

# ***Direct Characterization of Kerogen by X-ray and Solid-State $^{13}\text{C}$ NMR Methods***

***26<sup>th</sup> Oil Shale Symposium***

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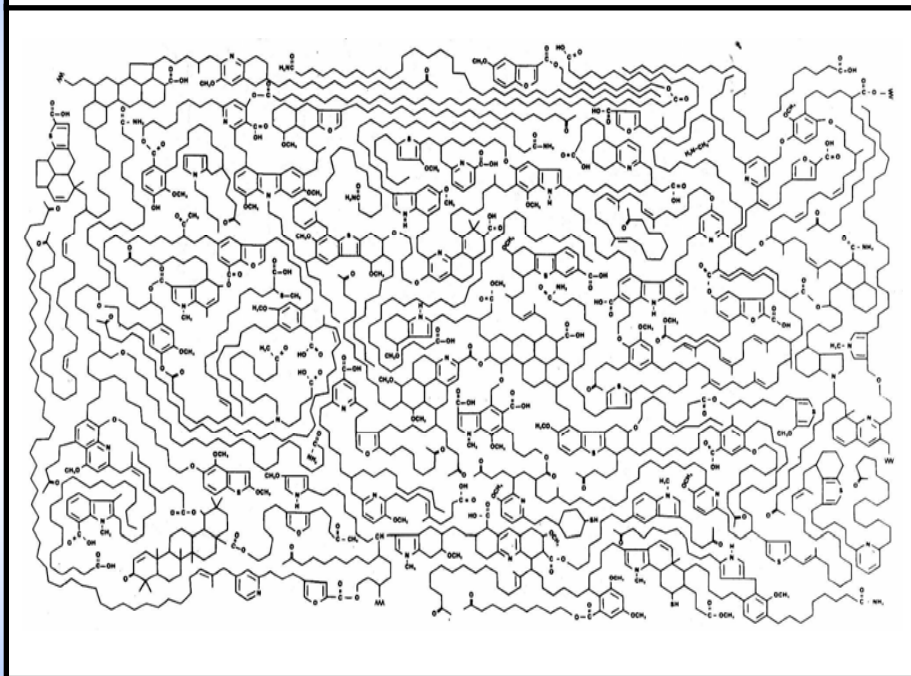
# ***Background***

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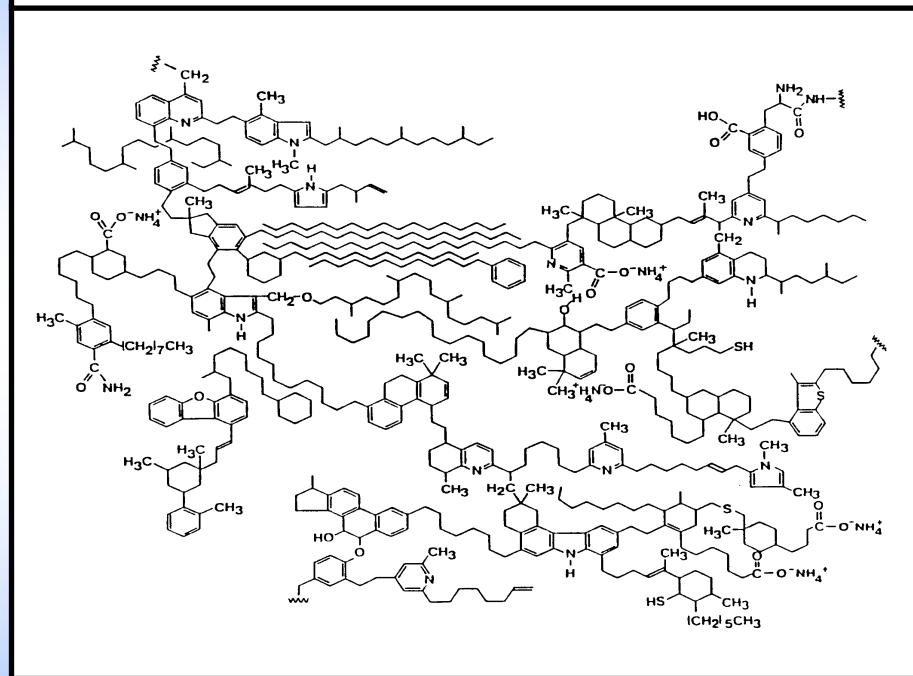
- **Understanding the chemistry of complex carbonaceous materials is aided by developing representative chemical structural models**
  - Ideally want to link chemical structure models to reactivity models
- **In the past, model development was aided by information gathered using an indirect characterization strategy**
  - Mildly decompose the organic solid, separate, identify and quantify the components using liquid and gaseous characterization methods
  - Employ selective nondestructive chemical derivatization and analysis
- **A large amount of chemical detail must be self-consistently integrated in order to derive a molecular level model of organic composition via indirect methods**
  - Approach has been used to elucidate chemical structure of the organic matter in Green River and Rundle Ramsey Crossing Oil Shale

# Original Organic Matter Models for Rundle and Green River Oil Shale from Indirect Characterization

## Rundle Organic Matter Model



## Green River Organic Matter Model



Scouten, C. G.; Siskin, M.; Scouten, C. G.; Rose, K. D.; Axzel, T.; Colgrove, S. G.; Pabst, R. E., Jr.; Prepr. Am. Chem. Soc., Div. Pet. Chem. **1989**, 36 (1), 43

Siskin, M.; Scouten, C. G.; Rose, K. D.; Axzel, T.; Colgrove, S. G.; Pabst, R. E., Jr.; in *Geochemistry and Conversion of Oil Shales*, ed. By C. Snape, NATO Series, **1995**

## ***Inherent Uncertainties with Indirect Characterization***

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- **Mildly decompose the organic solid and analyze products**
  - Incomplete decomposition of the organic solid
  - Chemical transformation during decomposition
- **Chemical derivatization and analysis**
  - Non-selective, incomplete or destructive derivatization of organic matter
  - Accuracy of methodologies to quantify derivatized products
- **Combination of Indirect characterization with new direct characterization methods can mitigate uncertainties**

# ***Direct Chemical State Probes for Carbonaceous Materials***

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- **Significant advances made over the past decade for different direct chemical state probes of complex carbonaceous samples**
  - Provides average chemical composition
- **X-ray Photoelectron Spectroscopy (XPS)**
  - Heteroatom (N, S, O), higher energy/spatial resolution, non-conducting samples
- **X-ray Absorption Near Edge Structure Spectroscopy (XANES)**
  - Sulfur, Carbon and Nitrogen
- **Solid-State NMR Spectroscopy**
  - $^{13}\text{C}$  NMR for Carbon structures & oxygen functionalities,  $^{15}\text{N}$  NMR for speciation
- **Multiple technique strategy developed to quantify the average chemical structure of kerogen including Green River and Rundle oil shale (Type I Kerogen)**

# Multiple Technique Strategy for Defining the Organic Composition of Complex Carbonaceous Solids

## Carbon (H) Chemical/Skeletal Features

Feature ↔ Approach	Feature ↔ Approach
H/C Elemental Analysis	Average Aromatic Ring Size <sup>13</sup> C NMR
% Aromatic/Aliphatic Carbon <sup>13</sup> C NMR XPS	Aromatic/Naphthenic Ring Size Distribution Indirect Methods
% Methyl Carbon <sup>13</sup> C NMR	Average Aliphatic Carbon Chain Length <sup>13</sup> C NMR
Fraction of Aromatic Carbon with Attachments <sup>13</sup> C NMR	Alkyl Carbon Chain Length Distribution (Isomerization) Indirect Methods

## Organic Forms of Oxygen

Feature ↔ Approach	Feature ↔ Approach
Aromatic C-O <sup>13</sup> C NMR	O/C Elemental Analysis XPS
Aliphatic C-O O-CH <sub>3</sub> <sup>13</sup> C NMR	Σ C-O XPS
C=O <sup>13</sup> C NMR	C=O, O-C-O XPS
O=C-O, O=C-N <sup>13</sup> C NMR	O=C-O, O=C-N XPS

## Organic Forms of Sulfur

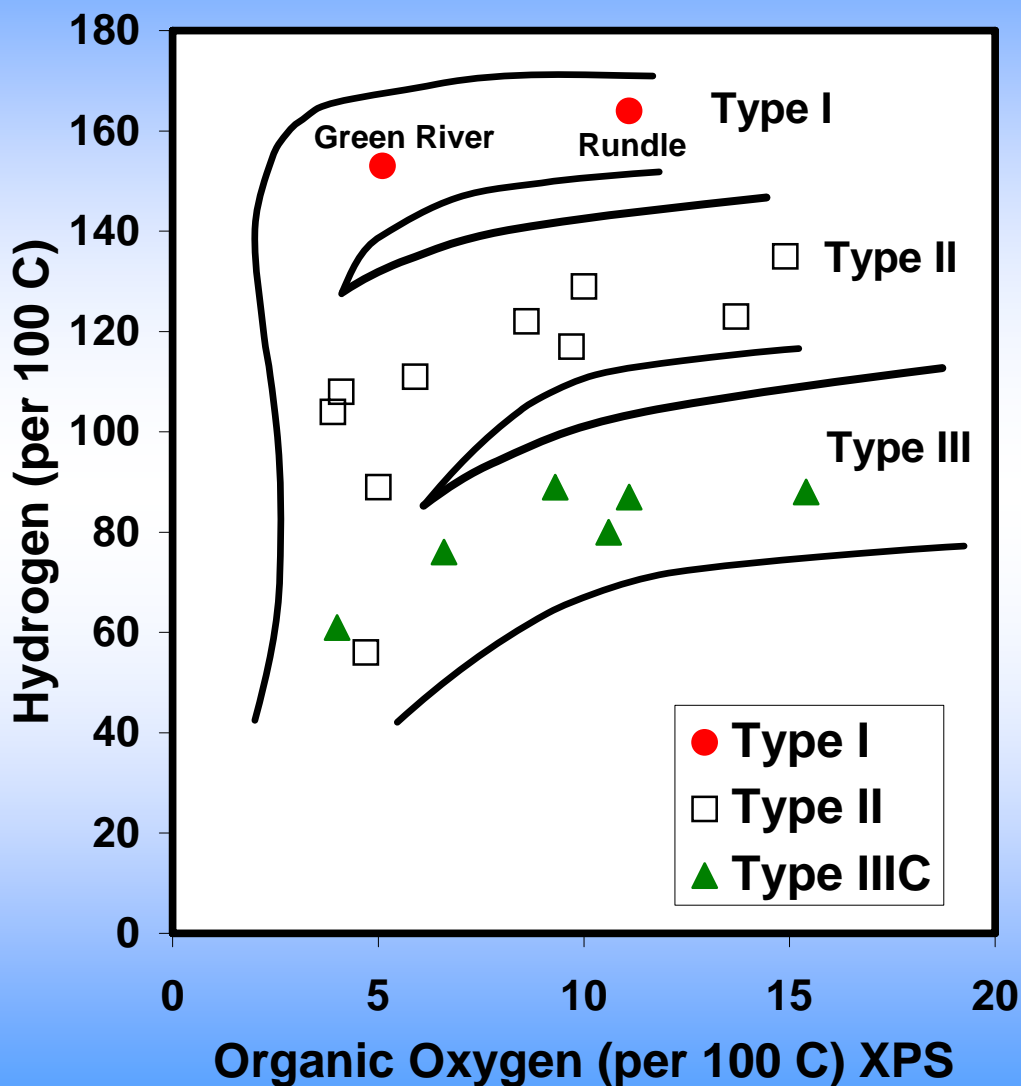
Feature ↔ Approach	Feature ↔ Approach
R-S-S-R XANES XPS	S/C Elemental Analysis XPS
R-S-R(H) XANES XPS	Thiophenic XANES XPS
Ar-S-Ar(H) XANES XPS	SO, SO <sub>2</sub> , SO <sub>3</sub> XANES XPS

## Organic Forms of Nitrogen

Feature ↔ Approach	Feature ↔ Approach
Pyridinic <sup>15</sup> N NMR XPS, XANES	N/C Elemental Analysis XPS
Amine <sup>15</sup> N NMR XPS, XANES	NO, NO <sub>2</sub> <sup>15</sup> N NMR XPS, XANES
Amide <sup>15</sup> N NMR XPS, XANES	Pyridinic (O-Environment) <sup>15</sup> N NMR XPS, XANES
Pyrrolic <sup>15</sup> N NMR XPS, XANES	Quaternary (Amonium Salt) (Pyridinium ion) (Ar-Bridgehead) <sup>15</sup> N NMR XPS, XANES

10-100 micron Spectroscopy (Yes)

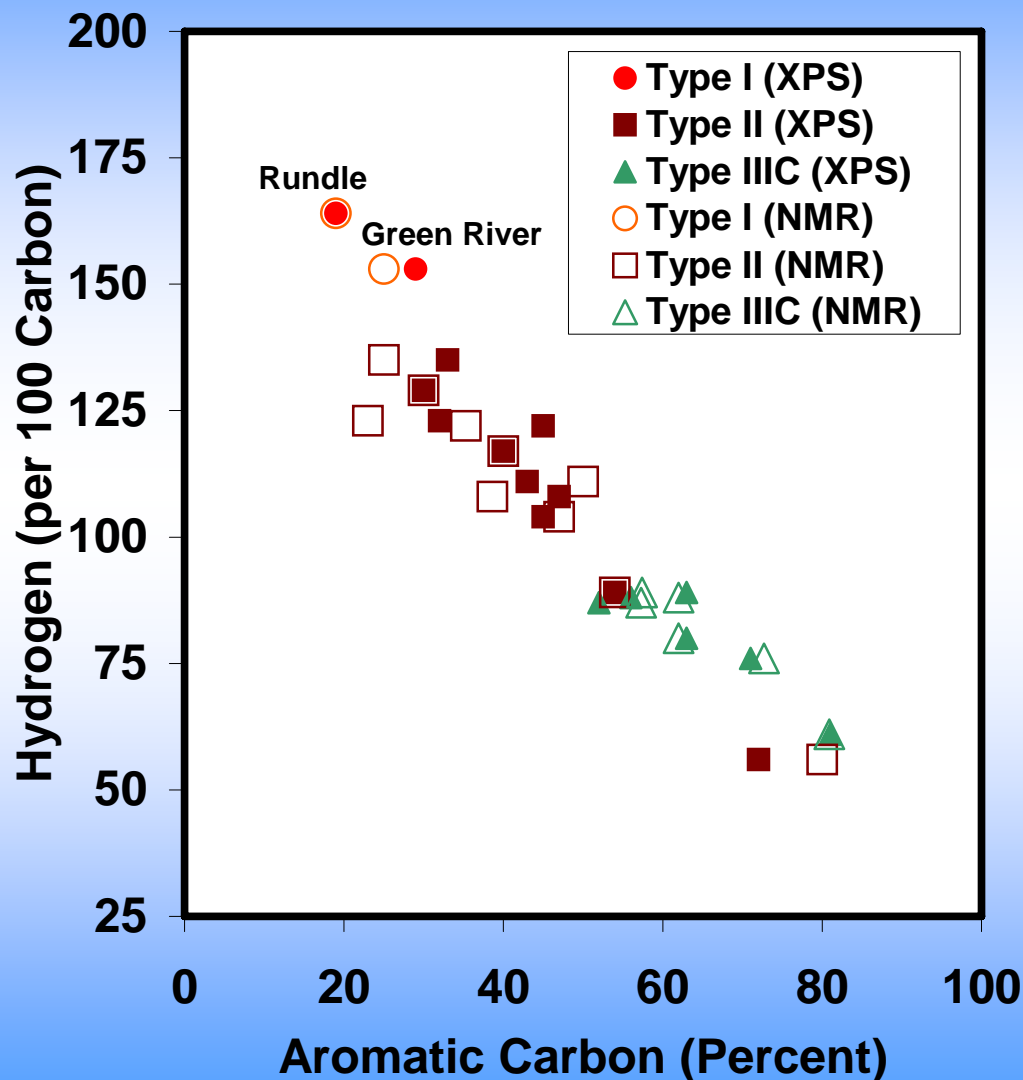
# Van Krevelen Diagram for Kerogen and Rock-Eval Data



Sample	Kerogen Type	Rock-Eval	
		Tmax (°C)	Hydrogen Index (mg/g)
Green River	I	446	739
Rundle	I	444	995
Duvernay (A)	II	414	532
Duvernay (B)	II	438	439
Duvernay (C)	II	443	242
Duvernay (D)	II	479	22
Oxford Clay	II	413	577
Paradox	II	438	401
Malm	II	420	670
Draupne	II	424	581
Bakken	II	419	580
Monterey	IIS	411	621
Gippsland (A)	IIIC	415	251
Gippsland (B)	IIIC	436	226
Proprietary (A)	IIIC	427	295
Proprietary (B)	IIIC	453	235
Proprietary (C)	IIIC	479	120
Fruitland	IIIC	424	237

- Lacustrine source rocks from the Green River and Rundle formations contain hydrogen-rich algal kerogen (Type I) derived primarily from cyanobacteria or various Chlorophyta and dinoflagellates, respectively

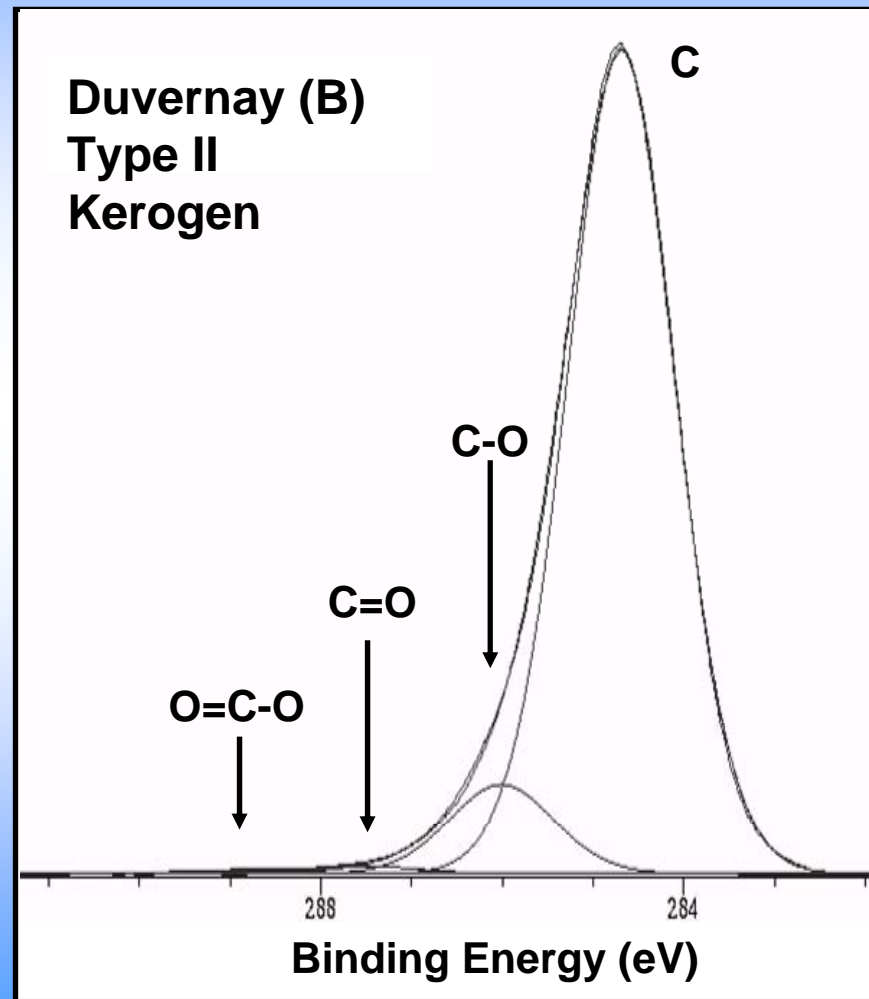
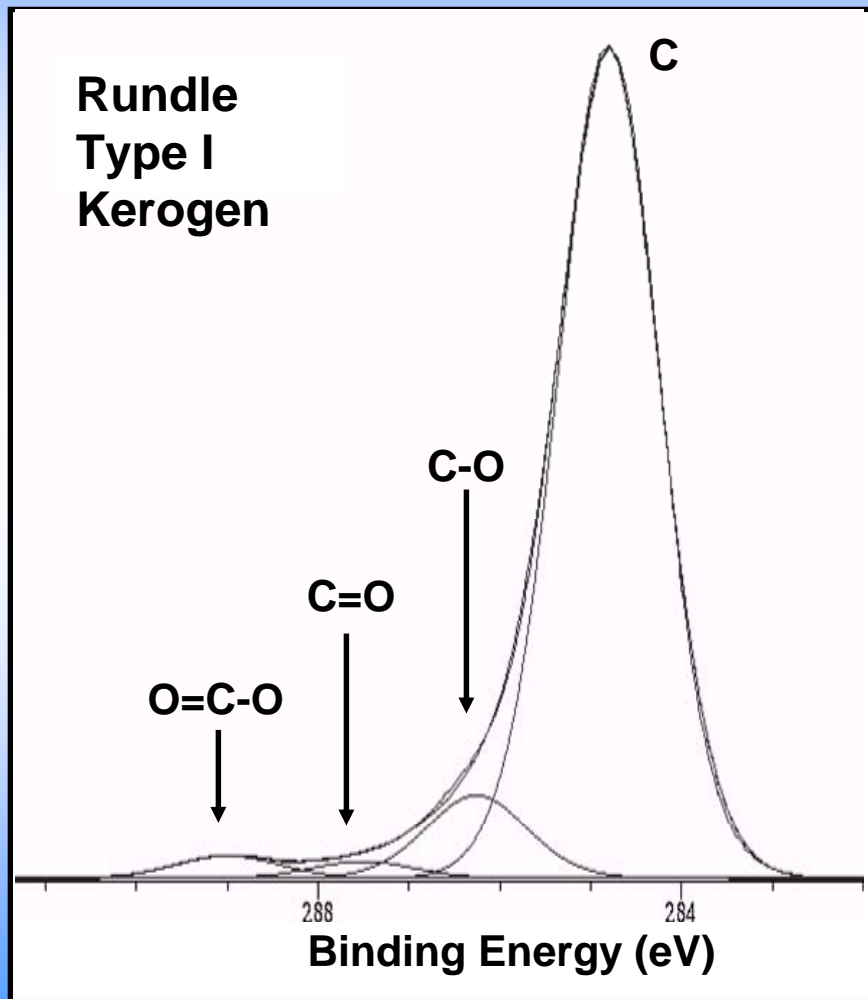
# Complimentary XPS and $^{13}\text{C}$ NMR Data for Aromatic Carbon



- The amount of aromatic carbon, measured by both  $^{13}\text{C}$  NMR and XPS, increases with decreasing H/C
  - Surface composition comparable to the bulk
  - XPS percent aromatic carbon from calibrated carbon (1s)  $\pi$  to  $\pi^*$  Signal (1)
- Green River and Rundle Kerogen (Type I) have less aromatic carbon than other organic matter types at comparable levels of maturity

(1) S. R. Kelemen et.al. Applied Surf. Sci., 1993, 64,167

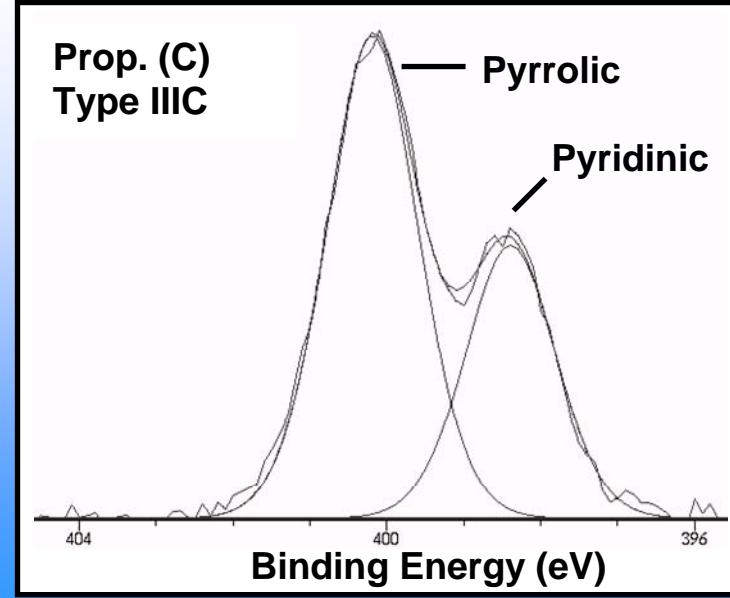
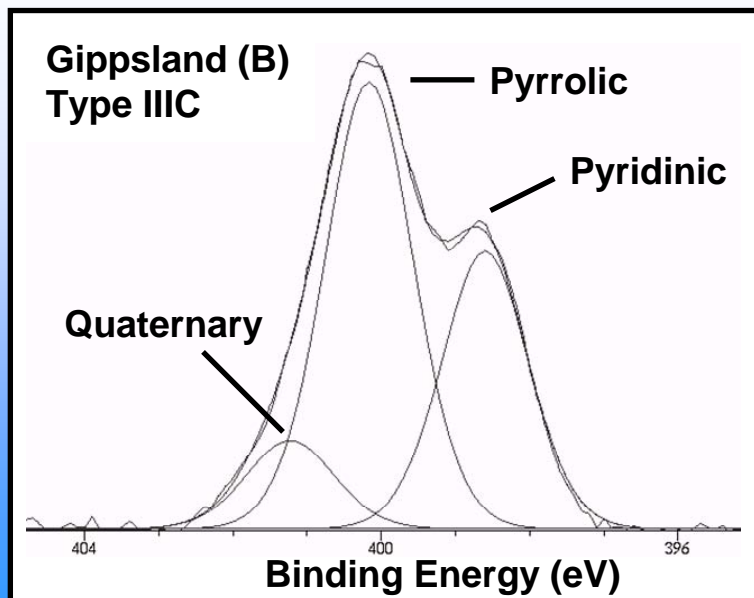
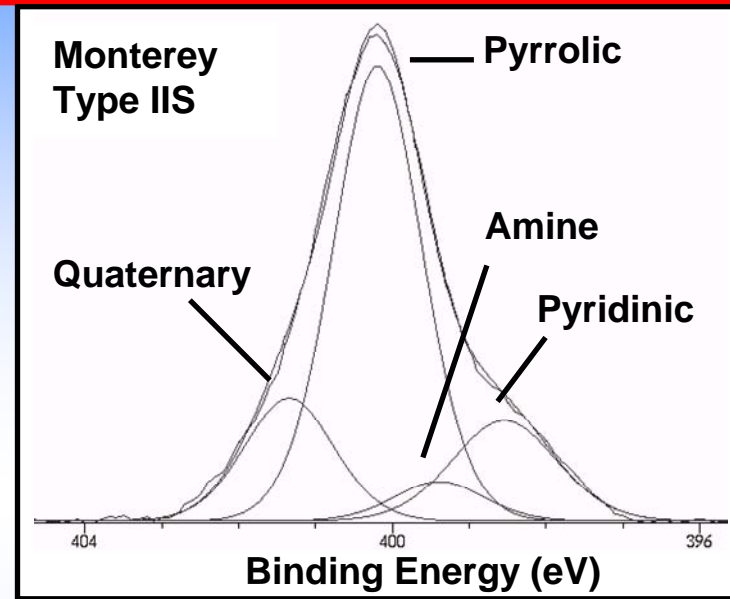
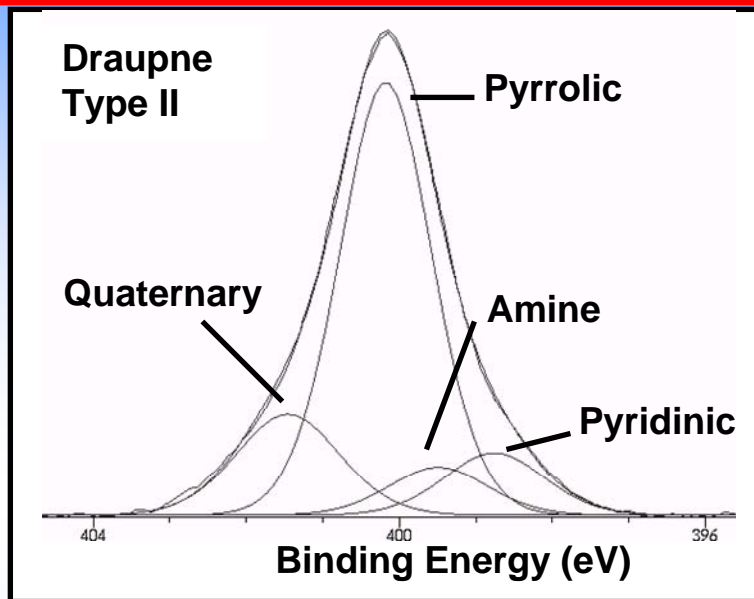
# XPS Carbon (1s) Spectra of Kerogen and Curve Resolution into Different Components



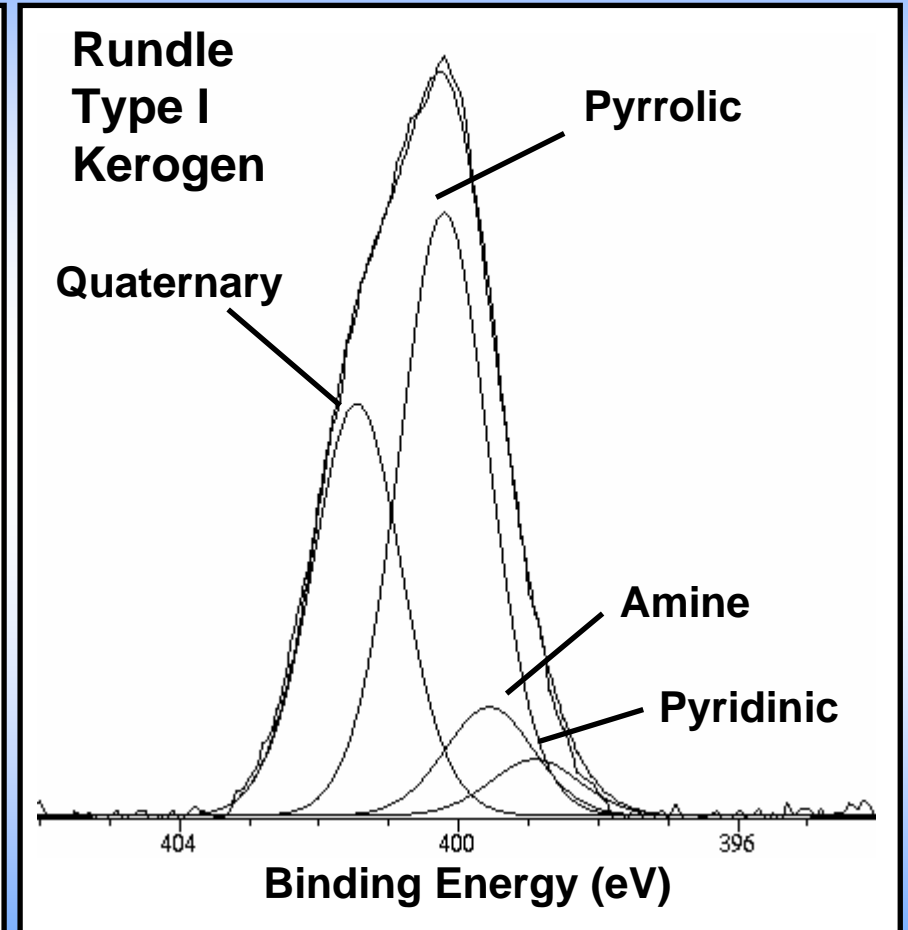
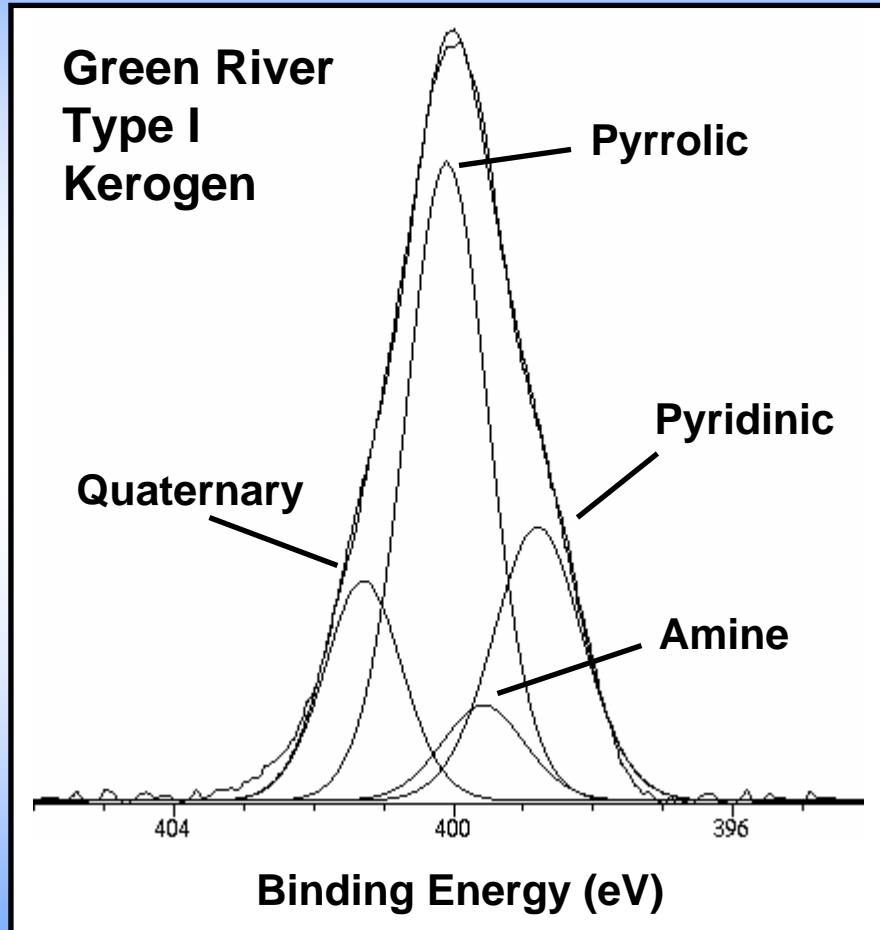
# Organic Oxygen Forms Quantified using XPS

<u>Sample</u>	Per 100 C	Mole Percent		
	<u>Total</u> <u>Org. Oxygen</u>	<u>C-O</u> (286.3 eV)	<u>C=O</u> (287.5 eV)	<u>O-C=O</u> 2x (289.0 eV)
<b>Green River</b>	<b>5.1</b>	<b>3.8</b>	<b>0.5</b>	<b>0.8</b>
Rundle	11.1	4.6	1.7	4.7
Duvernay (A)	9.7	5.0	3.4	1.3
Duvernay (B)	5.9	4.2	0.8	0.8
Duvernay (C)	5.0	3.5	0.8	0.7
Duvernay (D)	4.7	4.7	0.0	0.0
Oxford Clay	13.7	8.7	2.4	2.6
Paradox	<b>3.9</b> Low	2.2	0.6	1.1
Malm	10.0	6.8	2.8	0.4
Draupne	4.1	3.3	0.6	0.3
Bakken	8.6	6.5	1.8	0.3
Monterey	14.9	10.1	2.0	2.8
Gippsland (A)	<b>15.4</b> High	9.5	2.8	3.1
Gippsland (B)	10.6	8.3	1.6	0.7
Proprietary (A)	11.1	6.8	2.2	2.1
Proprietary (B)	6.6	6.6	0.0	0.0
Proprietary (C)	4.0	4.0	0.0	0.0
Fruitland	9.3	7.1	1.9	0.3

# XPS Nitrogen (1s) Spectra of Kerogen and Curve Resolution into Different Components



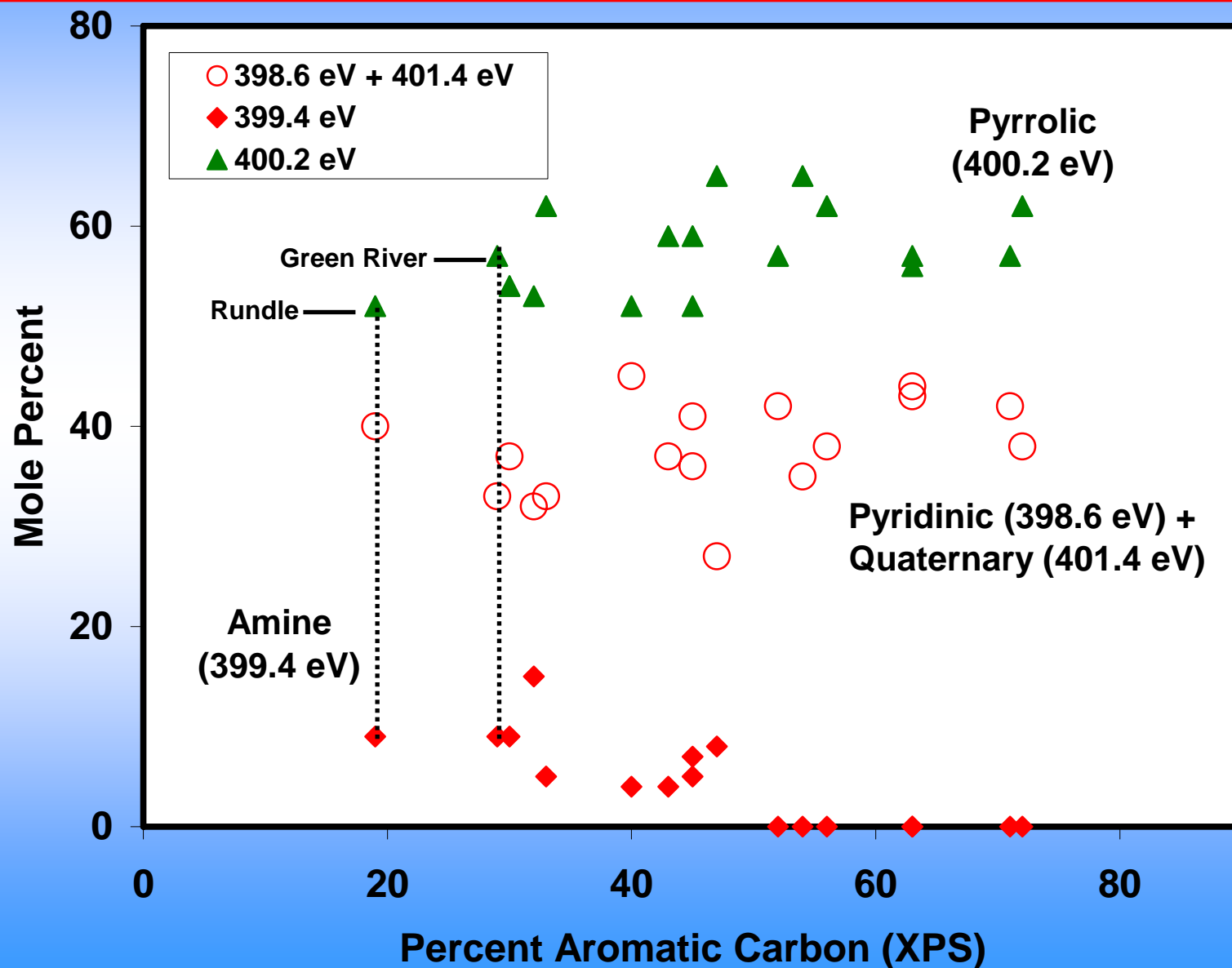
# XPS Nitrogen (1s) Spectra of Type I Kerogen and Curve Resolution into Different Components



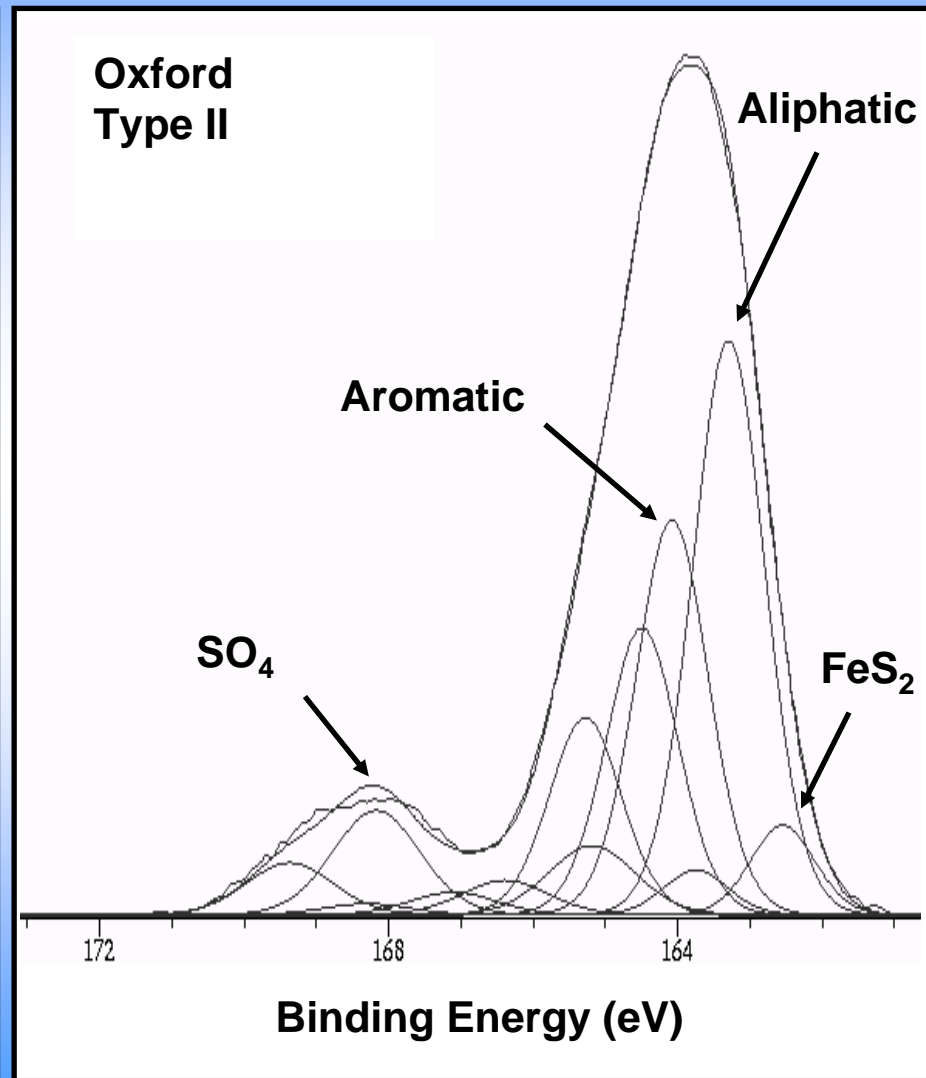
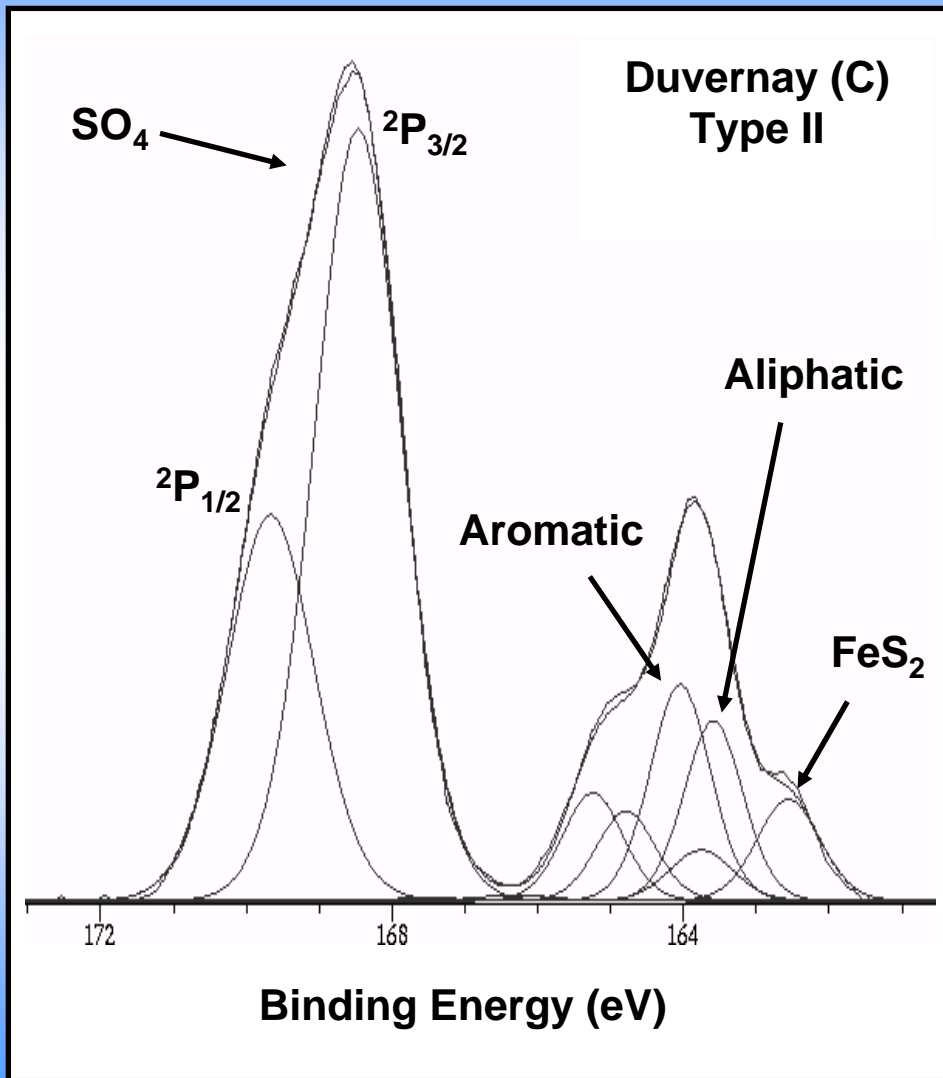
# Nitrogen Forms Quantified using XPS

Sample	Total Per 100 C	Mole Percent (XPS)			
		Pyridinic 398.6 eV	Amine 399.4 eV	Pyrrolic 400.2 eV	Quaternary 401.4 eV
Green River	2.2	20	9	57	13
Rundle	1.8	5	9	52	35
Duvernay (A)	2.9	27	4	52	18
Duvernay (B)	2.0	19	4	59	18
Duvernay (C)	2.1	18	0	65	17
Duvernay (D)	2.1	15	0	62	23
Oxford Clay	2.4	17	15	53	15
Paradox	3.1	23	5	59	13
Malm	2.3	15	9	54	22
Draupne	2.3	10	8	65	17
Bakken	3.5 High	20	7	52	21
Monterey	3.3	16	5	62	17
Gippsland (A)	0.8 Low	18	0	62	20
Gippsland (B)	1.9	34	0	56	10
Proprietary (A)	1.7	31	0	57	11
Proprietary (B)	1.1	35	0	57	7
Proprietary (C)	1.1	36	0	64	0
Fruitland	1.7	30	0	57	13

# Plot of Relative Amounts of Nitrogen Forms for Kerogen



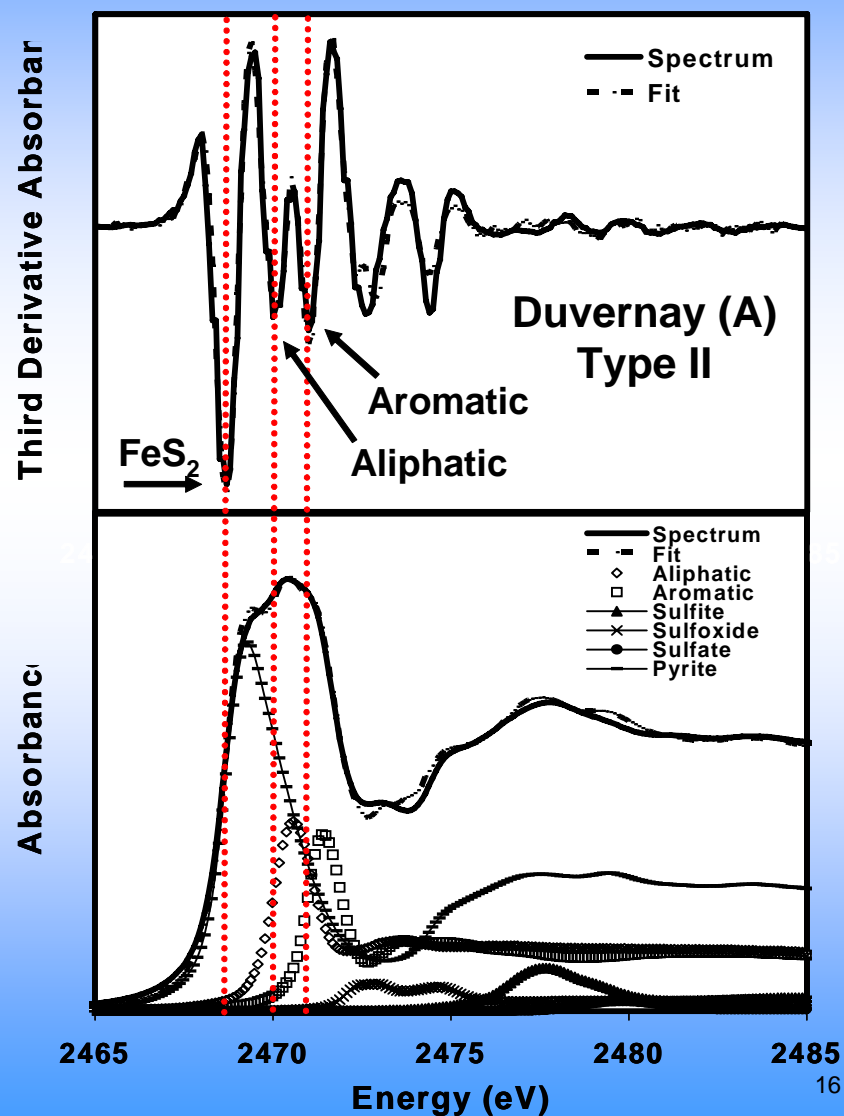
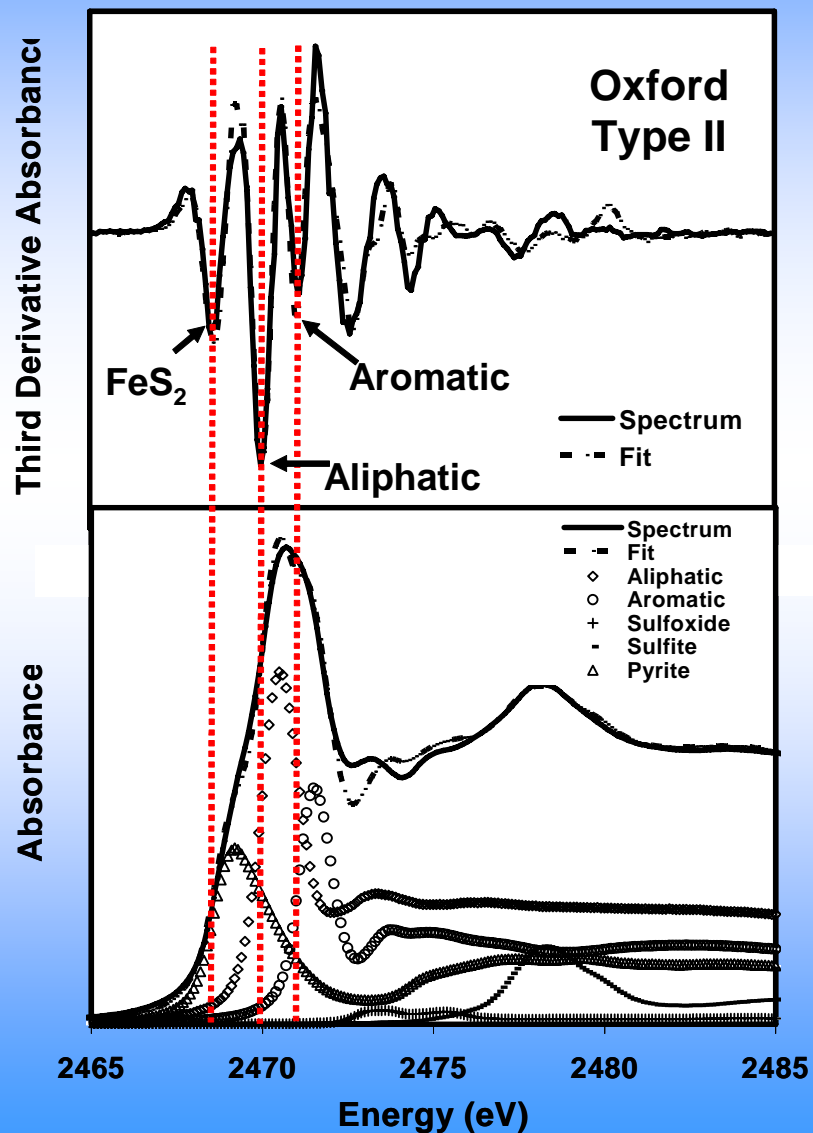
# XPS Sulfur (2p) Spectra of Kerogen and Curve Resolution into Different Components



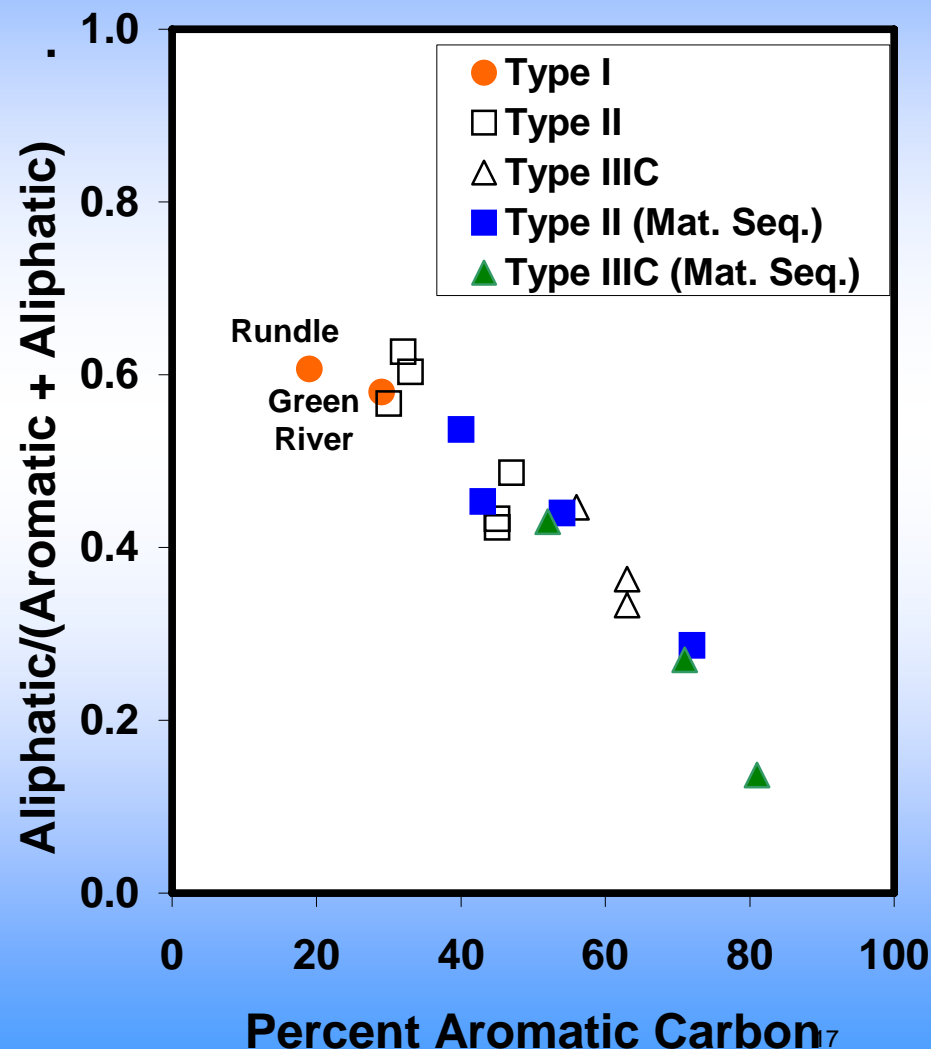
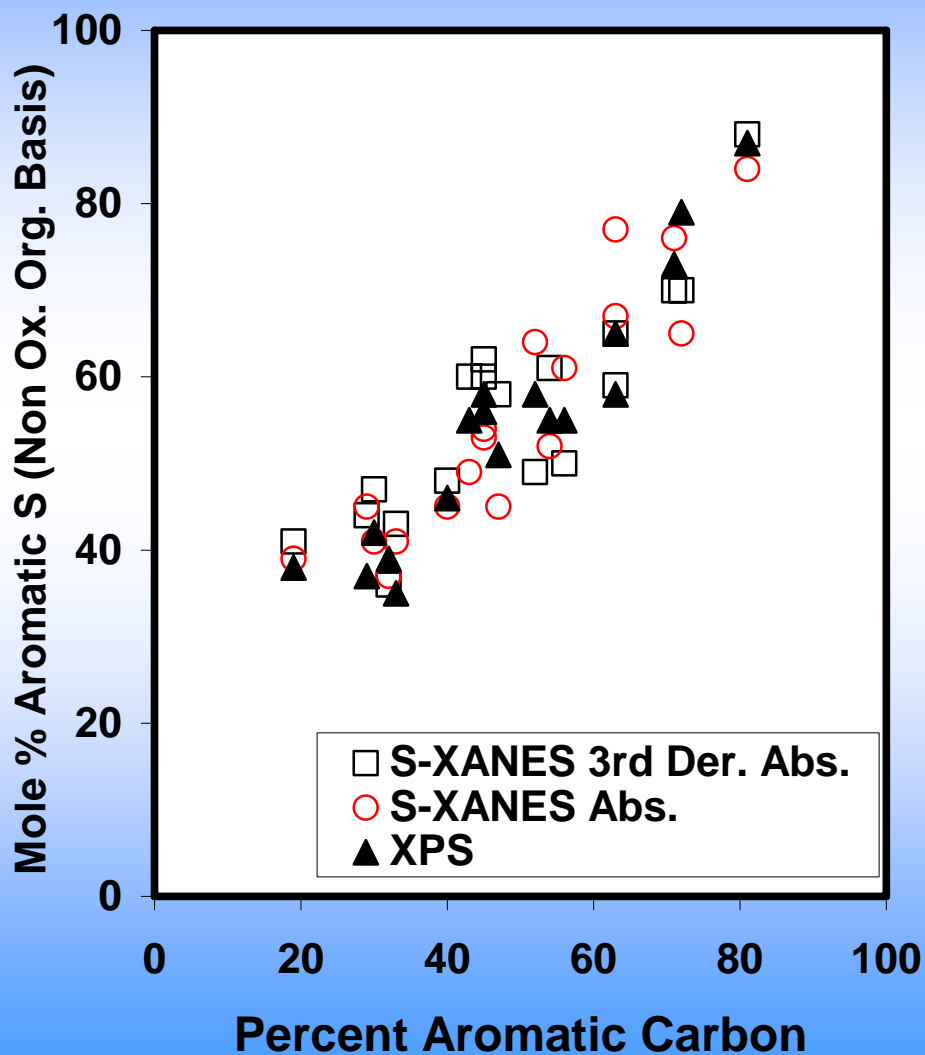
# Sulfur Forms Quantified using XPS

Sample	Total Org. S	Aliphatic Sulfide	Aromatic (Thiophenic)	Sulfoxide	Sulfate	Pyrite
Green River	0.5	17	10	9	50	14
Rundle	0.6	15	9	4	66	6
Duvernay (A)	1.4	33	28	13	25	2
Duvernay (B)	1.2	16	20	5	46	13
Duvernay (C)	0.6	11	13	0	69	7
Duvernay (D)	1.0	5	20	5	66	4
Oxford Clay	3.2 High	37	23	10	17	13
Paradox	1.4	16	22	2	45	15
Malm	1.9	22	16	7	45	10
Draupne	2.1	19	20	8	52	1
Bakken	2.2	25	32	10	30	2
Monterey	2.7	39	21	4	16	20
Gippsland (A)	2.7	36	44	8	10	2
Gippsland (B)	0.5	31	58	0	11	0
Proprietary (A)	0.2	24	33	0	42	0
Proprietary (B)	0.2	22	58	0	20	0
Proprietary (C)	0.1 Low	8	56	0	36	0
Fruitland	0.4	37	51	0	12	0

# S-XANES Absorbance and Third Derivative Absorbance Spectra of Kerogen



# Combined S-XANES and XPS Results for Sulfur Forms



# Summary

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- **A direct characterization strategy is used to quantify the average chemical structure of kerogen (mitigates indirect approach uncertainties)**
  - **Solid-state  $^{13}\text{C}$  NMR, XPS and S-XANES**
  - **Wide range of organic matter types and maturities**
  - **Basis for developing specific chemical structural models of kerogen linked to reactivity models**
- **Total amounts of organic nitrogen and sulfur vary among kerogen, however, patterns emerge for the relative abundances of nitrogen and sulfur forms**
  - **The relative amount of aliphatic sulfur decreases with increasing aromatic carbon**
    - + **High aliphatic sulfur levels for Green River and Rundle kerogen**
  - **The majority of nitrogen exists as pyrrolic nitrogen in all kerogens**
    - + **Pyridinic, amine and quaternary found in Green River and Rundle kerogen**
- **Green River and Rundle Kerogen (Type I) have more hydrogen than other kerogen organic matter types (at equivalent levels of maturity)**
  - **Both  $^{13}\text{C}$  NMR and XPS show aromatic carbon increases with decreasing H/C**
  - **Carbon structural features from solid-state  $^{13}\text{C}$  NMR appear in a companion poster**