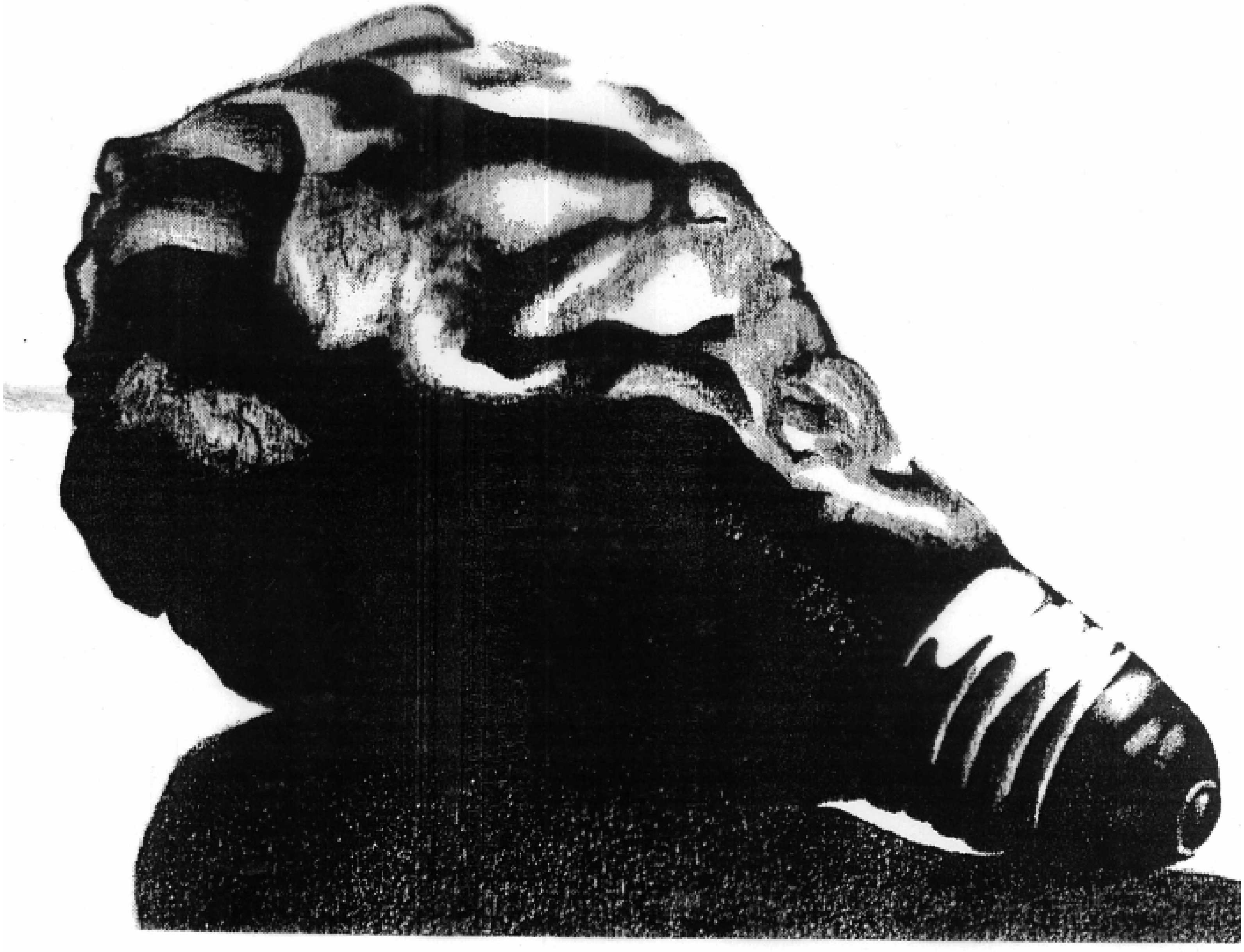


Business

- **Comments about book**
  - Not your normal textbook
  - Good reference material
  - Very heavy on organic chemistry
  - Do your best in the time allotted!

Class 3

- Coal Formation
- Lithotypes and macerals
- Coalification diagram
- What coal am I?
  - Dmmf
- Definitions
  - Aromaticity, etc.
- Cartoon molecules

1. Describe the major geologic factors that affected coal formation and discuss why this information is important. Based on these factors, explain why is there no coal in California or Nevada.

Coalification

Origin of Coal:

1. Subaquatic water plants and organic muds
2. Open marshes with sedges and reeds
3. Forest and bush swamps with vegetation rich in wood
4. Moss bogs

Peatification	==>	Coalification
(biochemical)		(geochemical)

Peatification Needs

- Appropriate amount of water and oxygen
- Aerobic bacteria to depth of 0.5 m
- Anaerobic bacteria to depth of 10 m
- Too much oxygen ---- oxidation
- Too much bacteria ---- complete methanation
- During peatification, carbon content increases from 45-50% to 55-60%

Coalification Needs

- **Pressure affects porosity and moisture content, but not coal rank**
- ***Time alone seems to have scarcely any influence on coalification beyond the coalification stage...***
- ***Neither can the presence of overburden be regarded as the cause of coalification...***
- ***This leaves only temperature as a possible explanation of metamorphosis.***

Van Krevelyn, p. 47-48

From National Geographic, 2014

2. Describe the difference between coal lithotypes and coal macerals, and compare the major classifications of each.

Petrography
(Coal as a Rock)

- **A. Lithotypes**
- **(Early broad classification by visual inspection performed by Stopes, 1919)**

	Vitrain	**no visible structure (glassy; "vitro")**
Bright		
	Clarain	**visible banded structure ("clare" meaning clear or bright)**
	Durain	**dull grey-black granular structure ("dur" meaning hard or tough)**
Dull		
	Fusain	**resembles charcoal, powdery or fibrous (origins from dry rot or forest fires)**

Petrography Cont.
(Coal as a Rock)

B. Macerals

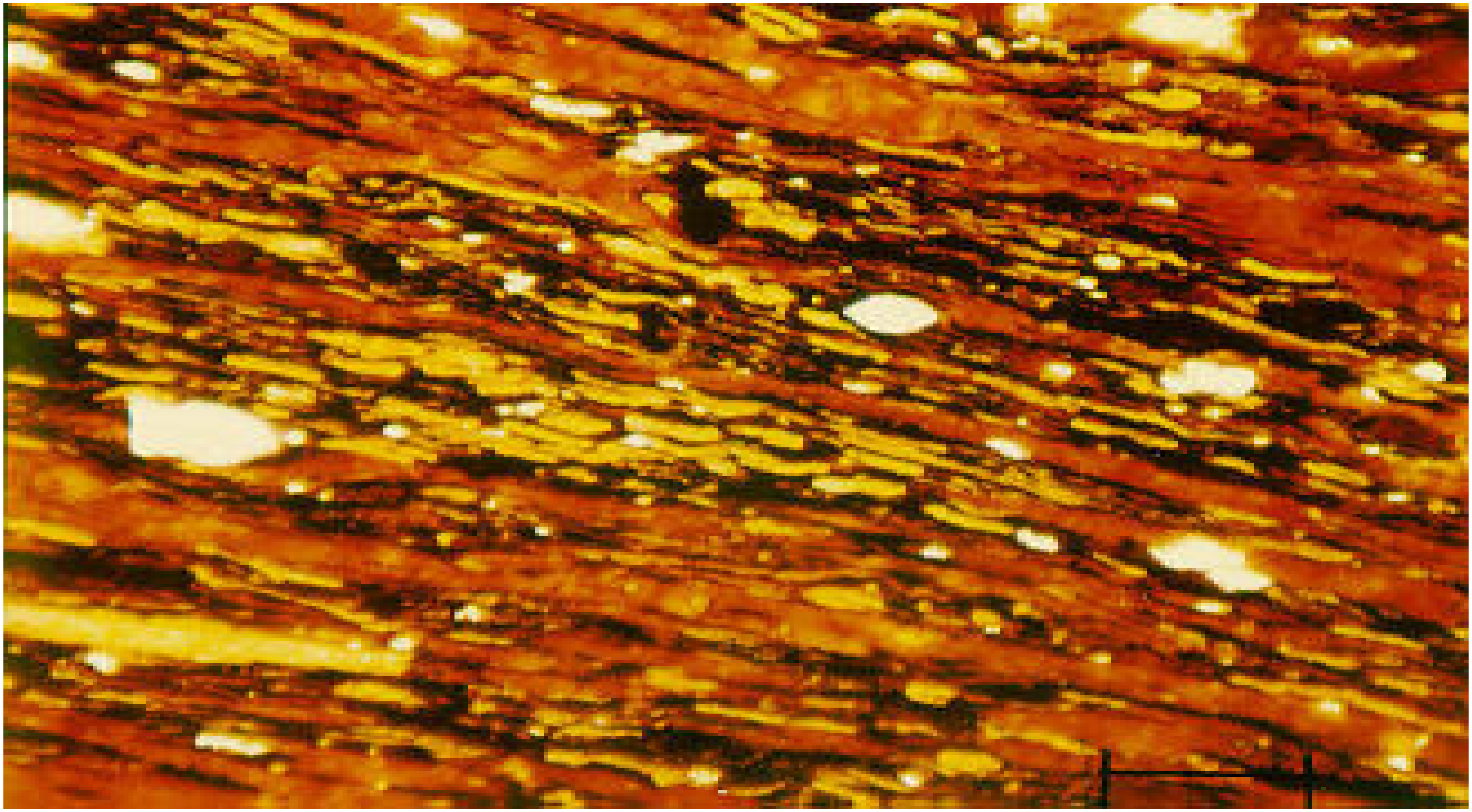
(Microscopic distinction, commonly accepted in the 1930's and modified as needed since then)

Vitrinite	**The principal coal maceral and primary constituent of bright coal. Higher in oxygen and aromatic content than liptinites**
Liptinite (exinite)	**From hydrogen-rich plant remains such as resins, balsams, spores, latex, pollen, algae, cuticles, waxes, fats, and oils of vegetable origin. Higher in hydrogen and aliphatic groups than vitrinite.**
Inertinite	**From "inert," referring to less reactive than the other macerals. Thought to come from charring (prehistoric forest fires), oxidation, moldering and fungal attack. Typically high in carbon, highly aromatic, and low in hydrogen and oxygen.**

Table 1: Maceral Nomenclature and Origins

Maceral Group	Maceral	Description	Origin
Vitrinite	Telinite	cell wall material derived from vegetable matter	trunks, branches, stems, leaves and roots
	Collinite	homogeneous structureless material filling cell cavities	humic gel precipitated from solutions of humic matter
	Vitro-detrinite	fragmental plant or humic peat particles	peat or plant particles degraded at an early stage by pressure
Exinite	Sporinite	flattened discs of original spores	spores and pollen grains
	Cutinite	outer layers of leaves or cuticles	leaves, needles, shoots and thin stems
	Resinite	secretions from plants resinated in plant metabolisms	essential oils and resins in plant tissue
	Alginite	algal remains	certain types of algae
	Lipto-detrinite	detrital remains of cutinite, resinite, alginite and sporinite	other members of the exinite group
Inertinite	Fusinite	cell wall material	charred trunks, branches and stems
	Semi-fusinite	intermediate stage between fusinite and telinite	partially charred trunks, branches and stems
	Macrinite	groundmass into which other macerals are embedded eg sporinite	variable
	Inerto-detrinite	fragmental fusinite, semifusinite, macrinite and sclerotinite	degradation of other members of the inertinite group by load pressure
	Sclero-tinite	tubular or cellular fungal hyphae	exclusively fungal remains

Microscopic View
(white light)



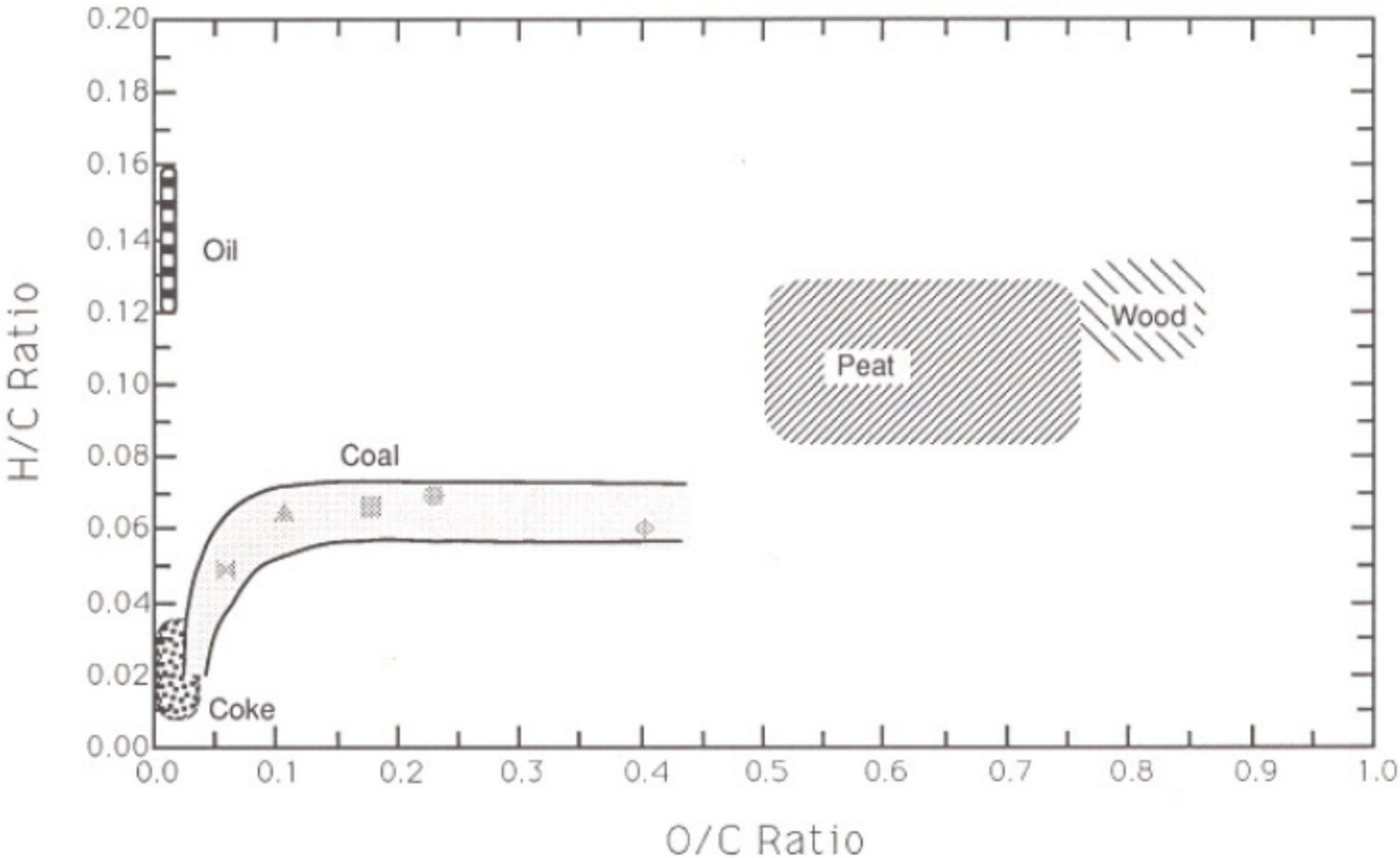
10 μm

3. A common way to describe coals is based on elemental composition, such as in Figure 2.3 (Ch. 2, Fig. 3) in the text. Note that the numerical values on the axes in this figure were misprinted.

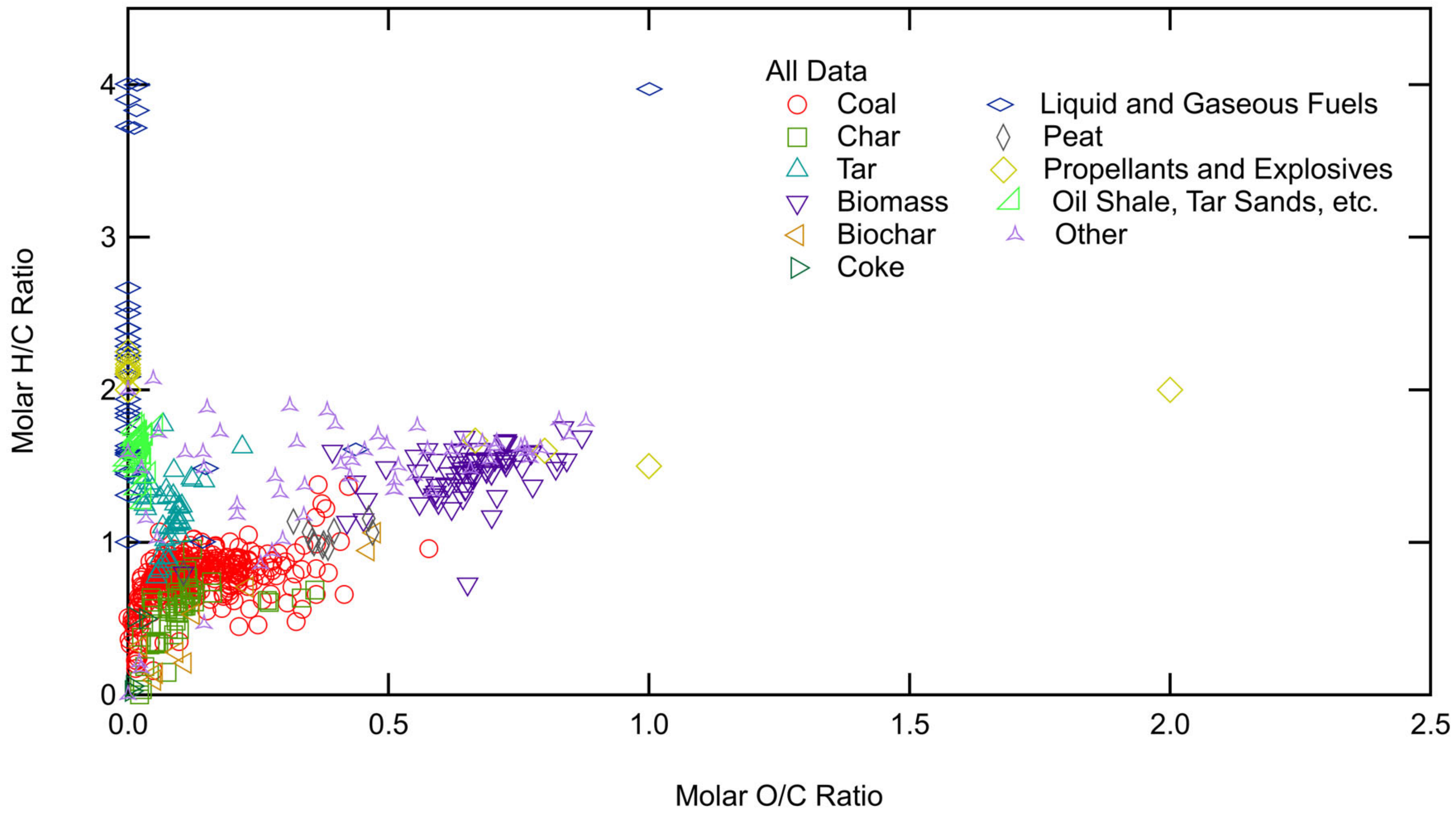
Please sketch a similar chart, showing
(a) the coals in Fig. 2.3 in a band (not each point),
(b) the region where oil (petroleum) would be on this chart,
(c) the region where peat would be, and
(d) the region where biomass/wood would be.

Cite your sources.

Fuel Compositions Relative to the Coalification Band



From Andrew Richards



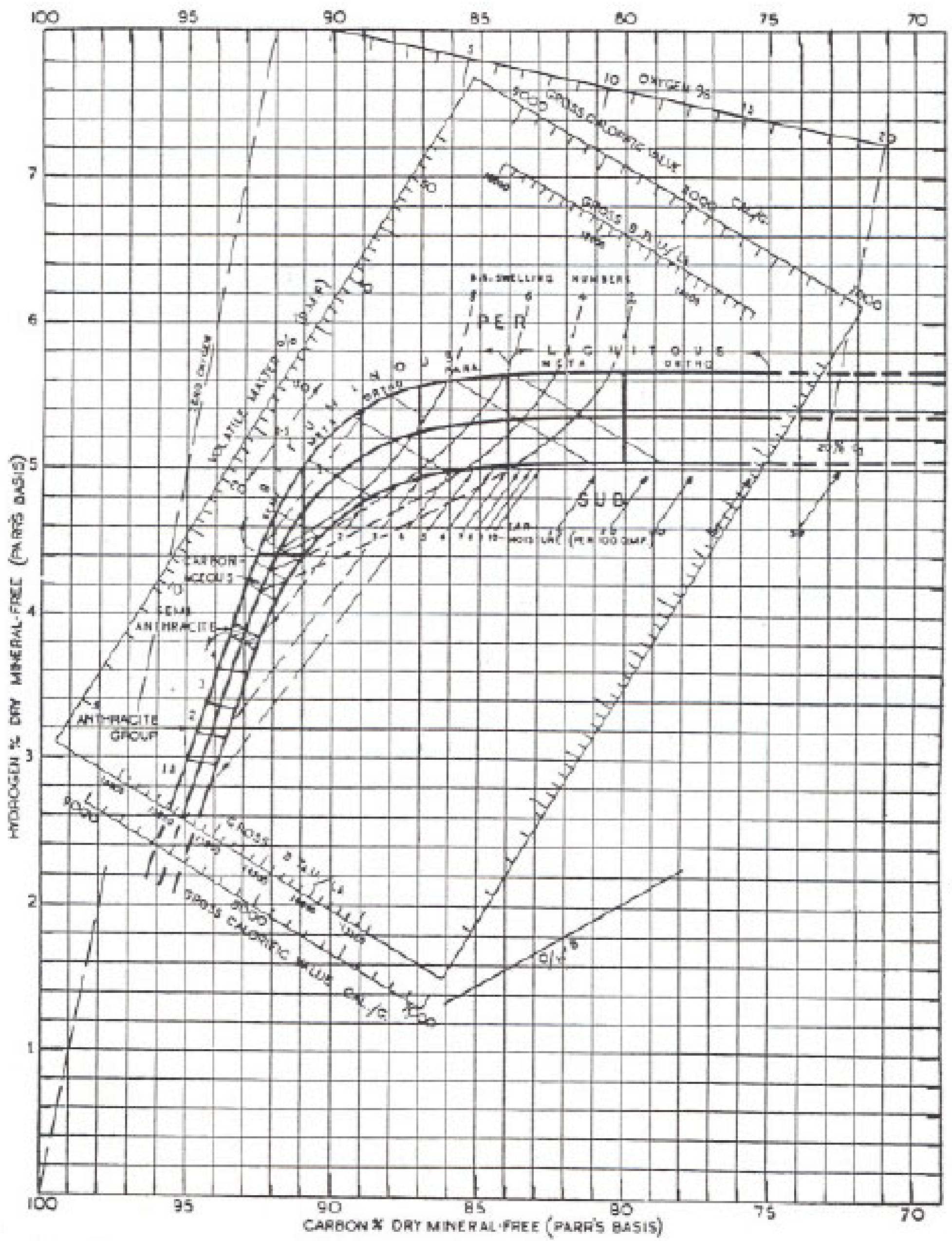
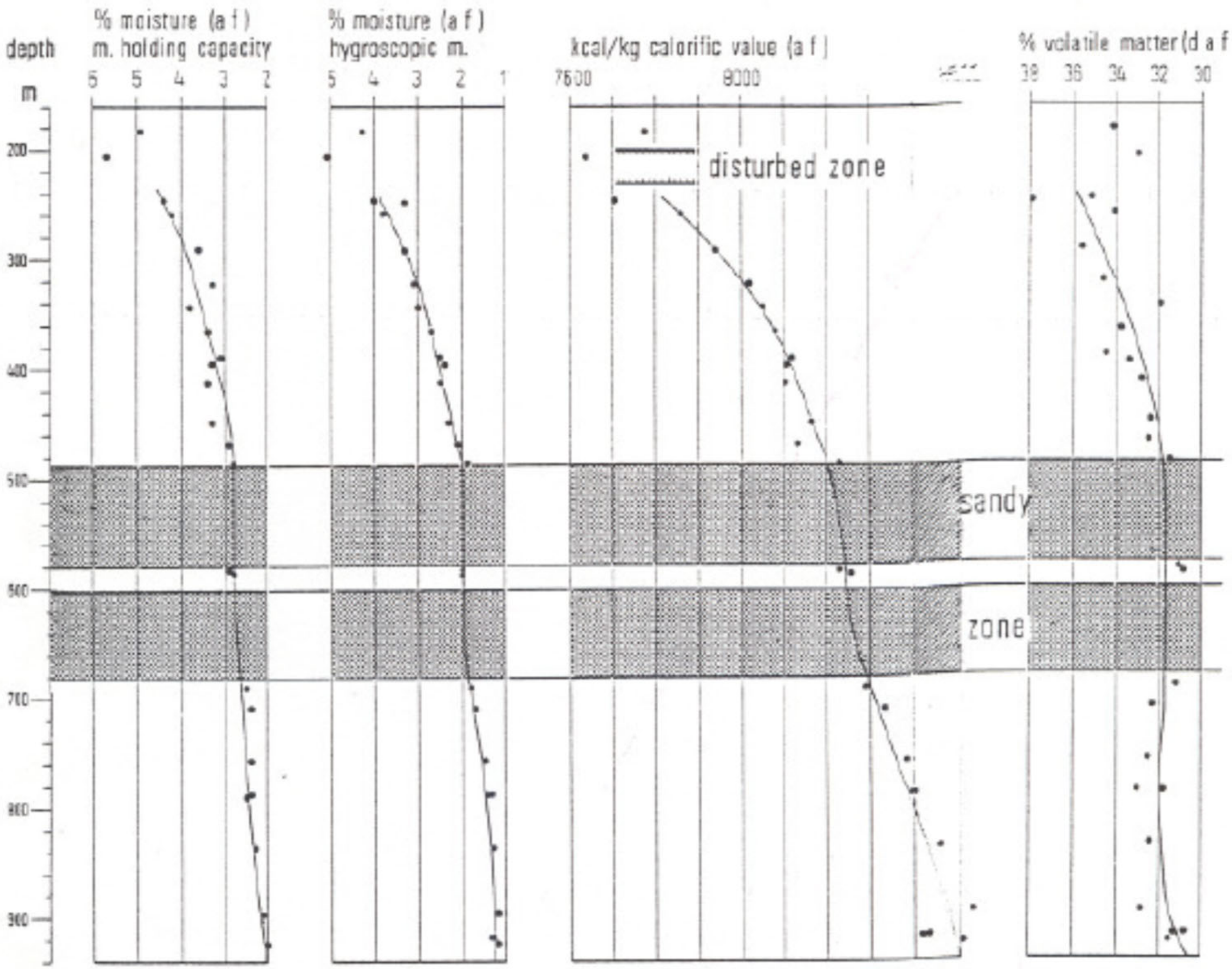


Fig. II, 5 SEYLER's coal chart.

Use of the coalification diagram for other characteristics

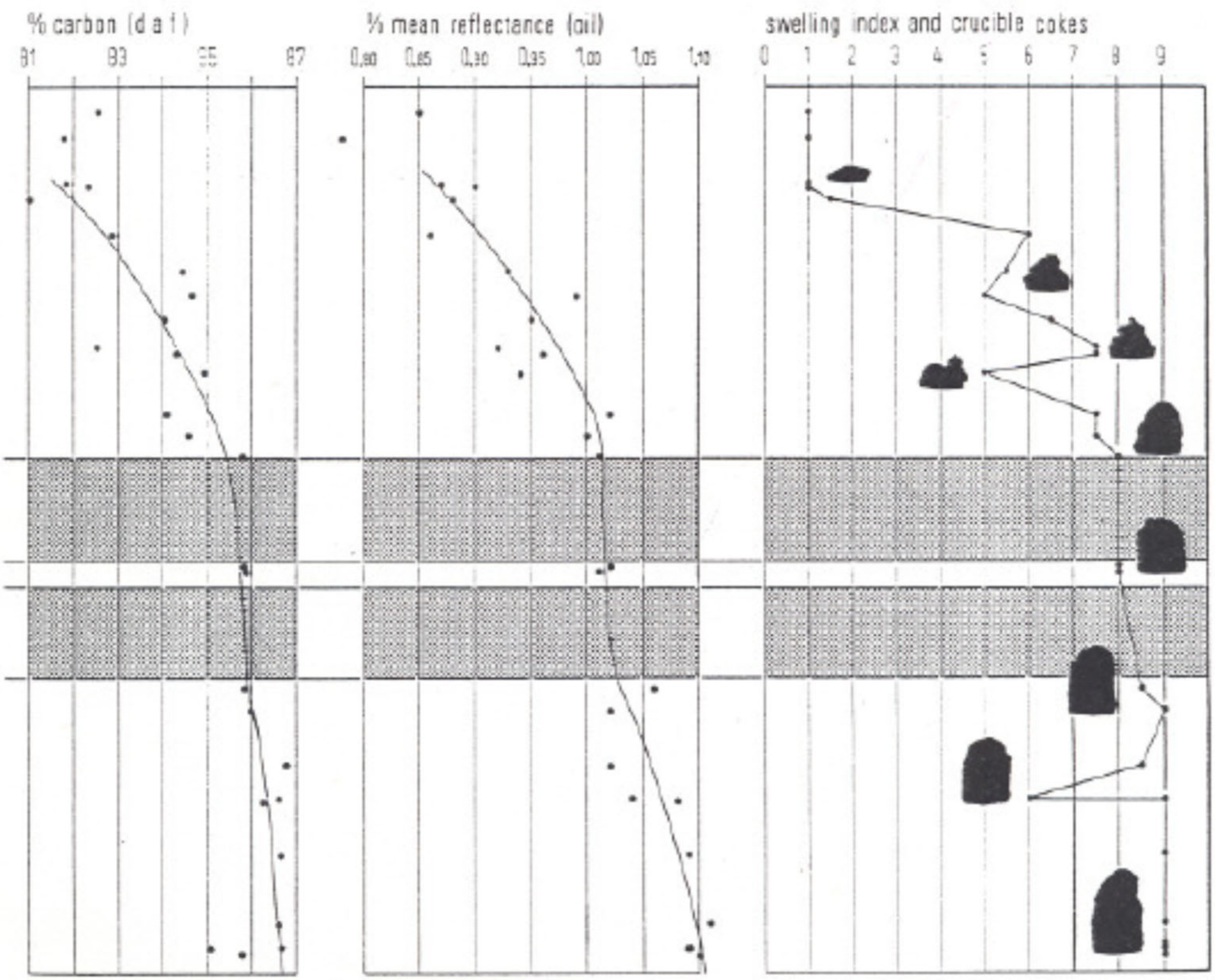
From van Krevelyn



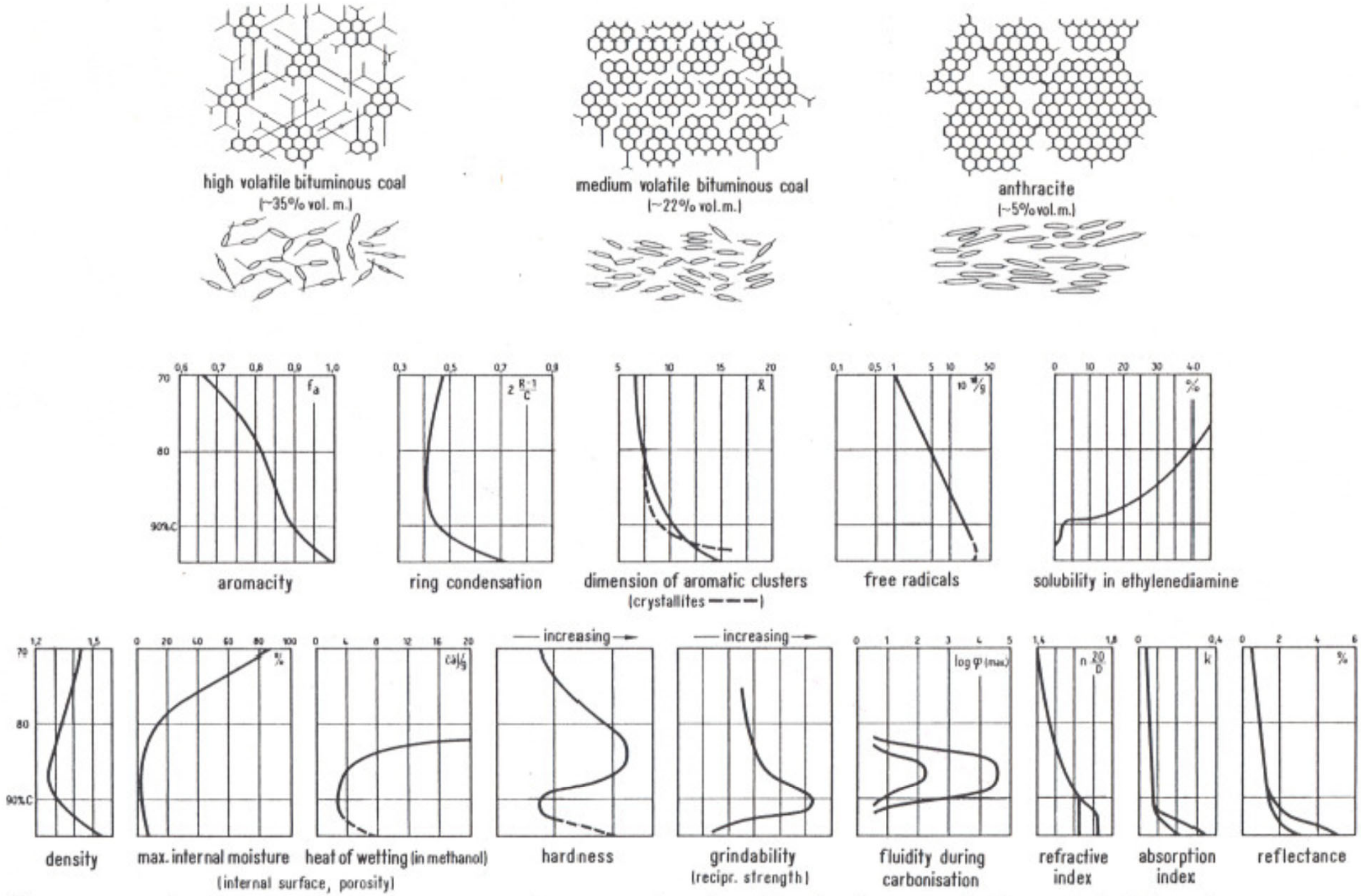
From Coal Petrology (Stach), p. 56 (1982)

Fig. 20. Increase of coal rank with depth in the Teufelspforte borehole (Saar district) based on different rank parameters (vitrite analyses). Note the break in the trend of the coalification tracks in the sandy zone (after M. & R. TEICHMÜLLER, 1968 a).

tion temperature of *ca.* 300 °C was necessary for the anthracitization of Wealden coals at a depth of 2000–3000 m above the Bramsche Massif (STADLER & R. TEICHMÜLLER, 1971).



From Coal Petrology (Stach), p. 56 (1982)



first row: molecular structure
-o- = hydrogen bonding
— = molecular bonding

second row: orientation of molecules perpendicular to the bedding plane
lenses = aromatic clusters
lines = non-aromatic elements

third row: development of chemical properties in relation to carbon content (daf)

fourth row: development of physical properties in relation to carbon content (daf)

Fig. 19. Physical, chemical and molecular changes of vitrite during the coalification of bituminous coals and anthracites (based on different authors: see M. & R. Teichmüller, 1954 a, 1968 a).

From Coal Petrology (Stach), p. 44 (1982)

4. Demonstrate how to convert proximate and ultimate coal analyses data to a dry, ash-free basis using the following coal data:

Moisture 6.17

Volatile Matter (moisture free) 37.87

Ash (mf) 9.90

H (mf) 4.69

C (mf) 71.12

N (mf) 1.39

S (mf) 3.80

O (mf) 9.11

Heating Value (Btu/lb, dry, ash-free) 14,102

What rank of coal is this, and which coals in Figure 2.3 are similar coals?

Bases for Comparison of Coals

Basis	Abbrev.	Description
As received	as rec'd	moisture + ash + organic
Moisture-free	dry	ash + organic
Dry ash-free	daf	organic
Dry mineral-matter free	dmmf	organic (corrected for loss of S, Cl, CO_2, etc., during ashing)

From Smith, L. and L. D. Smoot, PECS, **16**, 11 (1990)

Converting from DAF to DMMF

Parr formula (Parr, 1932):

m.m. = 1.08 ash + 0.55 S

Modified Parr formula (Given and Yarzab, 1975):

m.m. = 1.13 ash + 0.47 S_{pyr} + 0.5 Cl

Conversion of heating value to dmmf

The Parr formulas (Perry's ChE Handbook)

$$F' = 100 * \frac{(F - 0.15 * S)}{100 - (M + 1.08 * A + 0.55 * S)}$$

F = Fixed carbon (char)
V = Volatiles
Q = Heating value

$$V' = 100 - F'$$

$$Q' = \frac{100 * (Q - 50 * S)}{100 - (1.08 * A + 0.55 * S)}$$

Practice Problem (in class)

- Data
  - 14,926 Btu/lb as rec'd
  - 4.74% ash as rec'd
  - 0.65% moisture as rec'd
  - 18.48% volatile matter as rec'd
  - 0.15% S_{pyr} (dry)
  - 0.19% Cl (dry)
- Find
  - Heating value on moist mmf basis
  - Volatile matter on dmmf basis
  - Rank

TABLE I *Classification of Coals by Rank*

Class	Group	Fixed carbon limits (%) (dry, mineral-matter-free basis)		Volatile matter limits (%) (dry, mineral-matter-free basis)		Calorific value limits (Btu/lb) (moist mineral-matter-free basis)		Agglomerating character
		⩾	<	>	⩾	⩾	<	
I. Anthracitic								
	1. Meta-anthracite	98	—	—	2	—	—	nonagglomerating
	2. Anthracite	92	98	2	8	—	—	nonagglomerating
	3. Semianthracite	86	92	8	14	—	—	nonagglomerating
II. Bituminous								
	1. Low volatile bituminous coal	78	86	14	22	—	—	commonly agglomerating
	2. Medium volatile bituminous coal	69	78	22	31	—	—	commonly agglomerating
	3. High volatile A bituminous coal	—	69	31	—	14,000	—	commonly agglomerating
	4. High volatile B bituminous coal	—	—	—	—	13,000	14,000	commonly agglomerating
	5. High volatile C bituminous coal	—	—	—	—	11,500	13,000	commonly agglomerating
						10,500	11,500	agglomerating
III. Subbituminous								
	1. Subbituminous A coal	—	—	—	—	10,500	11,500	nonagglomerating
	2. Subbituminous B coal	—	—	—	—	9,500	10,500	nonagglomerating
	3. Subbituminous C coal	—	—	—	—	8,300	9,500	nonagglomerating
IV. Lignitic								
	1. Lignite A	—	—	—	—	6,300	8,300	nonagglomerating
	2. Lignite B	—	—	—	—	—	6,300	nonagglomerating

Definitions

- Raw Coal
- Char
- Ash
- Volatiles
- Moisture

5. Define the following:

a. carbon aromaticity

b. hydrogen aromaticity

c. aliphatic carbon

d. aromatic clusters

e. bridges between clusters

Definitions

- Aromaticity
  - Carbon
  - Hydrogen
- Aliphatic material
- Aromatic cluster
- Ether, carbonyl

Proposed coal molecules

Criteria often used

- Elemental composition
- Aromatic and aliphatic C
- Molecular weight of aromatic clusters
- Functional groups attached to clusters
- Molecular weight of bridges
- Reaction behavior during devolatilization

Cartoon coal molecules

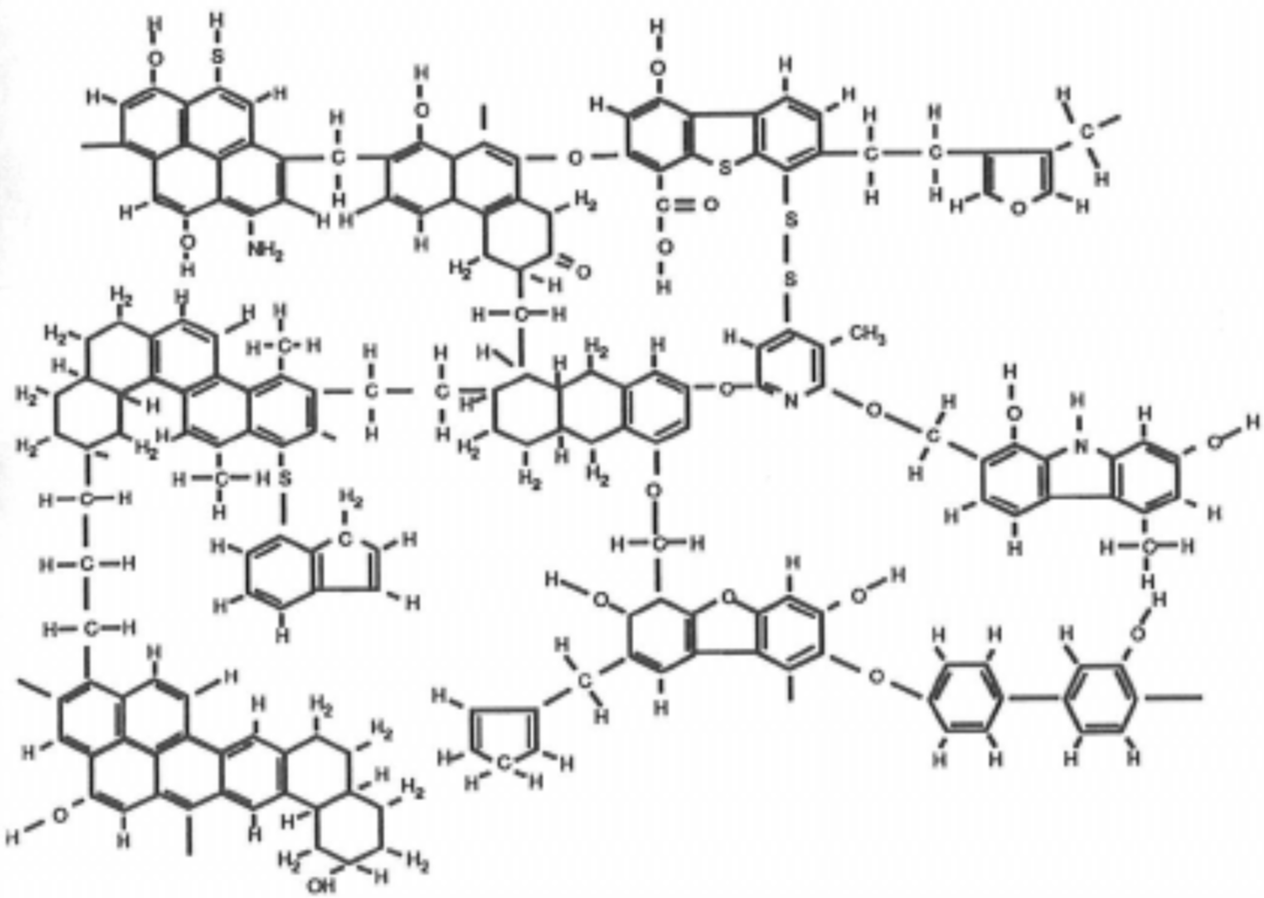
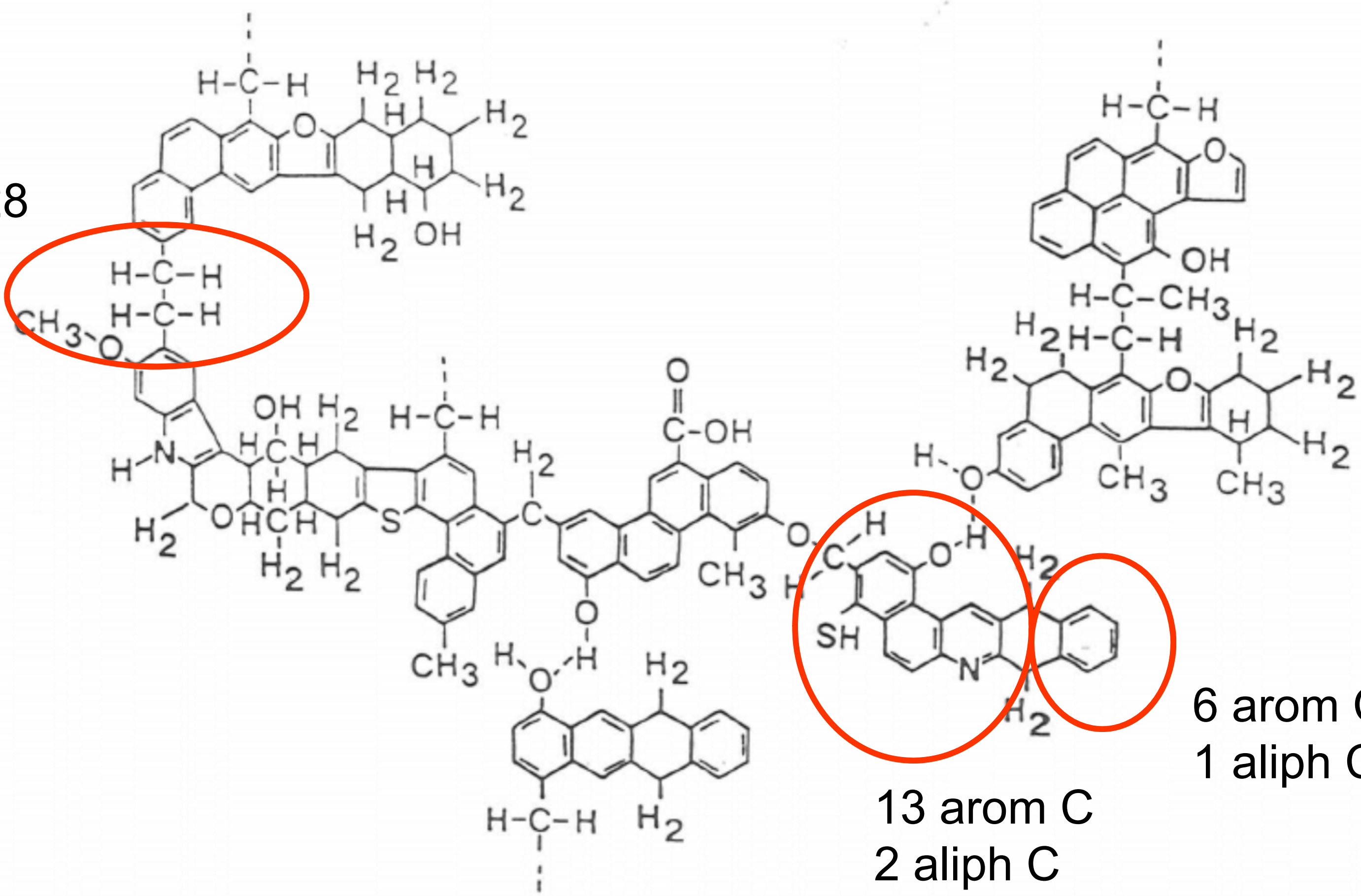


Figure 11. The Wiser (1975) model of a high-volatile bituminous coal.

Solomon coal model

MW$_b$ = 28



13 arom C
2 aliph C

6 arom C
1 aliph C

Figure 12. The Solomon (1981) model of a Pittsburgh high-volatile bituminous coal.

6. For Solomon's proposed coal molecule, please find the following:

a. elemental composition (wt% C, H, O, N, S)

b. carbon aromaticity

c. average number of aromatic carbons per cluster

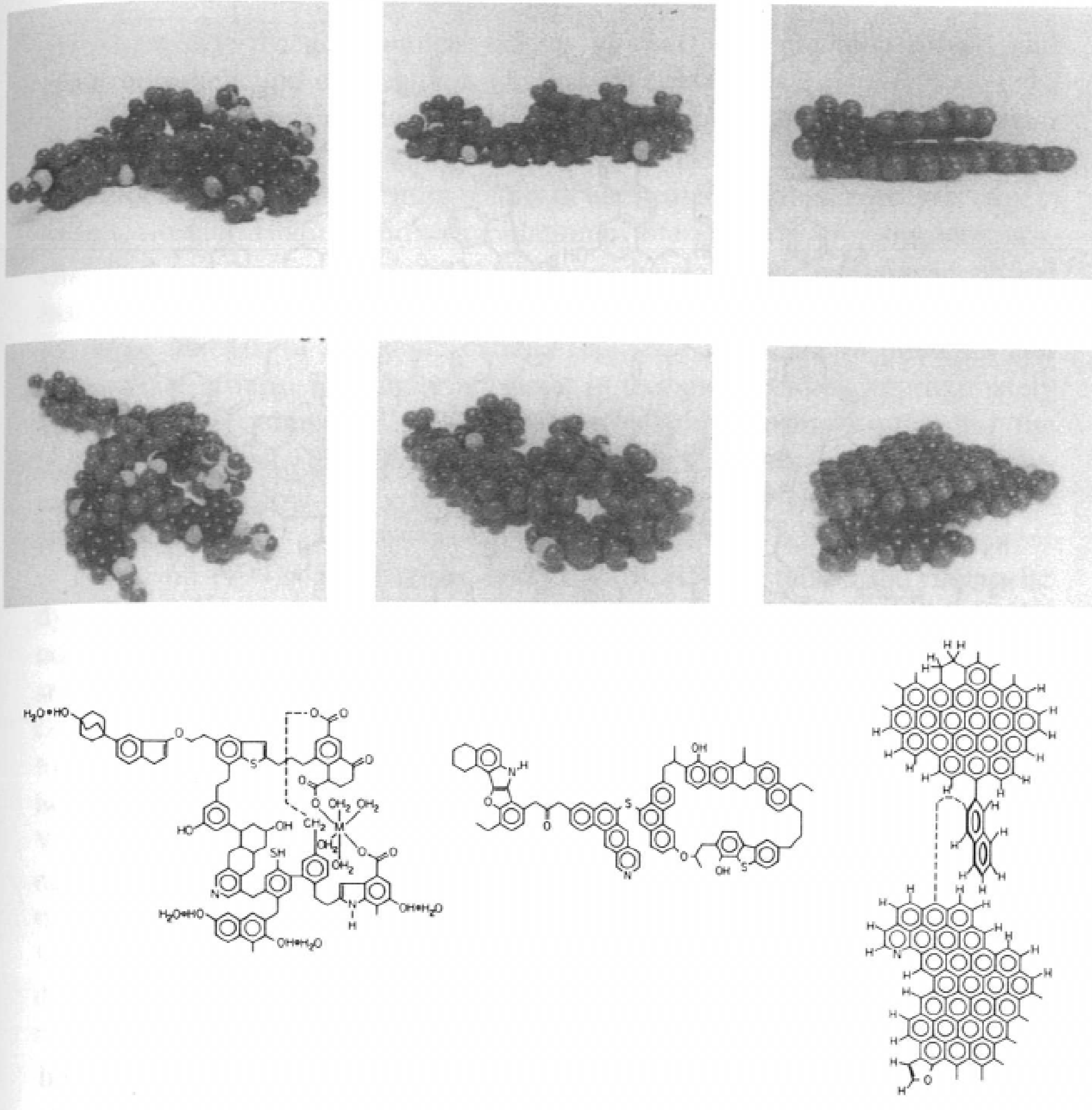


Figure 13. Spiro and Kosky (1982) models for a low-, intermediate-, and high-rank coal.

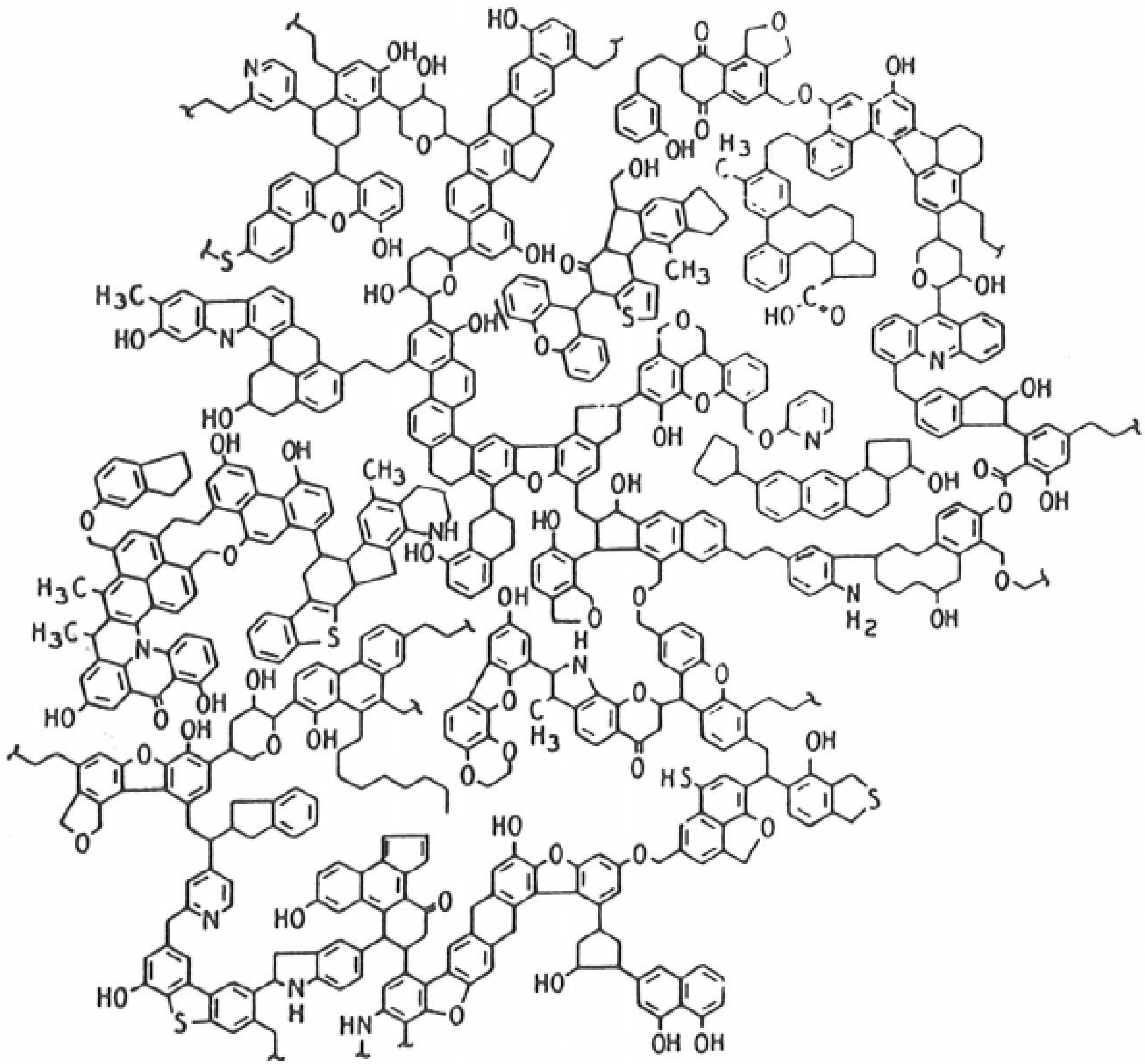


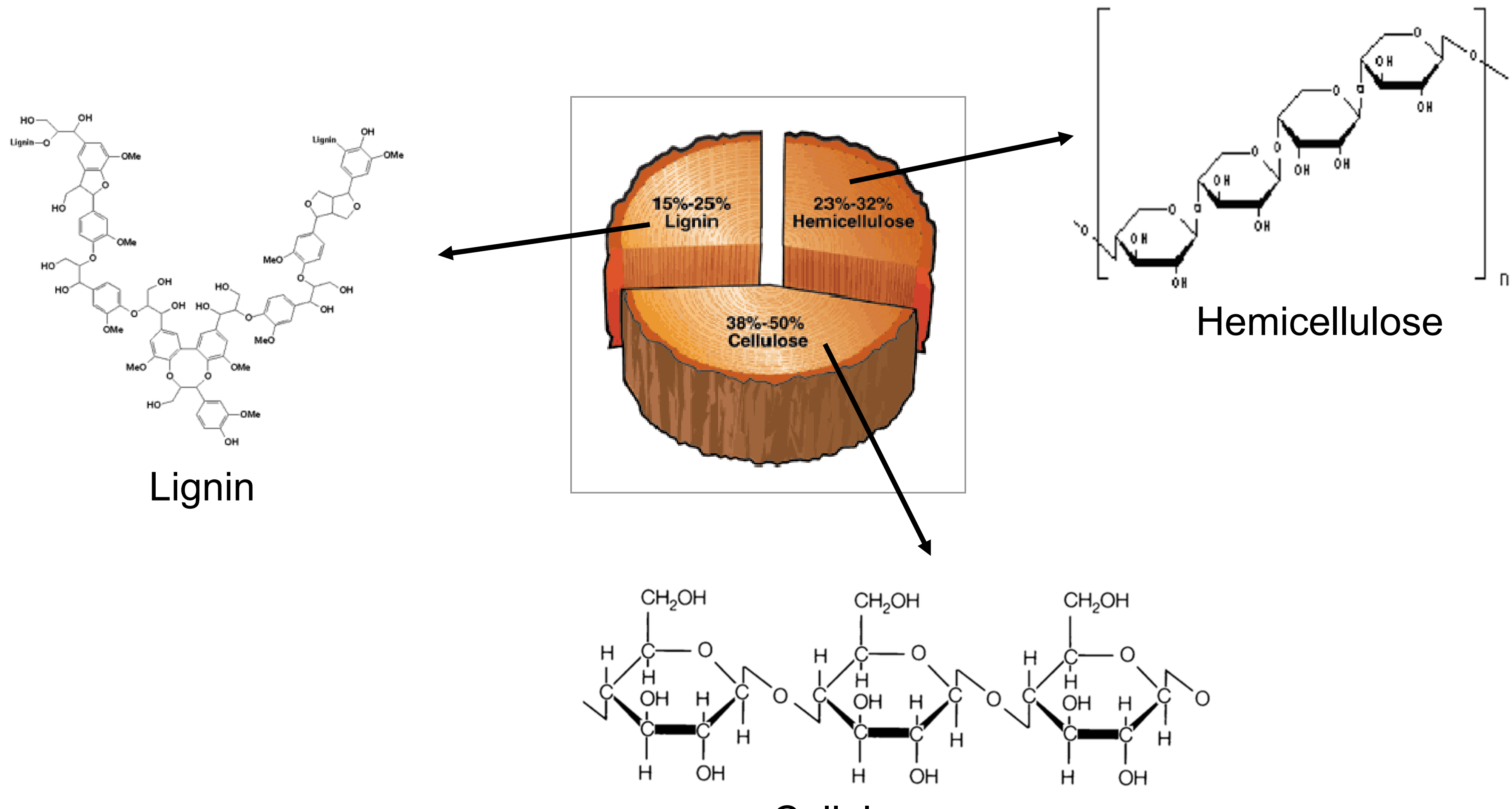
Figure 14. The Shinn (1984) model of a bituminous coal structure.

Cautions about proposed coal molecules

- A significant part of the proposed coal molecule is the … (the idea of an infinite network)
- Coal is heterogeneous, and these molecules represent average characteristics
- No particular model is totally accepted
- The models help formulate ideas about how the coal comes apart, and help to rationalize activation energies for reaction rates

7. Biomass is composed of cellulose, hemicellulose, and lignin. Please describe these three molecules, and contrast them with coal molecules. (Hint: search for these structures on the internet)

Composition of Biomass



Lignin is branched with aromatics

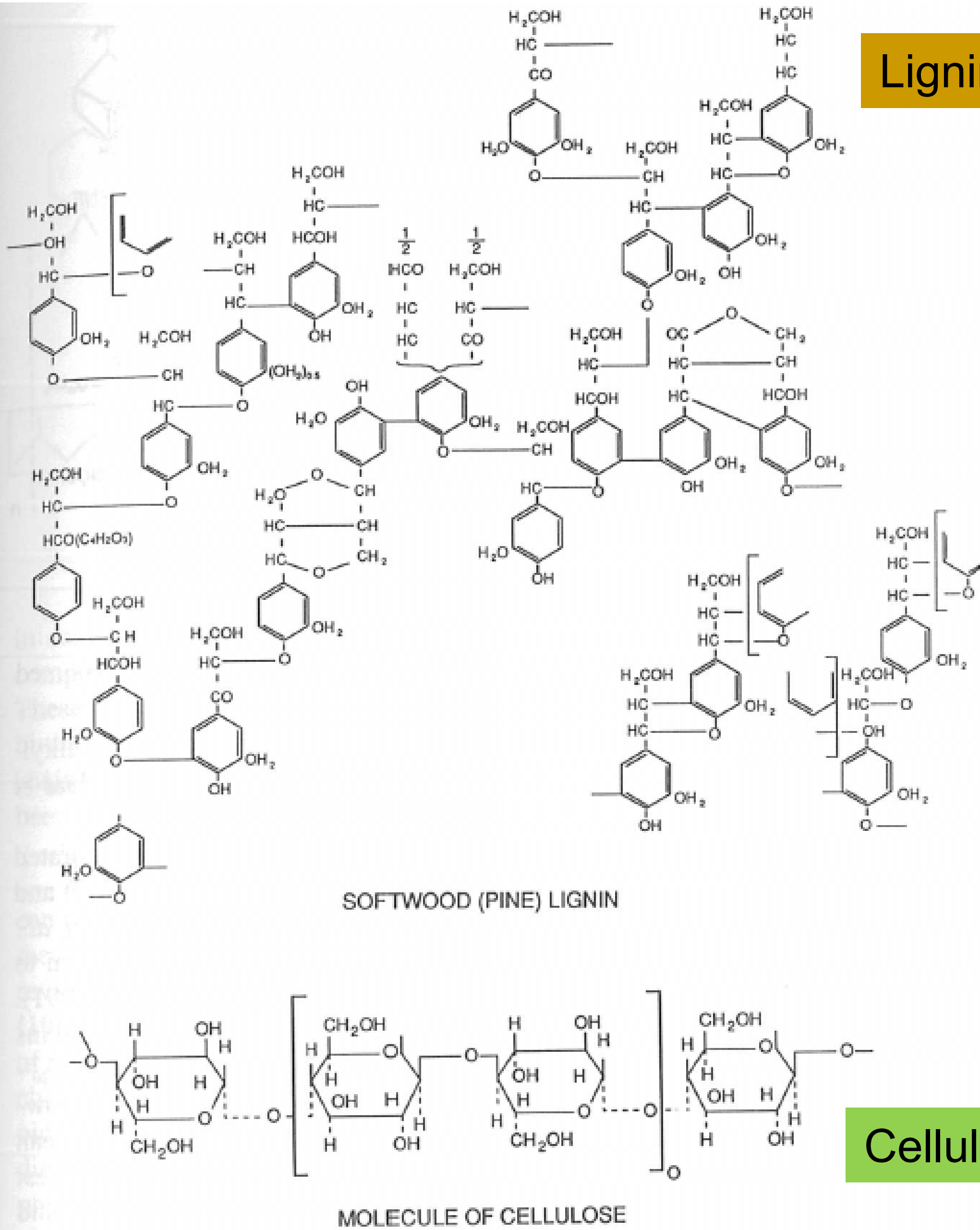
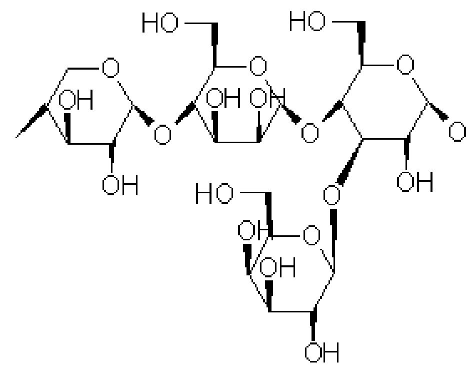


Figure 6. Some precursors of vitrinite: lignin and cellulose (Flaig, 1968; Given, 1984b).

Hemicellulose is branched



- Xylose - ß(1,4) - Mannose - ß(1,4) - Glucose -
- alpha(1,3) - Galactose

Hemicellulose

By BerserkerBen - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=19378315

Cellulose is a straight chain

Composition of Leaves

Plant Species	Pectin	Arabanan	Galactan	Xylan	Mannan	Glucan	Cellulose	Hexosan	Pentosan	Hemicellulose	Klason lignin	KL ash	KL silicates	KL protein	Phenols	Structural Lignin	C+H+L
Saw palmetto	0.7	4.3	0.9	12.5	0.7	12.9	11	1.9	16.8	18.7	35.79	3.02	4.83	1.19	4.82	29.77	59.47
Dwarf palmetto	2	3	1.5	13.6	0	29.7	28	1.5	16.5	18	22.27	0.7	1.13	4.06	7.94	17.09	63.09
Swamp bay	1.8	1.5	1.5	7.5	0	21	18.3	1.5	9	10.5	34.94	0	0	2.05	5.28	32.89	61.69
yaupon	1.9	1.5	2.5	2.6	0.5	12	11.8	3.2	4.1	7.3	35.19	0.24	0.38	9.63	6.6	25.18	44.28
inkberry	2.6	2.3	1.9	1.2	0	16.4	11.1	1.9	3.5	5.4	25.94	0	0	0.97	9	24.96	41.46
wax myrtle	2.7	1.1	1.8	7.6	0	18.7	17.6	1.8	8.7	10.5	34.11	0.16	0.25	5.78	2.39	28.09	56.19
live oak	1.7	1.9	1.9	7	0	21.4	19.2	1.9	8.9	10.9	27.51	0	0	3.76	5.82	23.74	53.84
fetterbush	1.8	1.9	1.5	3.5	0	19.8	19.8	1.5	5.4	6.9	33.29	0.21	0.33	2.69	3.45	30.27	56.97
water oak	2.9	2.7	2.3	0	0.6	18.2	15.7	3	2.7	5.8	33.27	2.7	4.31	3.64	13.49	25.32	46.82
longleaf pine	2	2	2.5	3	5.6	22.8	19	10	5.1	15	27.5	0.39	0.62	3.34	3.09	23.54	57.54
wiregrass	0	3.2	0.9	22	0	34.8	34.8	0	25.2	22.8	18.7	1.5	0	0	2.8	18.7	76.3
little bluestem	0.5	3.2	1.3	17	0	32	31.3	1.3	20.2	21.5	21.2	1.7	0.03	0	3.1	21.2	74

Matt et al., *Energy & Fuels* (2020)

Composition of Leaves

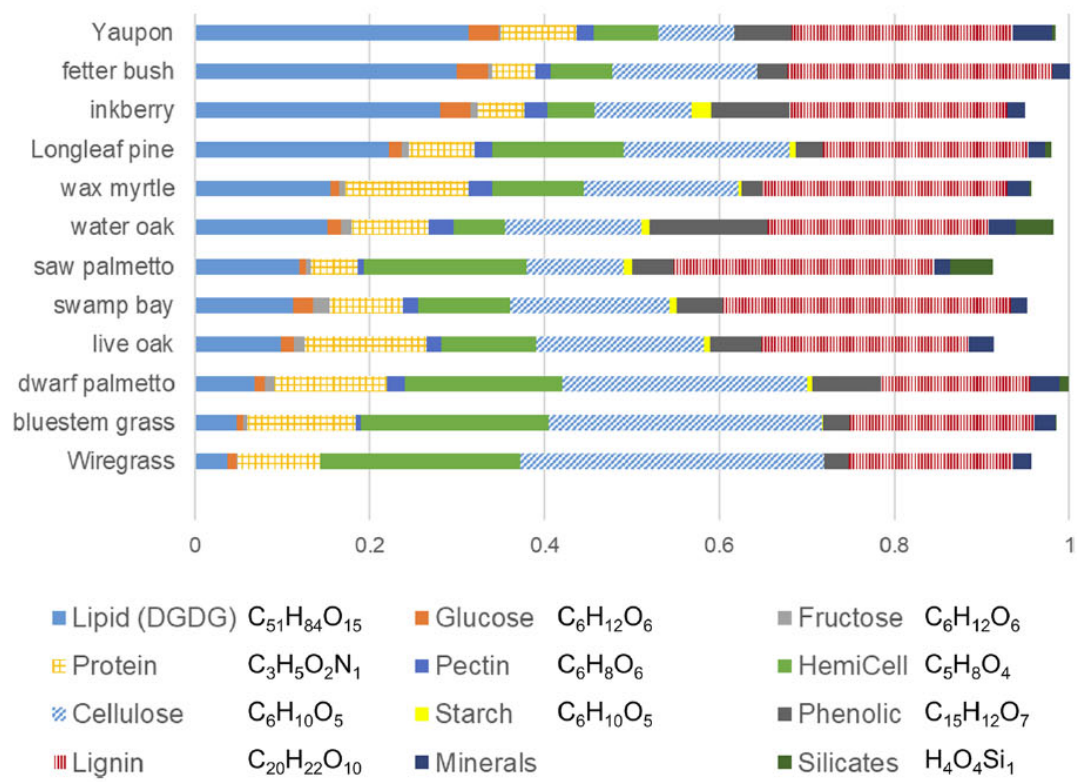


Figure 7. Leaf components with species arranged in the order of increasing lipid content with empirical formulas of modeling compounds.

Matt et al., *Energy & Fuels* (2020)

Pretreatment Prior to Enzymatic Breakdown for Biofuels