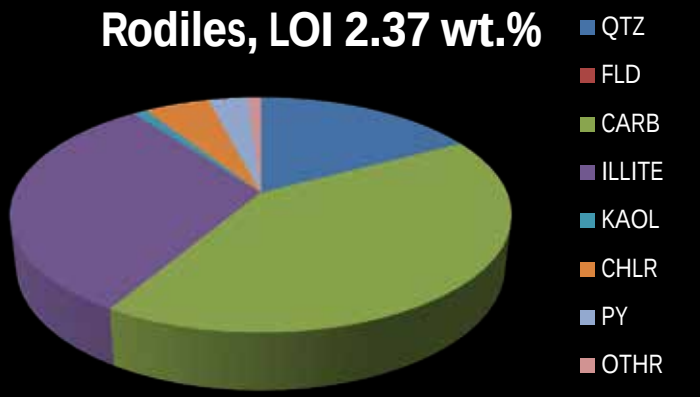


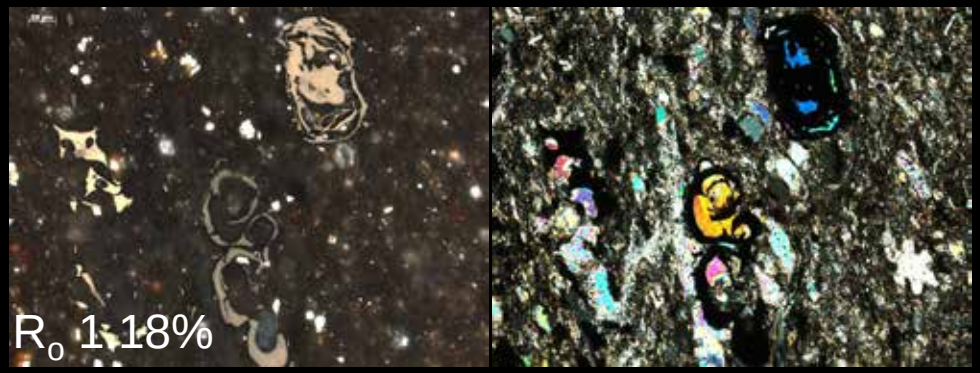


Vitrinite is rare or absent; four petrographers reported bitumen reflectance. Tasmanites is abundant (some misidentified for vitrinite or mega-spores) with strongly red-shifted fluorescence. Weathering (sulfates, oxides) prevalent.

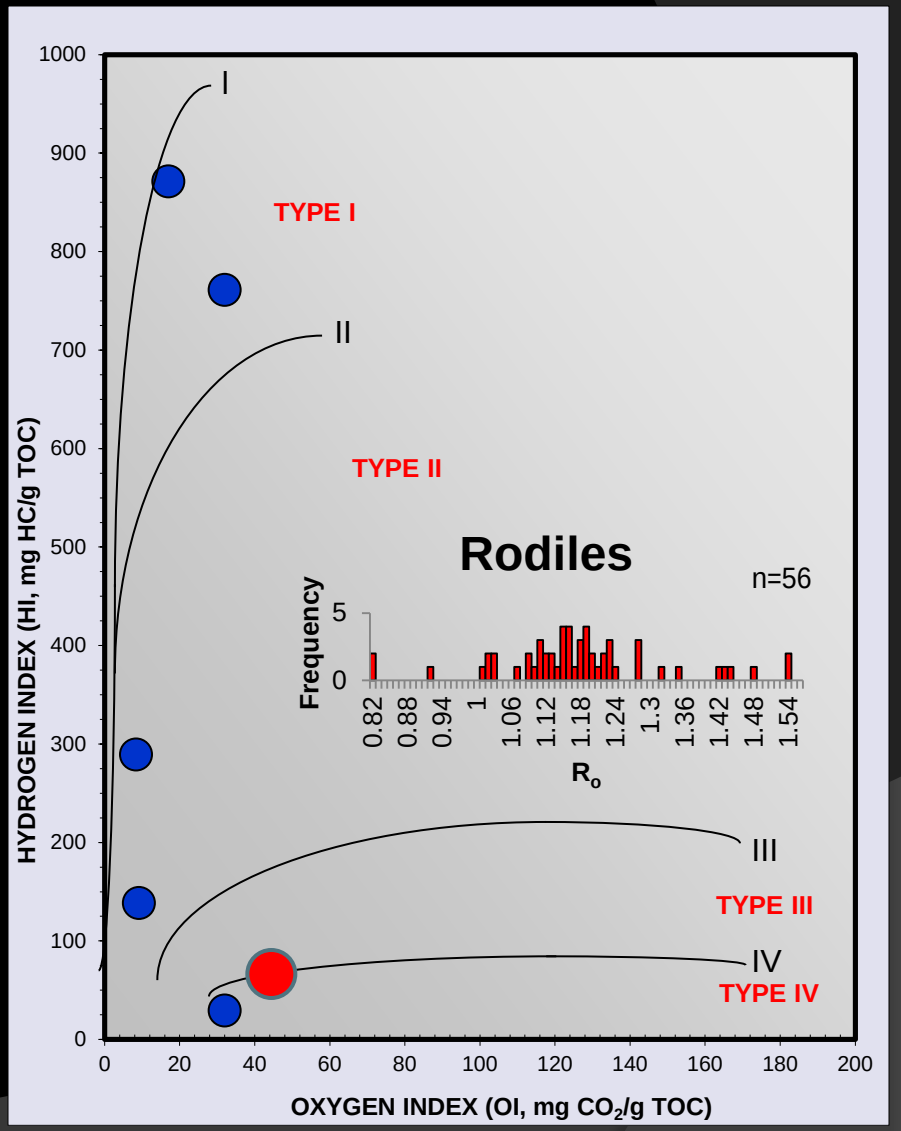


Sample 4 – Rodiles Shale, Jurassic

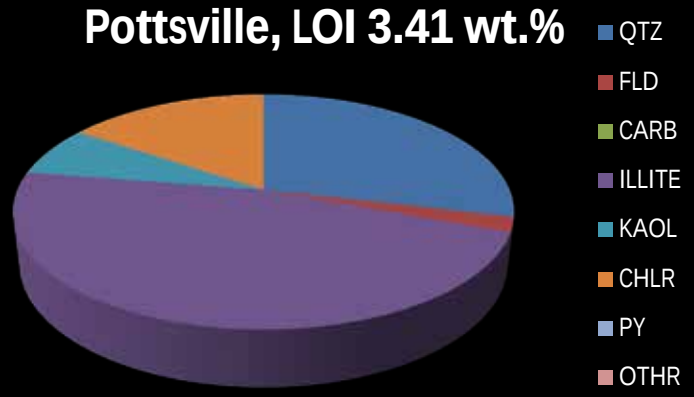




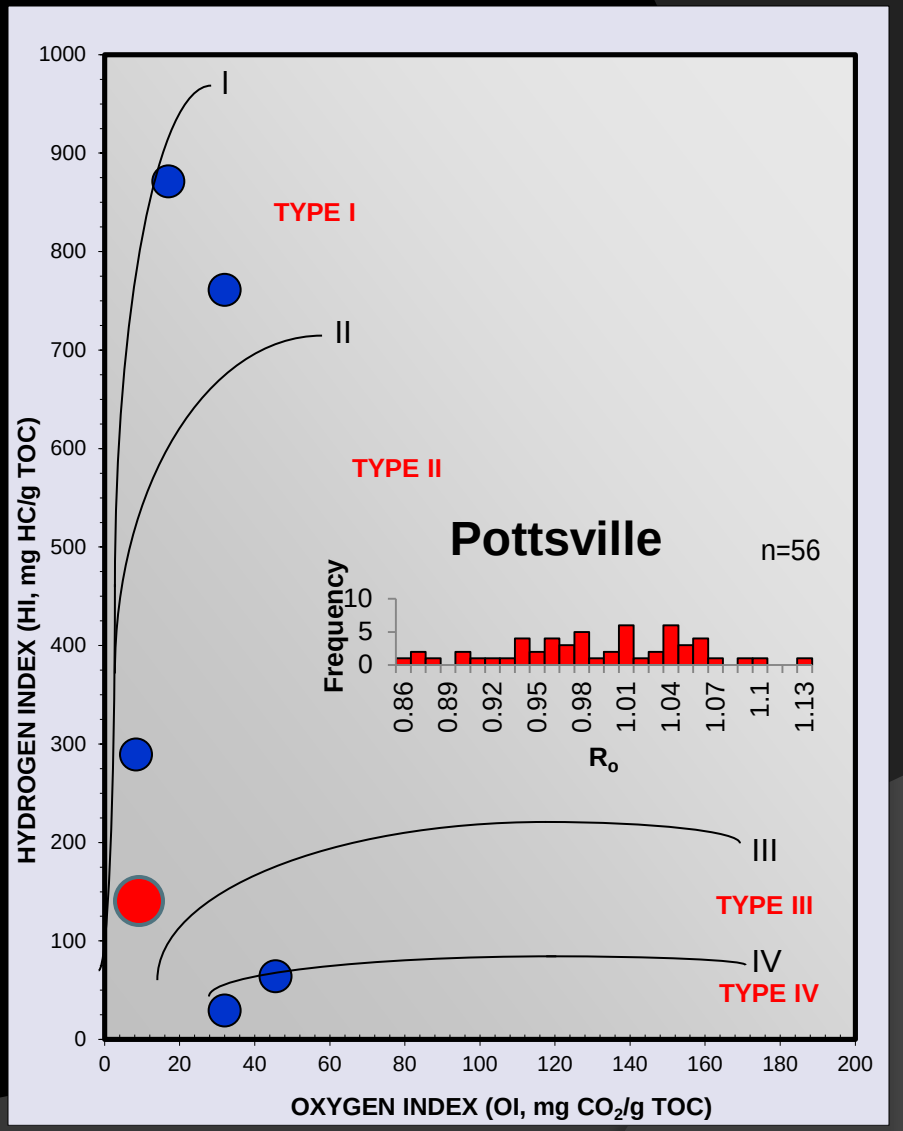
Sample contains multiple populations of recycled vitrinite/semifusinite. Contains bitumen with same reflectance as the indigenous vitrinite. Char particles abundant; six and eight spindle calcareous fossils



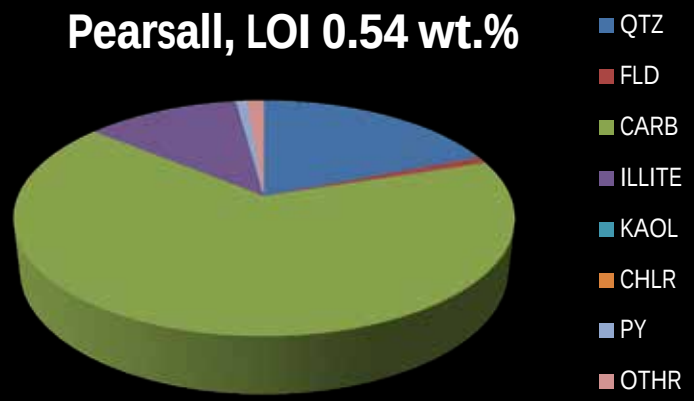
Sample 5 – Pottsville Shale, Carboniferous

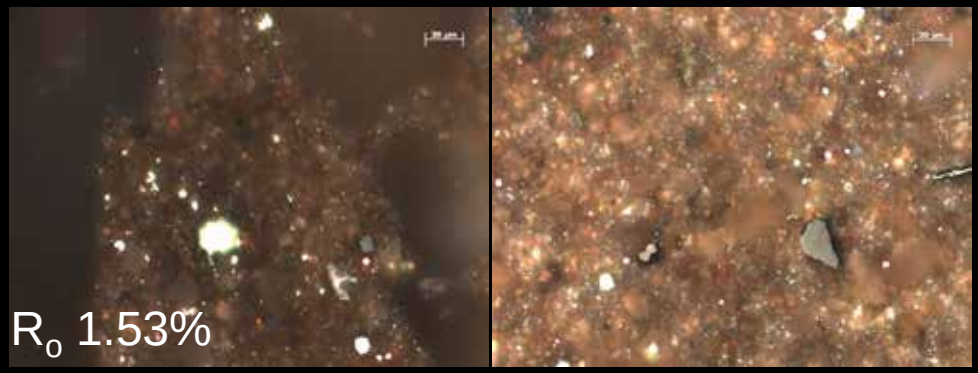


Sample is from coal measures, very organic rich; organic fluorescence is present but dim. High level of agreement in measurements (0.06 GSD). Some petrographers confused highly structured semifusinite for vitrinite.

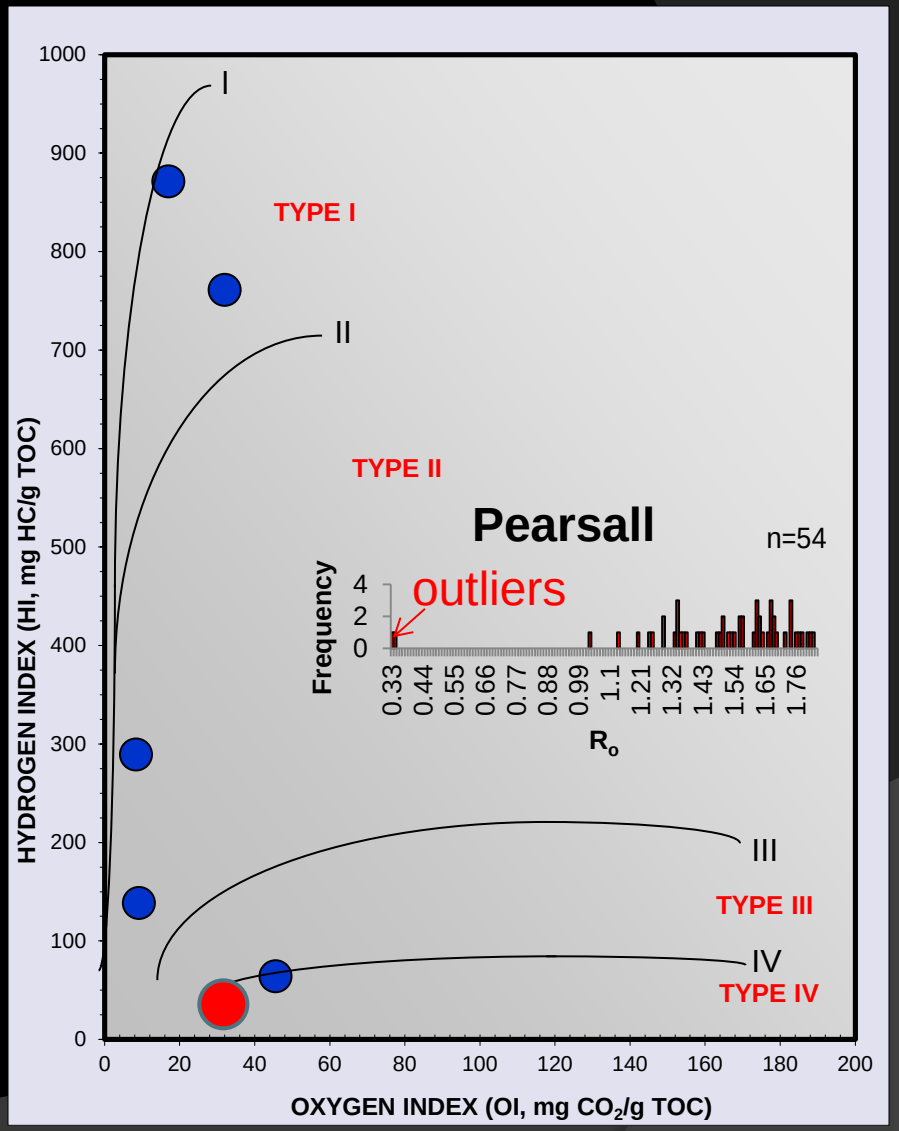


Sample 6 – Pearsall Shale, Lower Cretaceous





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



Comments from participants and some observations

- More difficult than daily work; samples need supporting data such as Rock-Eval, TAI/SCI, geological information
- Not easy but representative of rocks being analyzed in the oil and gas industry
- Only 2 persons asked about samples prior to analysis
- All petrographers (except the first to submit results) were provided preliminary feedback and opportunity to submit edited results
- Six petrographers submitted edited results: instrument calibration mistakes, sample preparation mistakes, identification mistakes
- Measurements on “semifusinite” included in precision statistics for sample 6
- Measurements on “bitumen” included in precision statistics for samples 1, 3, 4, and 6
- All petrographers reported proper order of increasing maturity: 1, 2, 3, 5, 4, 6

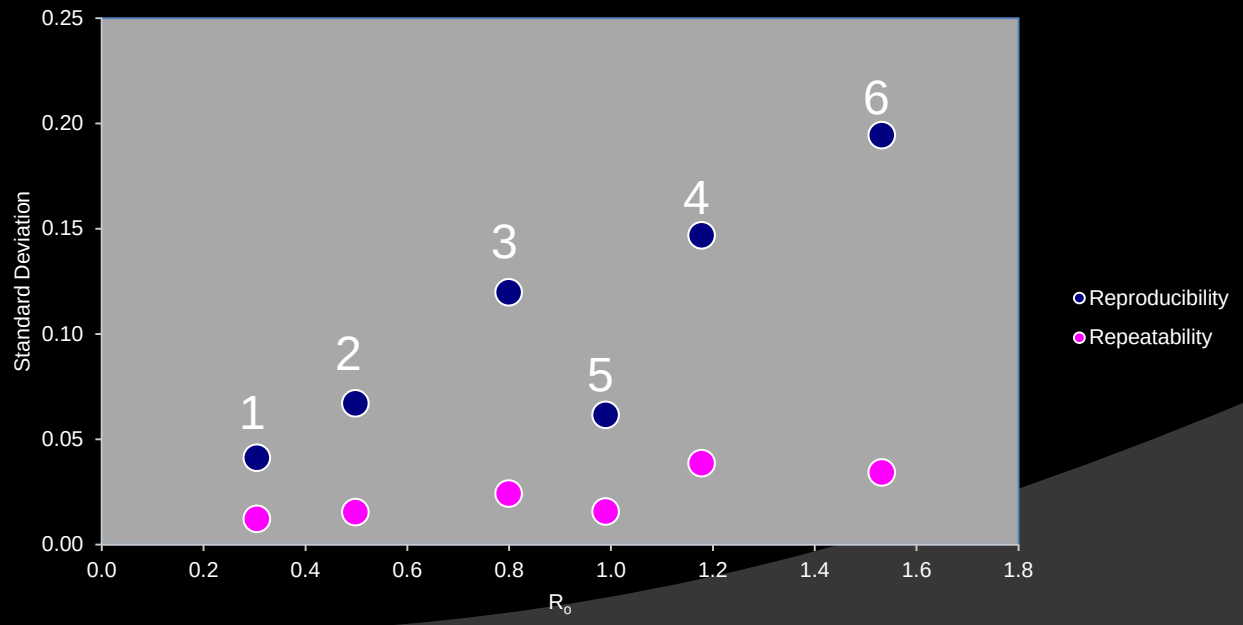
Results – Precision Statistics

	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 will be balloted ASAP

DISCUSSION

- Equipment impacts interpretation – an analyst unable to see Tasmanites fluorescence in sample 3 (Huron shale, R_o 0.80%) reported higher values than group mean. Require reporting of equipment type if fluorescence is noted? Require reporting of equipment type in general?
- Difficulty in obtaining minimum of 20 measurements for compliance with ASTM. Add statement to reporting requirements that non-compliant values can be used as a *qualitative* thermal maturity indicator?
- Do repeatability conditions assume that the analyst is aware they are analyzing an identical sample?
- Additional ICCP round robin exercises? Send out similar samples – one with supporting information and one without? To test the hypothesis that supporting information will improve accuracy of test?
- 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. Which one?

DISPERSED VITRINITE REFLECTANCE REPORT

SAMPLE INFORMATION

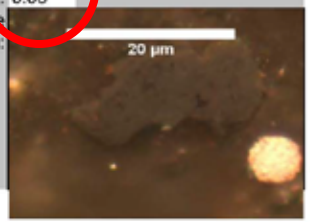
Submitted by: P. Warwick
Date Submitted: 4.25.11
Project: Gulf Coast

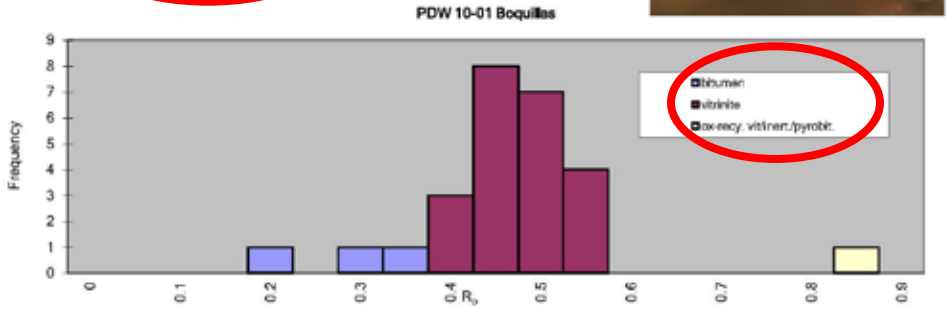
Sample ID: PDW 10-01 Boquillas
Lab ID: 1743
Sample Type: outcrop
Date Analyzed: 8.25.11
Operator: P. Hackley

Standard: ASTM D7708-11

RESULTS

No. measurements: 22
macerals type: vitrinite
mean: 0.45
std.: 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

USGS

newmanenergyresearch

2 Rose Street
Christchurch
New Zealand 8025
phone 64 3 3381 887
fax 64 3 3381 033
email j.newman@newmanenergyresearch.com

FINAL REPORT TO: Paul Hackley
U.S. Geological Survey
Reston, VA 20192
USA

DATE: 25 March 2013

Dispersed vitrinite reflectance[1], sample 1A

Sample	Ro ran %	N=	Standard deviation	Range %
1A	0.26	30	0.048	0.17 – 0.34

Table 1 Analysis results for Sample 1A. A chart and list of values appear on page 2 as Figure1 and Table 2.

Preparation & analysis: Samples are whole rock, prepared in broad agreement with ASTM D2797 with the exception that a hydraulic mounting press is not used. Measurements are made on a Zeiss UMSP50 petrological microscope using sapphire and garnet standards and Zeiss "F" immersion oil.

Polish: The polish on Sample 1A ranks "1A" (Excellent) on the alphanumerical scale defined by the ASTM D7708 test method. The criteria for this scale are reproduced on page 2 of this report.

Lithology: Sample 1A is a dominantly carbonate lithology with significant amorphous organic matter. There is evidence of microstructural disturbance and the rock matrix is sometimes intensely fluorescent particularly along fracture zones, which suggests a complex burial history. There is mineralogical evidence of hydrothermal activity.

Confidence in the vitrinite reflectance result as an indicator of thermal history: Sample 1A contains a restricted organic assemblage. Subjects with vitrinite morphology are considered likely to have an unusual chemistry. Although the reflectance of these subjects has been measured the result is considered unlikely to represent true vitrinite with orthohydrous chemistry. The subjects are also considered unlikely to be true vitrinite with perhydrous chemistry. Confidence in the reflectance result as an indicator of thermal history is consequently rated Very Poor according to Newman Energy Research Ltd criteria. The result is expected to substantially underestimate the maximum temperature experienced by the sample interval during burial history.

Recommendations: VIRF analysis might provide a more reliable indication of thermal history than standard VR but should be complemented by analysis of a more diverse suite of lithologies and by definition of a well constrained maturity profile for the entire succession, if suitable samples can be obtained.

Analyst: Jane Newman

[1] Performed according to ASTM standard D7708 unless otherwise noted

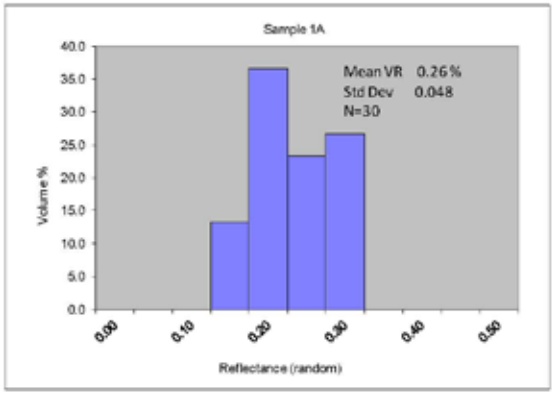


Figure 1 Reflectance data as histogram.

Table 2 Tabulated measurements

0.183	0.237
0.207	0.293
0.341	0.173
0.227	0.239
0.219	0.184
0.317	0.299
0.236	0.304
0.279	0.300
0.312	0.267
0.321	0.307
0.199	0.231
0.306	0.220
0.233	0.299
0.293	0.259
0.220	0.227

ASTM D7708 polish rating criteria

Proportion of the sample which has remained coherent at the polished surface:

1. Organic matter and associated mineral grains have remained coherent with binder and polished with minimal relief over >90% of the examination surface.
2. Organic matter and associated mineral grains have remained coherent with binder and polished with minimal relief over most of the examination surface.
3. Sample has suffered differential erosion; organic matter and associated mineral grains have remained coherent with binder and polished with minimal relief over a minority of the examination surface.

Quality of the polish on organic materials:

A. Within the coherent areas of the examination surface with minimal relief, >90% of the organic materials are free of pitting and scratching.
B. Within the coherent areas of the examination surface with minimal relief, >50% of the organic materials are free of pitting and scratching.
C. Within the coherent areas of the examination surface with minimal relief, most of the organic materials are pitted and scratched.

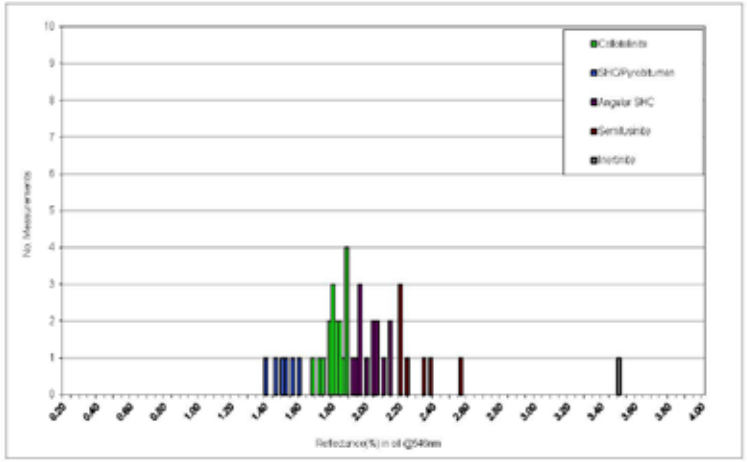
	1	2	3
A	**1A** Excellent	**2A** Very good	**3A** Poor
B	**1B** Good	**2B** Good	**3B** Very poor
C	**1C** Poor	**2C** Poor	**3C** Unusable

Reflectance Histogram

Weatherford LABORATORIES

WELL: DEPTH:

SAMPLE DATA					
API#		Country		Formation	
Operator		State		Age	
Client		County		WFT ID	BH-53405-3402923560
ClientID		Location		Sample Type	



VR READINGS *

1.39	1.46	1.50	1.52	1.55	1.59	1.67	1.72	1.73	1.77	1.78	1.79	1.80	1.80	1.82	1.82	1.83	1.83
1.86	*1.87*	*1.87*	*1.87*	*1.88*	*1.91*	*1.93*	*1.95*	*1.96*	*1.96*	*2.00*	*2.04*	*2.04*	*2.06*	*2.06*	*2.10*	*2.13*	*2.14*
2.19	2.19	2.20	2.24	2.34	2.38	2.56	3.49										

STATISTICS	Representative Vitrinite	Collodetrinite	Reworked Vitrinite
Mean:	1.81		
STDEV:	0.06		
Variance:	0.00		
Minimum:	1.67		
Maximum:	1.88		
Number:	17		

PHASE	MATURITY
Immature	<0.6%
Oil	1.1%
Wet Gas	1.1 - 1.4%
Dry Gas	1.4 - 4.0%
Postmature	>4.0%

UV COLORS	Landplant	Algal
Min. Color		Absent
Max Color		Absent
Min Maturity		>1.1
Max Maturity		>1.1

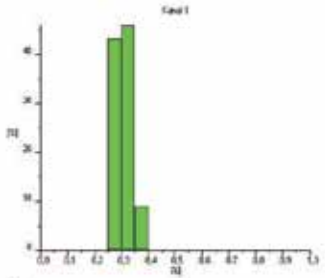
Comments

* Representative Vitrinite measurements in italics.

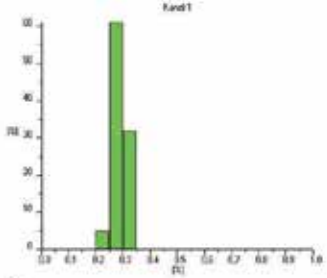
Report of Analysis Data: 1a and 1b

11.1.1:

ID Number	Lims Number	Mean random VR	SD	Number of Measurements
1a	1215836	0,31	0,0249	32
1b	1215837	0,29	0,0276	34



1a



1b

11.1.2:
Sample preparation: in compliance with DIN 22020-2:1998 (Investigations of raw material in hard coal mining – Microscopical examination of hard coal, coke and briquettes – Part 2: Preparation of polished surface from lump material and particulate blocks). Water free preparation technique was adopted.
Measuring equipment: in compliance with Test Method D7708

11.1.3:
Presence of fluorescence in the vitrinite: none
Presence of fluorescence in the liptinite: yes

Vitrinite reflectance suppression due to intense fluorescence: possible

11.1.4:
Presence of abnormal reflectance values at a given depth in an interval or profile: does not apply

11.1.5:
Distinguishing features of the first cycle vitrinite: stripes
Presence or absence of organic materials similar to first cycle materials: none observed
Distinguishing features of the organic materials similar to first cycle material: does not apply

11.1.6:
Check of measurements after re-polish: does not apply

11.1.7:
Quality of the sample preparation: (1)
Quality of the polish on organic materials: (A)

11.1.8:
Additional accompanying information such as depth and stratigraphic information: not provided.

Plate 2 A-D Vitrinite Reflectance Measurements, Histogram and Images

Company: USGS Round Robin Exercise
Formation N/A
Location: N/A
Depth (ft): N/A Well: Outcrop

Min Value	0.40
Max Value	0.53
Mean Value	0.44
# of Measurements	21
Strd Deviation	0.04

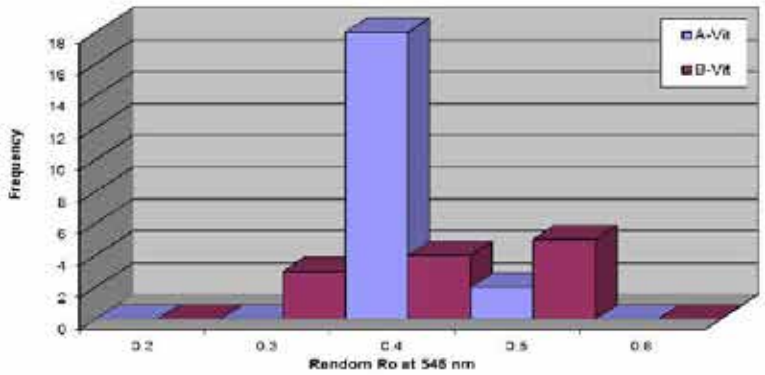
List of Ro Values in Increasing Order: (A)

0.40	0.40	0.41	0.41	0.41	0.41	0.41	0.41	0.42	0.42
0.43	0.43	0.43	0.44	0.45	0.45	0.48	0.49	0.52	0.53
0.53									

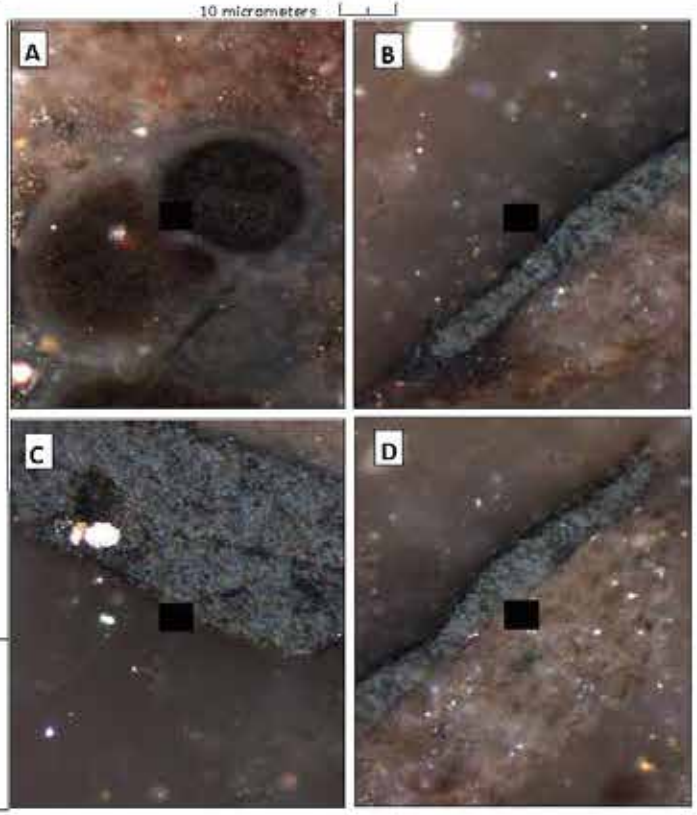
List of Ro Values in Increasing Order: (B)

0.38	0.39	0.40	0.41	0.41	0.41	0.43	0.51	0.51	0.52
0.53	0.53								

Histogram



10 micrometers



General Description

Photo Captions

Template and more discussion

- If we develop a template, how do we get petrographers to use it?
- Word? Excel? PowerPoint? Or simply an example included in D7708 in the ASTM book of standards?
- Make it available from the ASTM website?
    - **OTHER QUESTIONS**
- Is an exercise with kerogen concentrates necessary? What is the benefit to identifying primary vitrinite if textures are removed?
- Is extraction with organic solvents necessary? What is the benefit to identifying primary vitrinite if bitumens are not digested?
    - **NEXT DIRECTIONS**
- ICCP peer-reviewed publication: Draft 2013-2014
- Presentations at AAPG 2014, others, articles for newsletters, Oil and Gas Journal, etc.

Acknowledgments

- Participants in the DOMVR survey of 2009
- All members of the writing committee for ASTM D7708: Angeles Borrego, Carla Araujo, Brian Cardott, Maria Hámor-Vidó, João Graciano, Jane Newman, Mark Pawlewicz, Judith Potter, Isabel Suarez-Ruiz, Kees Kommeren
- Participants in the 2012-2013 ASTM D7708 round robin
- All Commission II members

- **THANKS ICCP!**