Geokimia –TKG 2201

Geokimia Organik: Material Organik

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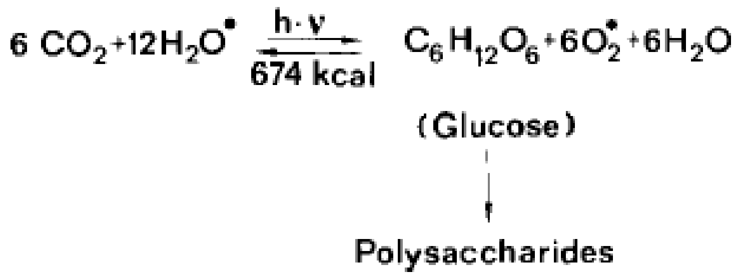
Outline

- Introduction
- Organic carbon cycles
- Chemical composition of biomass
- Sedimentary processes and accumulation of organic matter

Organic matter (OM)

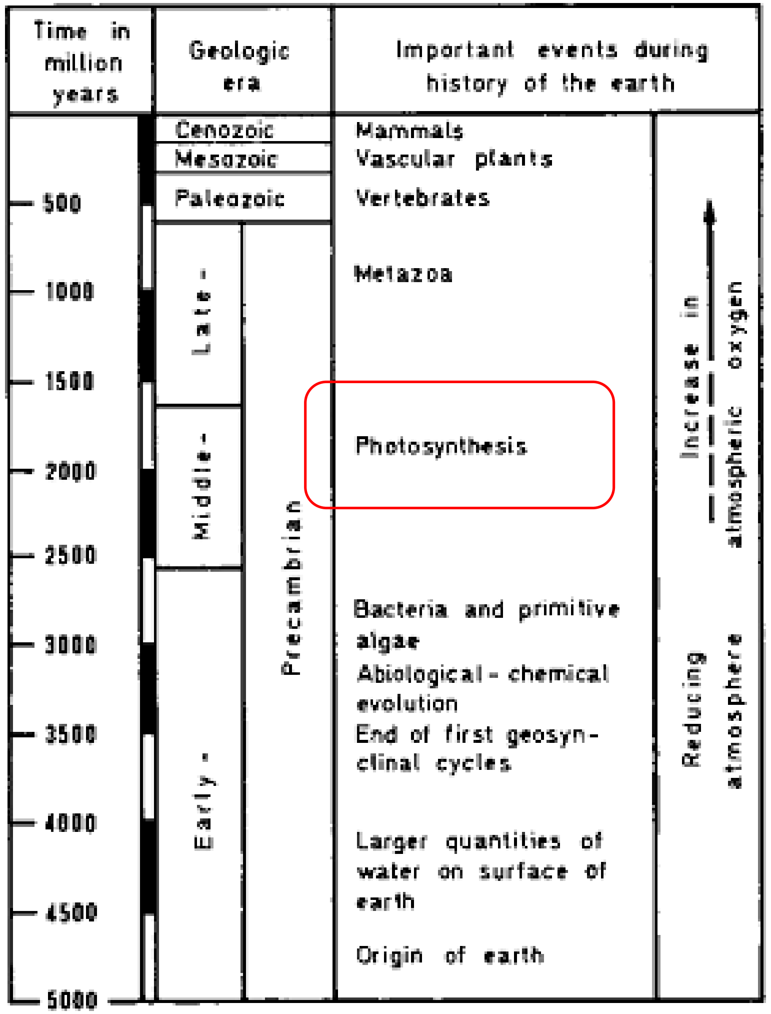
- Material comprised of organic molecules in monomeric or polymeric form derived directly or indirectly from the organic part of organism.
- Mineral skeletal parts, such as shells, bones, and teeth are not include
- Photosynthesis is the basic process that accomplishes the mass production of organic matter on earth



Photosynthesis is basically a transfer of hydrogen from water to carbon dioxide to produce organic matter in the form of glucose and oxygen

Tissot and Welte (1984)

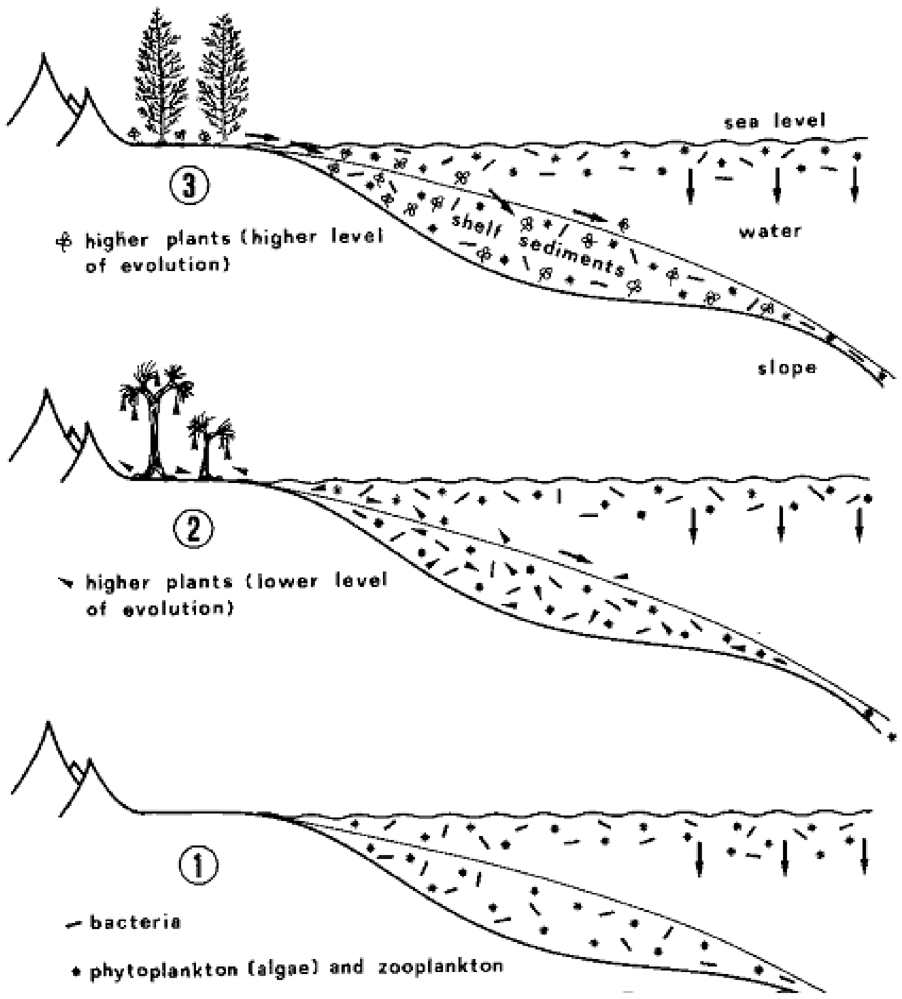
Photosynthesis



- The early earth's atmosphere: H_2, CH_4, NH_3, N_2 and H_2O. No Oxigen
- Heterotroph organism
- 2 billion years ago: start photosynthesis → autotroph organism : blue green algae (the first oxygen-producing organism)
- The portion of the spectrum utilized by most photosynthetic organisms is between 4000 to 8000 A : ~ visible light
- Photosynthesis is the basis for mass production of OM
- The average preservation of primary organic production: 1 – 4 %

Tissot and Welte (1984)

Main natural associations of OM in aquatic sediment during geological history



Main natural associations of organic matter during geologic history		(1) CAMBRIAN-SILURIAN	(2) DEVONIAN-JURASSIC	(3) CRETACEOUS-RECENT
Bacteria, algae and zooplankton		+ + +	+ + +	+ +
Higher plants	degraded, partly oxidized reworked by microorganisms	o	+	+ +
	little to moderately altered	o	+	+ + +

deltas, continental margins

Tissot and Welte (1984)

Processes and pathways involving Carbon

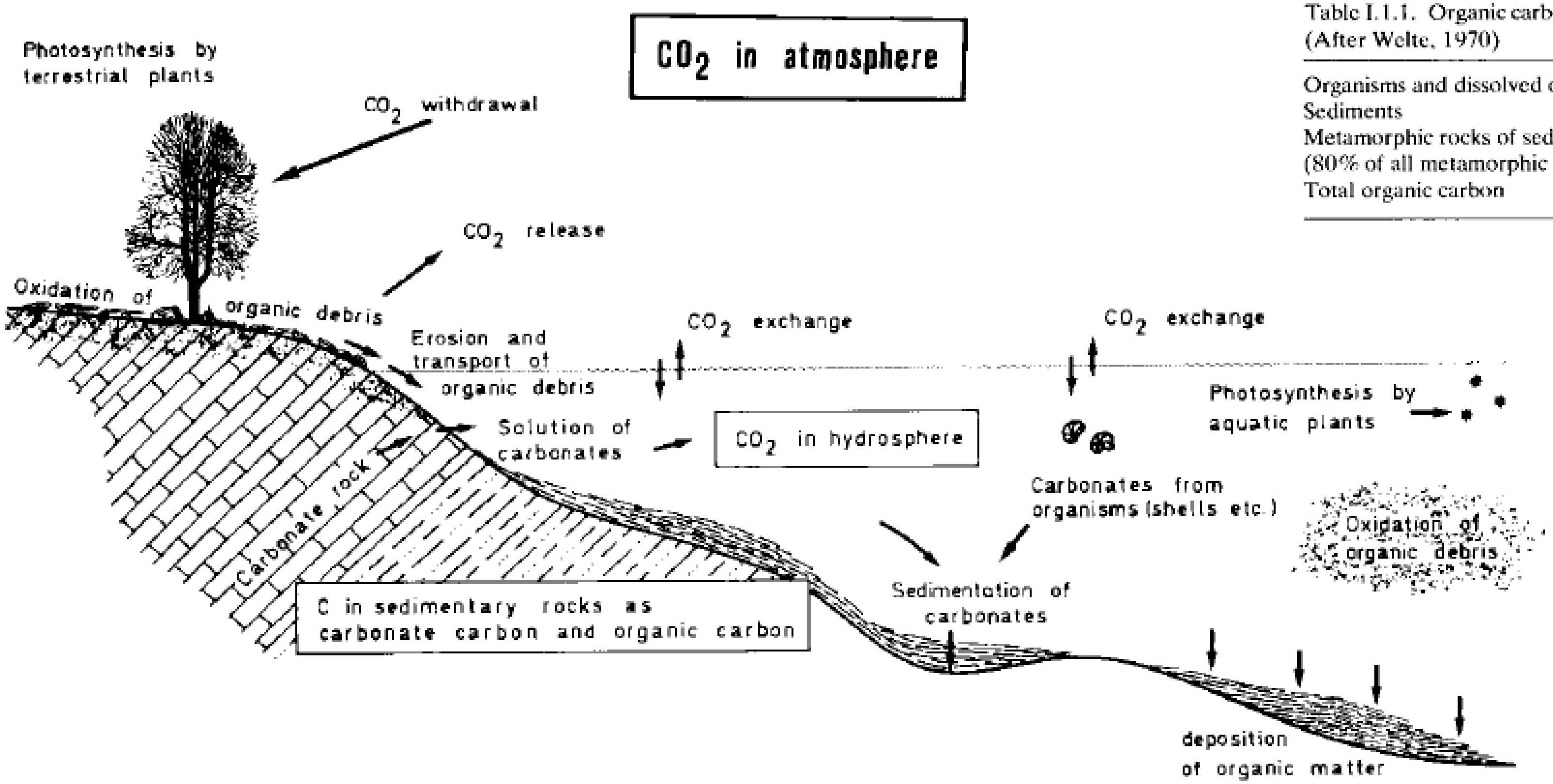


Table I.1.1. Organic carbon in the earth's crust expressed in 10^{15}t. (After Welte, 1970)

Organisms and dissolved organic C	0.003
Sediments	5.0
Metamorphic rocks of sedimentary origin (80% of all metamorphic rocks)	1.4
Total organic carbon	6.4

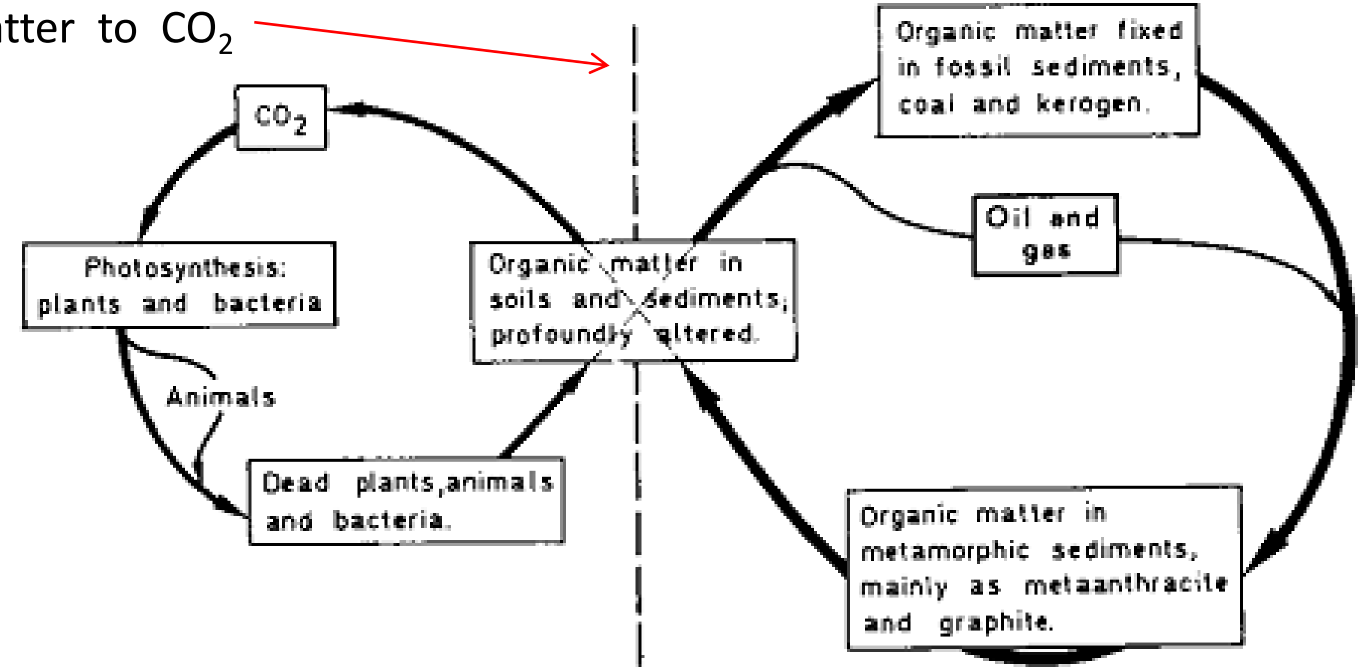
Fig. I.1.5. Main processes and pathways involving the element carbon. Most carbon on earth is concentrated in sediment, about 18% as organic, and about 82% as carbonate carbon. Most organic carbon produced by organisms is quickly oxidized to CO_2 and recycled to the atmospheric and hydrospheric CO_2 reservoirs

Tissot and Welte (1984)

Cycle of organic carbon

Cycle 1 / Cycle 2

Interconnected by the tiny leakage of about 0.01 % to 0.1% of the total organic carbon, representing oxidation of sedimentary organic matter to CO_2



Tectonic events:

Uplift →
→ Erosion
→ Eroded and oxidized

Subsidence →
→ Increase in burial
→ OM preserved

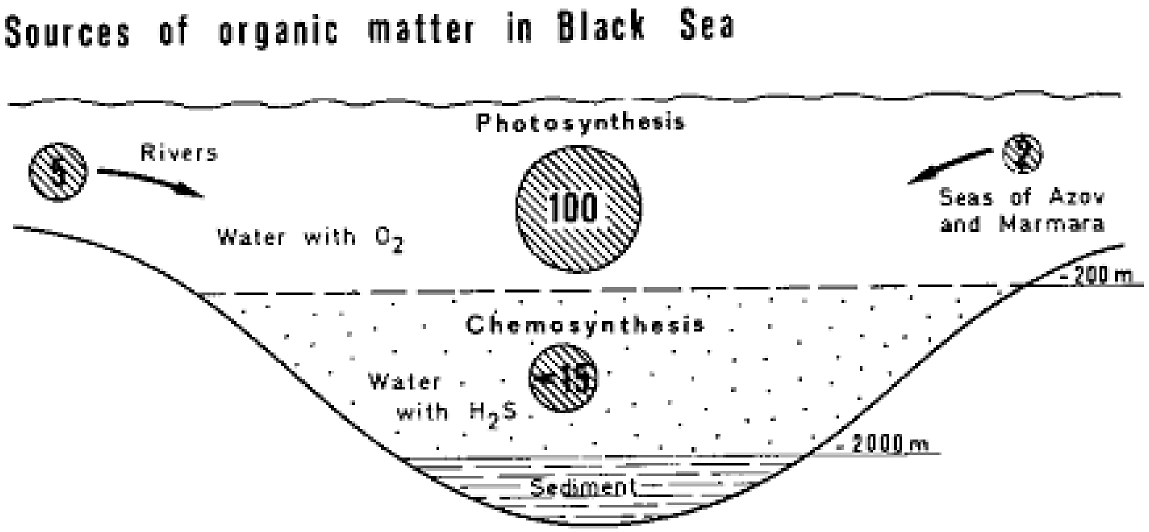
- Small cycle
- a turnover of about 2.7 to 3.0 x 10^{12} t of organic carbon, and
- a half-life of days up to tens of years

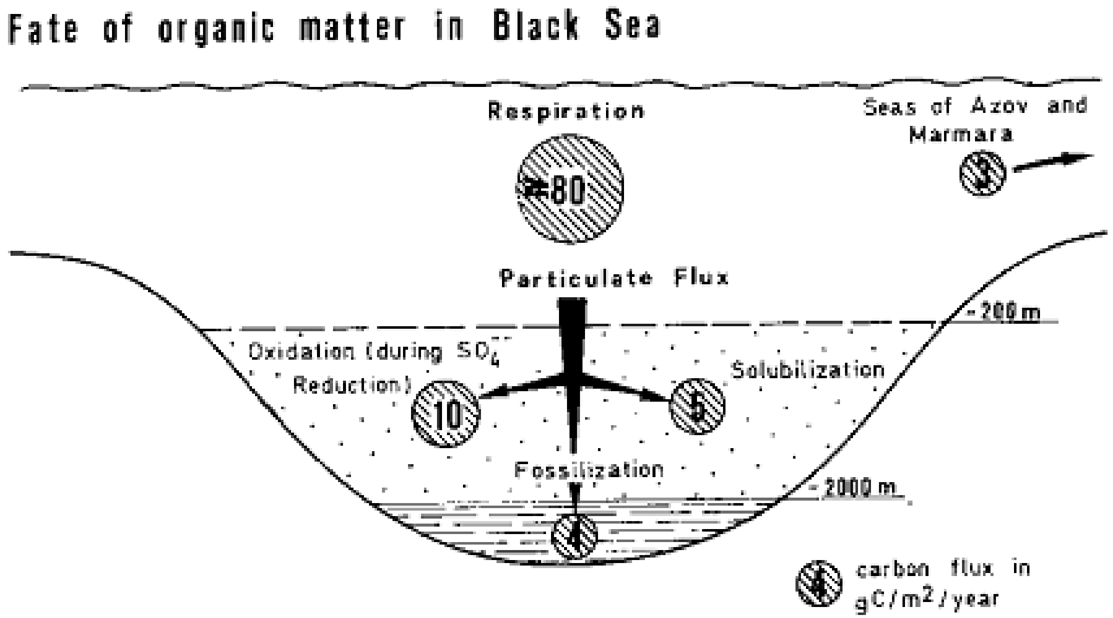
- Large cycle
- 6.4 x 10^{15} t
- a half-life of several million year

Tissot and Welte (1984)

Organic carbon budget

- An example from Black sea





- 100 g organic carbon/m2 -yr have been produced by photosynthetic organisms
- < 10 % as detrital material by rivers and seas
- Chemosynthesis → OC resynthesized by autotrophic bacteria

- Primary organic carbon cycle (cycle 1): 80-95 %
- ~10 %: Oxidation
- ~ 5 %: Solubilization
- Max. 4 %: Fossilized

Tissot and Welte (1984)

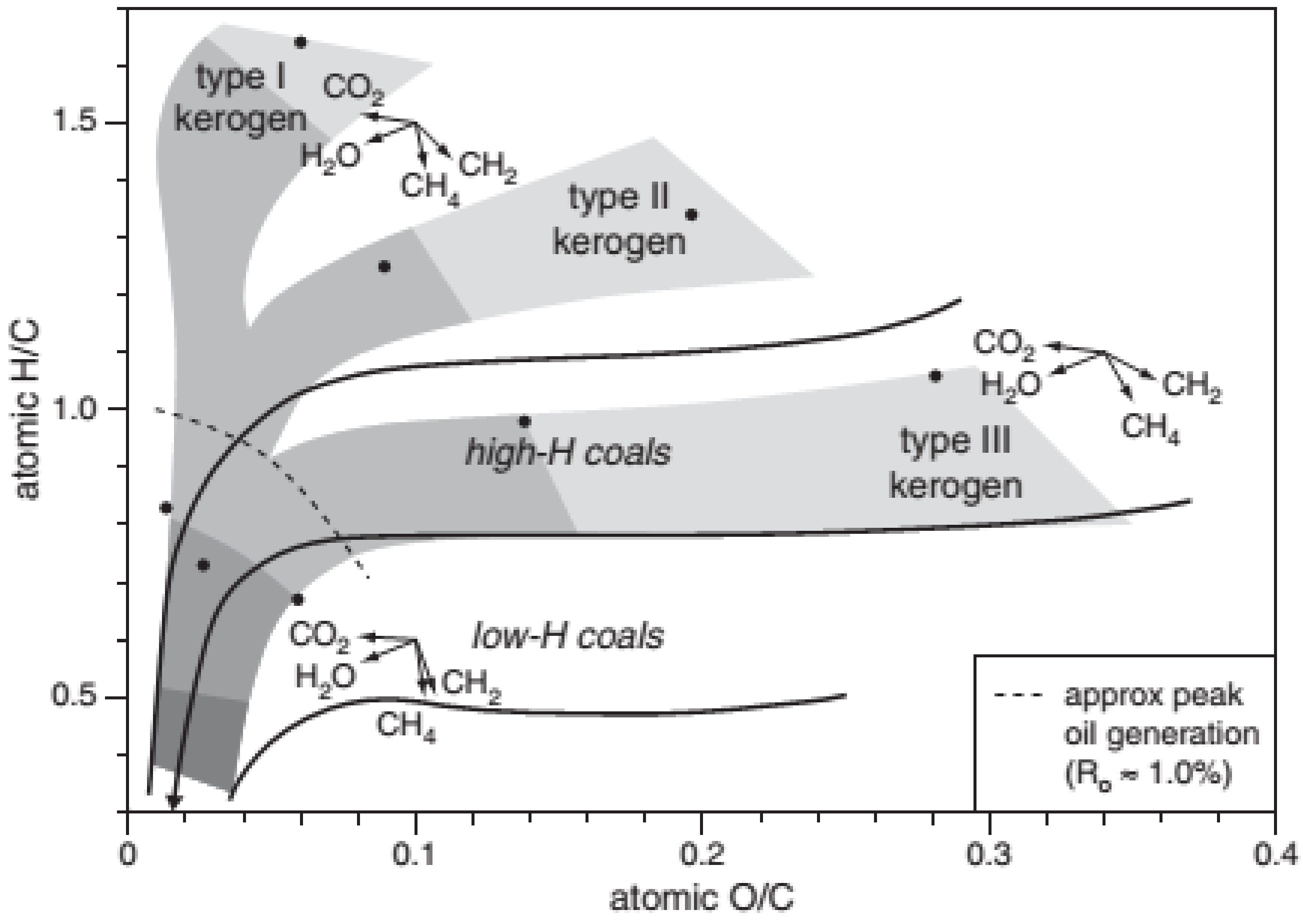
Chemical composition of biomass

- Chemical constituents of organisms: lipids, proteins, carbohydrates and lignins (higher plants).
- Lipids: fat substances, waxes and lipid-like components, such as oil-soluble pigments, terpenoids, steroids and many complex fats.
- Chemical composition of marine planktonic algae vs. terrestrial higher plant:
  - The OM of marine planktons: mainly composed of proteins (up to 50% and more), a variable amount of lipids (5 to 25%), and, generally not more than 40% carbohydrates.
  - Higher terrestrial plants are largely composed of cellulose (30 to 50%) and lignin (15 to 25%)

Chemical composition of biomass

- Lignin is the major primary contributor of aromatic structures in organic matter of recent sediments
- Predominantly land-derived organic matter with high contents of lignin and carbohydrates has H/C ratios around 1.0 to 1.5 and is more of an aromatic nature.
- Organic material mainly derived from autochthonous marine plankton reaches H/C ratios around 1.7 to 1.9 and is more of an aliphatic or alicyclic nature

van Krevelen plot: Kerogen types & coals



stage	zone	main fluids evolved	approx vitrinite reflectance (R_o)
diagenesis	immature	carbon dioxide & water	
			0.5–0.6%
catagenesis	oil	liquid hydrocarbons	
			1.3%
	wet gas	gaseous hydrocarbons	
			2.0%
metagenesis	dry gas	methane	

Killops and Killops (2005)

General condition for formation of organic-rich sediments

1. A sufficient and large amount of OM is needed
   → Higher plant on land and phytoplankton in aquatic environments
2. Low-energy depositional environment
   → Low water current velocities and limited wave action
3. Input of inorganic mineral matter should not overwhelm the organic matter and dilute it significantly
4. Conditions must favour preservation of organic matter within the sediment, rather than degradation by detritivores and decomposers

Estimated annual production of OM in the oceans

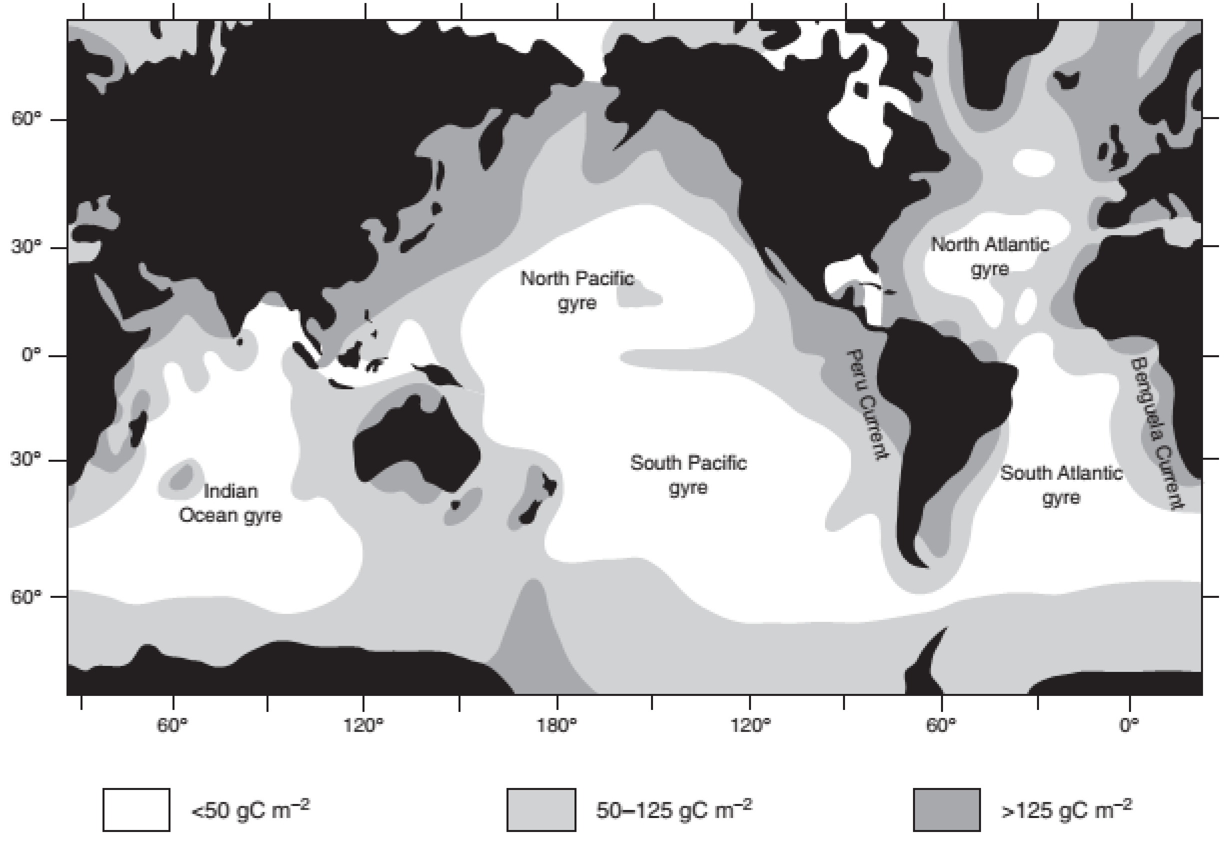
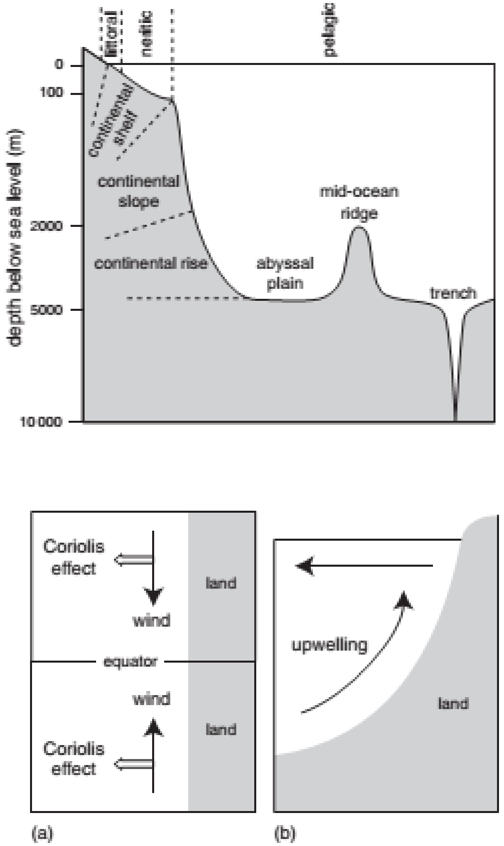
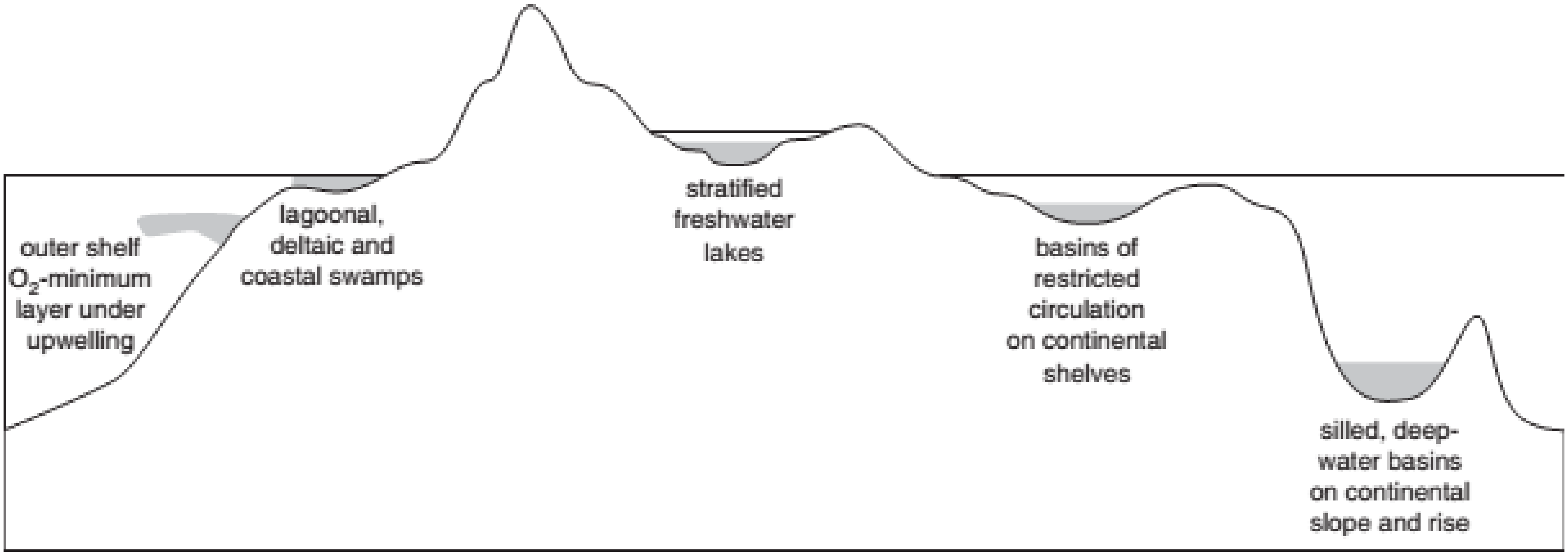


Fig. 3.8 Estimated annual production in the oceans (after several sources, including FAO 1972; Koblenz-Mishke et al. 1970).



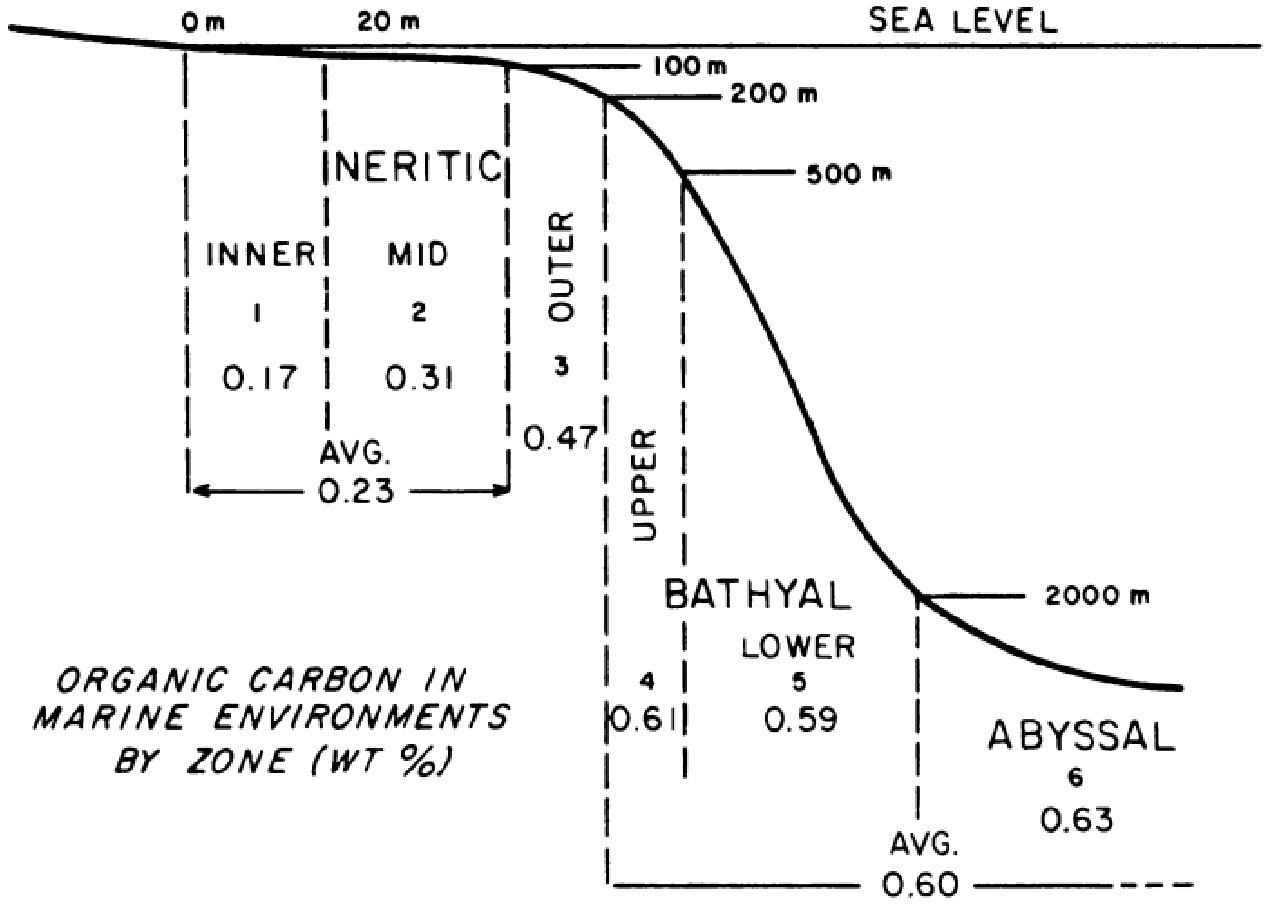
Killops and Killops (2005)

Oxygen-depleted environments



Killops and Killops (2005)

Organic carbon in marine environments by zone (wt,%)



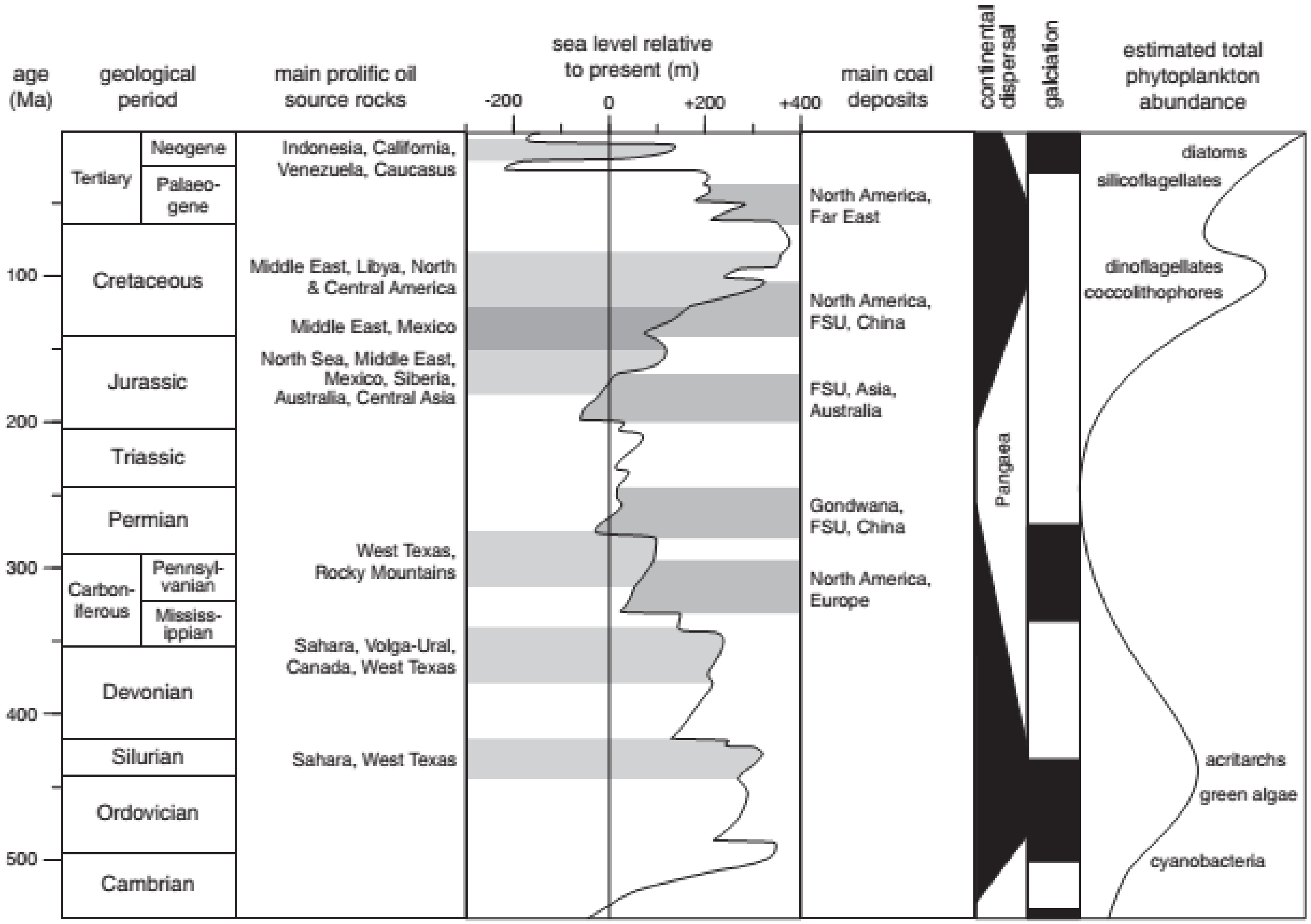
The amount of organic matter in a sediment is a function of three variables:

(1) the rate of organic productivity of the system;
(2) the rate of destruction by biologic or inorganic processes; and
(3) the rate of dilution by detrital sediment

Figure 14-1. Mean total organic carbon (TOC) content of environmental depth zones in the Gulf Coast Tertiary section of Louisiana. (From Dow, 1978.)

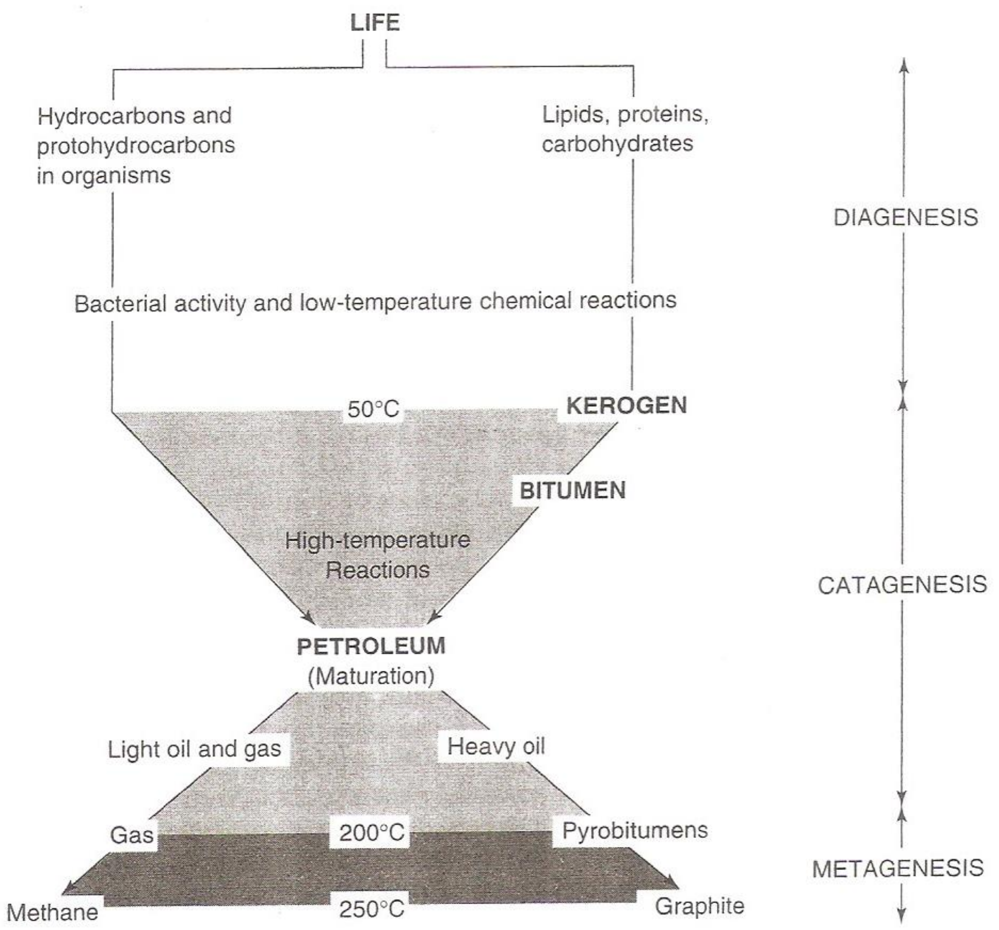
Galloway and Hobday (1983)

Depositional periods of coal and petroleum SR



Killops and Killops (2005)

The origin and maturation of petroleum



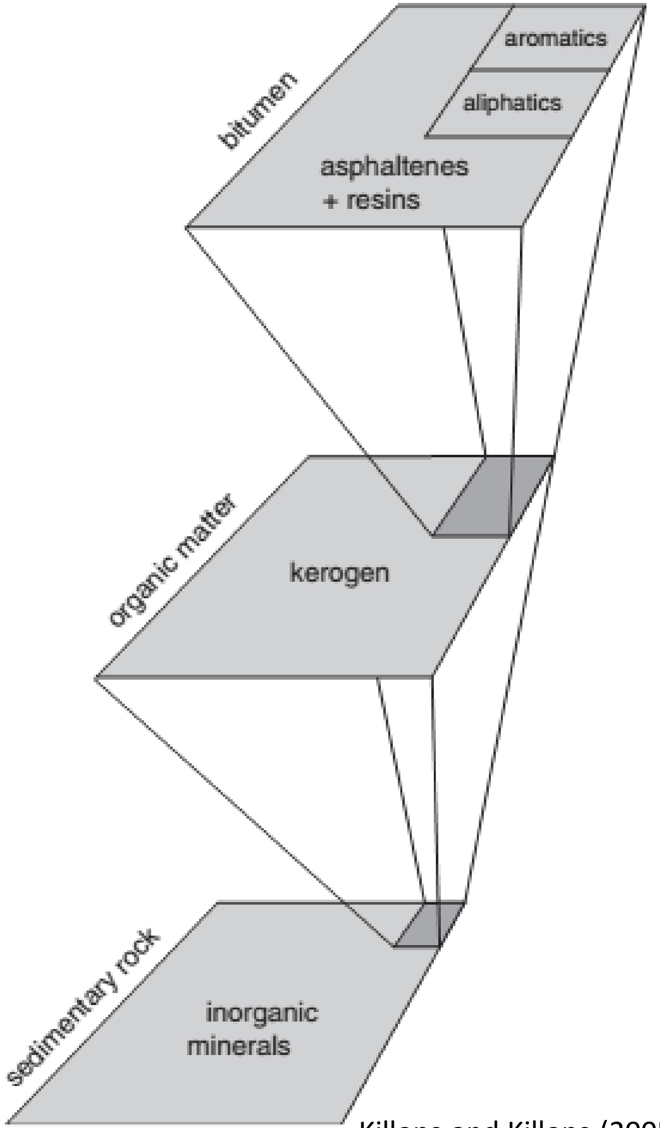
Hunt, 1995

Evolution of OM

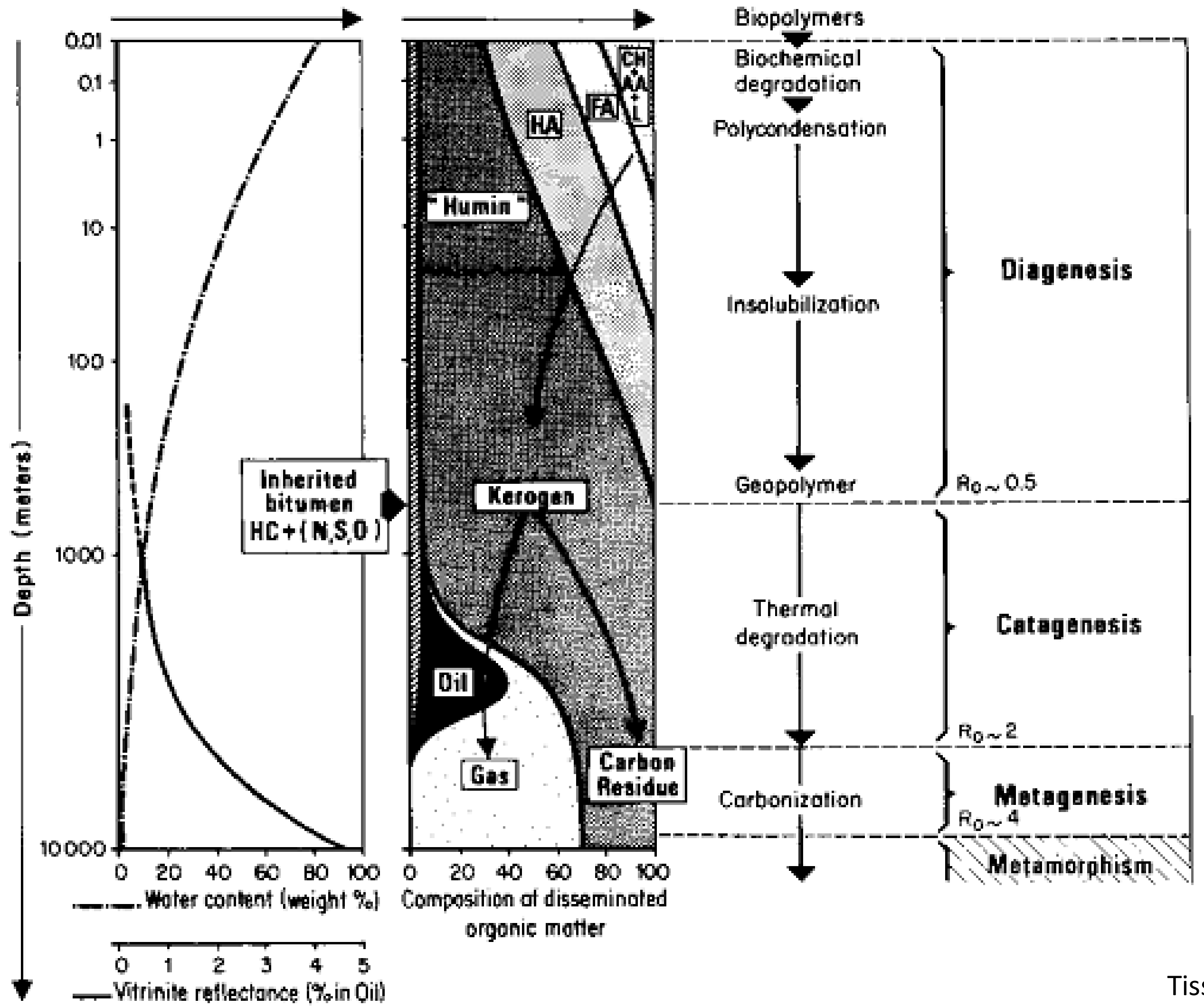
- Diagenesis begins in recently deposited sediments where microbial activity is one of the main agents of transformation. Chemical rearrangements then occur at shallow depths: polycondemation and insolubilization. At the end of diagenesis, the organic matter consists mainly of kerogen.
- Catagenesis results from an increase in temperature during burial in sedimentary basins. Thermal degradation of kerogen is responsible for the generation of most hydrocarbons, i. e., oil and gas.
- Metagenesis is reached only at great depth. However, this last stage of evolution of organic matter begins earlier (vitrinite reflectance approximately 2 %) than metamorphism of the mineral phase (vitrinite reflectance of about 4 %, corresponding to the beginning of the green-schist facies)

Tissot and Welte (1984)

Evolution of OM



Killops and Killops (2005)

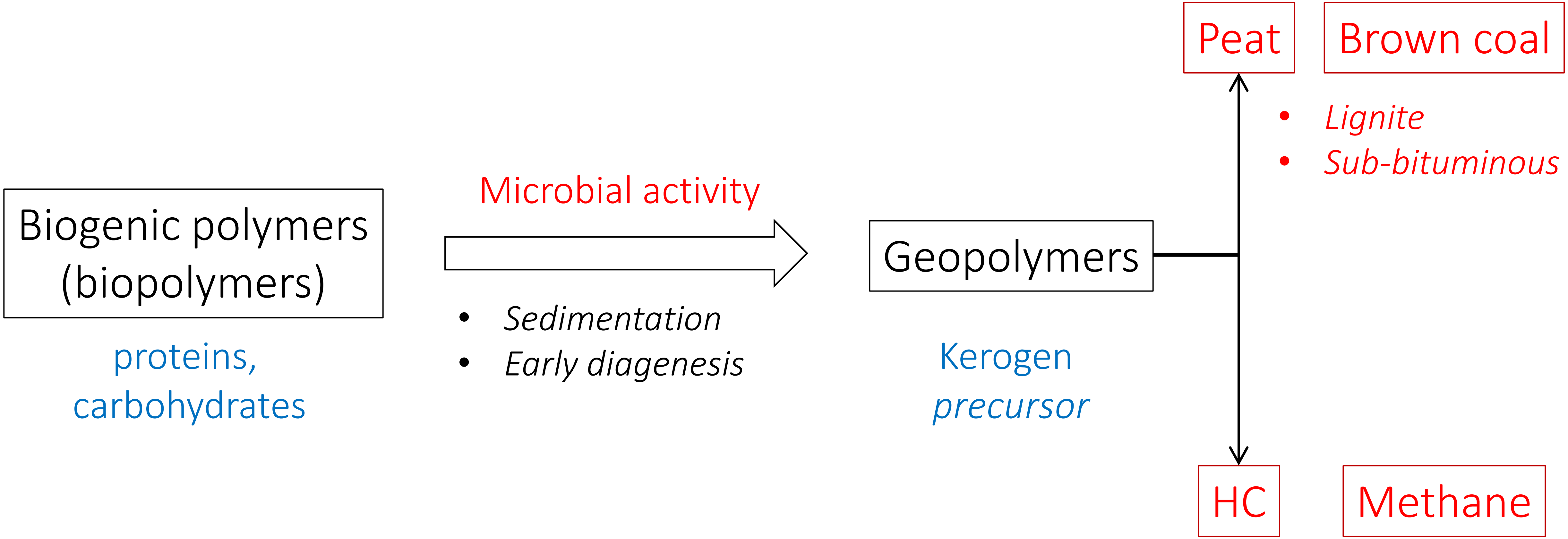


Tissot and Welte (1984)

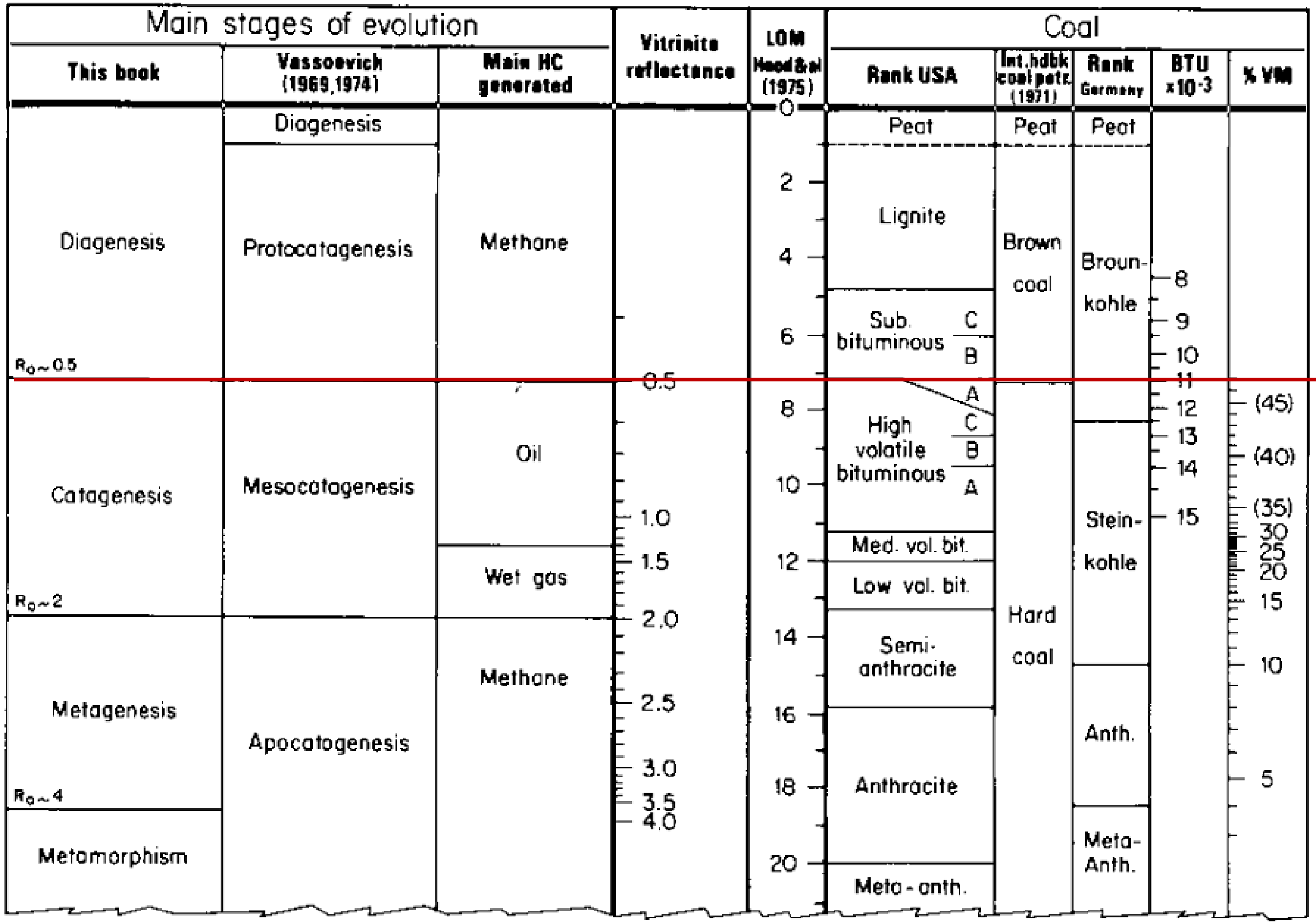
Diagenesis

- A process through which the system tends to approach equilibrium under conditions of shallow burial, and through which the sediment normally becomes consolidate
- Depth: a few hundred meters – (a few thousand meters-occasionally)
- Increase P & T : small
- Transformation: mild condition
- Main agent: microbial activity

Diagenesis


Biogenic polymers (biopolymers)
proteins, carbohydrates
Microbial activity
Sedimentation
Early diagenesis
Geopolymers
Kerogen precursor
Peat
Brown coal
Lignite
Sub-bituminous
HC
Methane

Diagenesis



The end of diagenesis of sedimentary OM

- *Decreasing extractable humic acids*
- *Most of carboxyl groups have been removed*
- *~ Boundary between brown and hard coal*

Tissot and Welte (1984)

Diagenesis

- Biosphere → to geosphere: below water-sediment contact (first few meters of sediment)
- 1-m section = 500 to 10000 years
- .The residence time of organic compounds in this. zone of the sedimentary column is long compared to the lifetime of the organisms but very short compared to the duration of geological cycle
- Sediment deposits → is buried → OM → insoluble: increasing polycondensation associated with loss of superficial hydrophilic functional group → humin + pollen, spores, etc

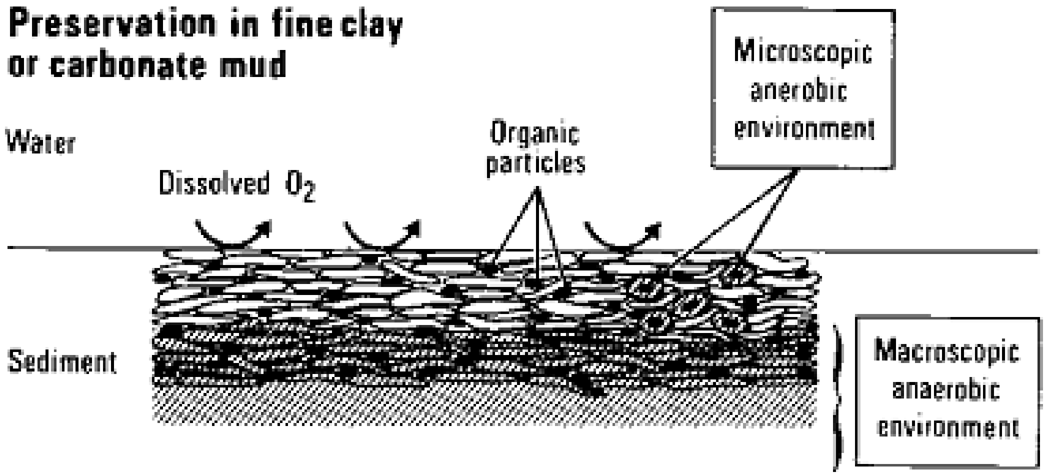
Diagenesis

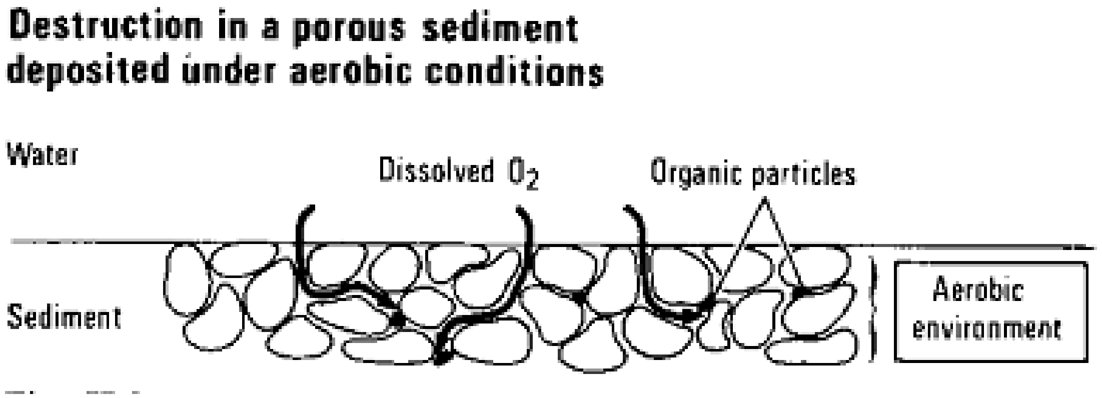
- Biochemical degradation: micro-organism activities

  biopolymer (protein & carbohydrate) →individual amino acids & sugars
- Polycondensation

  residue (not used by micro-organism) → brown compound fulvic and humic acid
- Insolubilization
  - Increasing polycondensation & loss of functional groups
  - Fulvic&humic acids → kerogen
- Product: biogenic methane

Preservation or destruction of OM



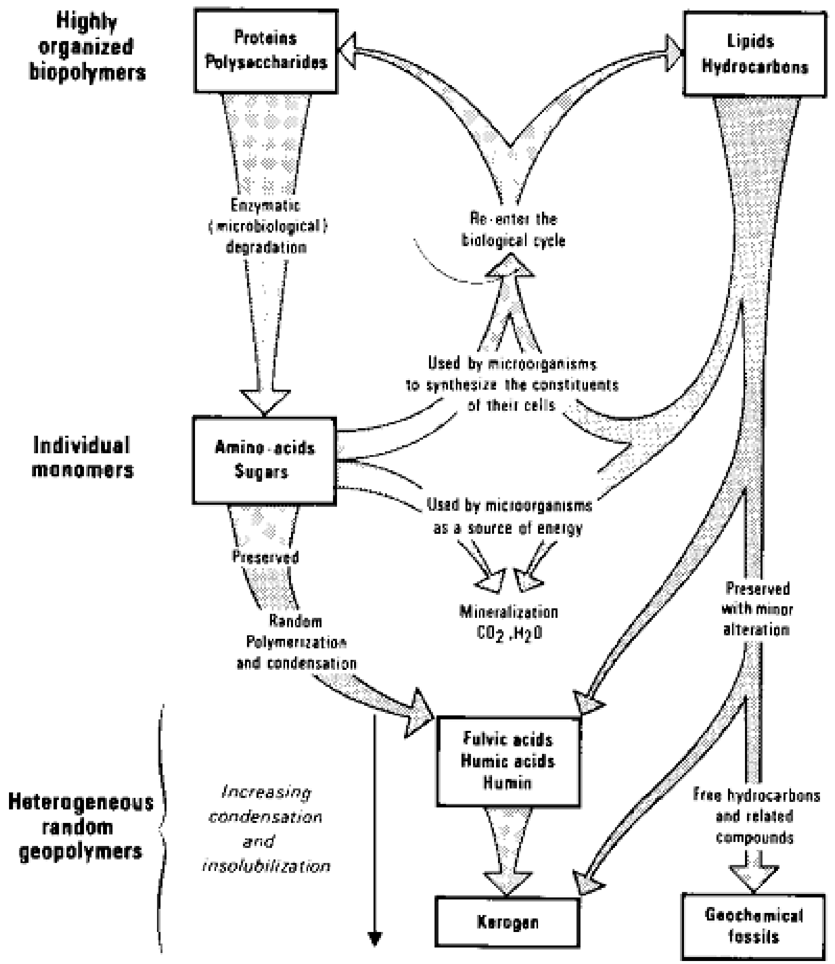


In a fine clay or carbonate mud, pore water becomes a nearly closed microenvironment. There is no replenishment of oxygen, and anaerobic conditions are rapidly established, first on microscopic, then on a macroscopic scale.

In a porous sand deposited under aerobic conditions, free circulation of water containing dissolved oxygen results in the destruction of the organic matter.

Tissot and Welte (1984)

Results and balance of Diagenesis



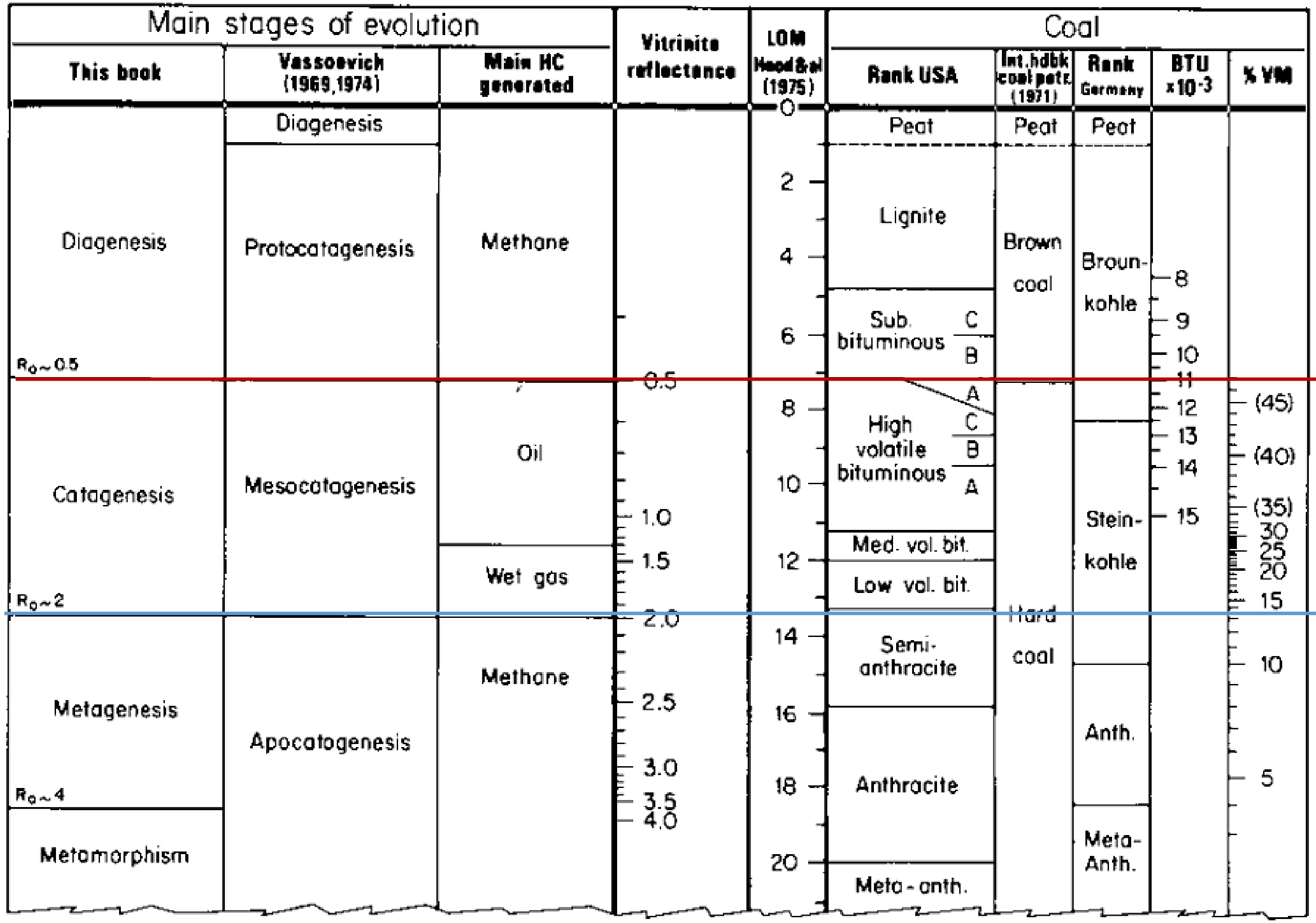
Tissot and Welte (1984)

Catagenesis

- Depth: several kilometers
- Increasing P&T (*tectonics may also contribute)*
- T: 50 to 150°C; P: 300 to 1500 bars
- Kerogen → *liquid petroleum* → wet gas → condensate + methane
- Hard coal + methane

  (*massive organic deposits*)
- End of catagenesis:
  - disappearance of aliphatic carbon chain
  - ~ vitrinite reflectance 2.0 : beginning of anthracite ranks

Catagenesis

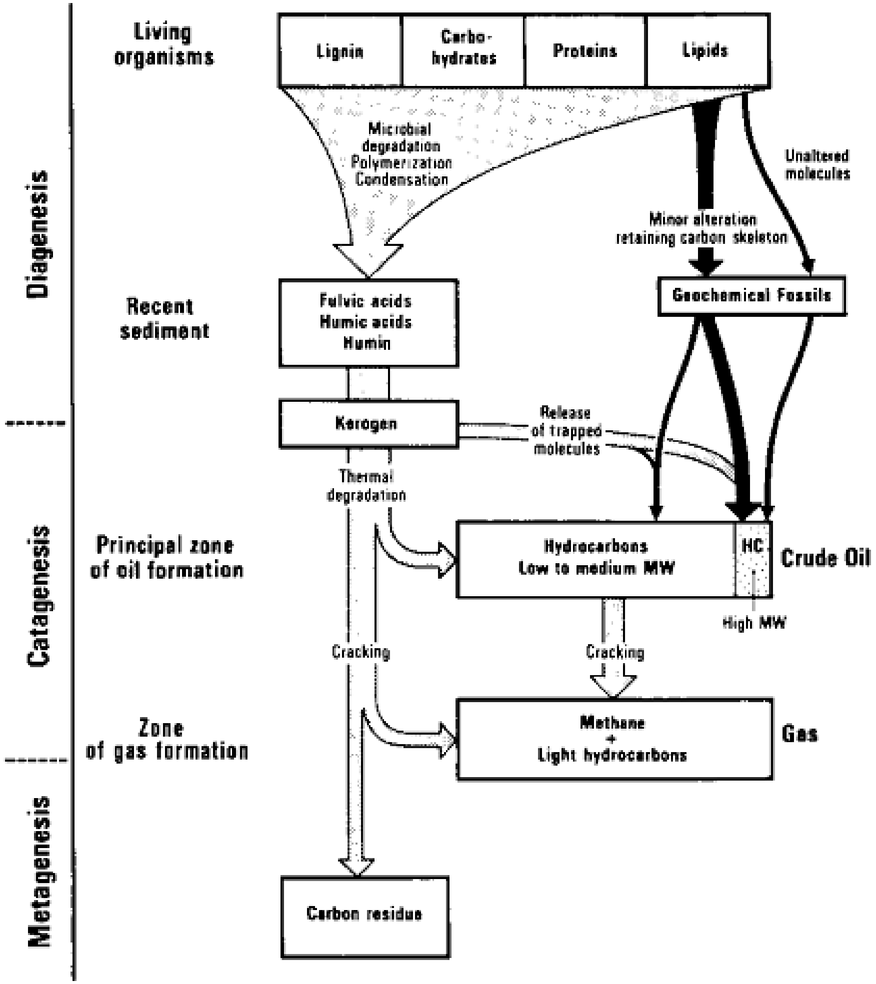


The end of diagenesis

The end of catagenesis

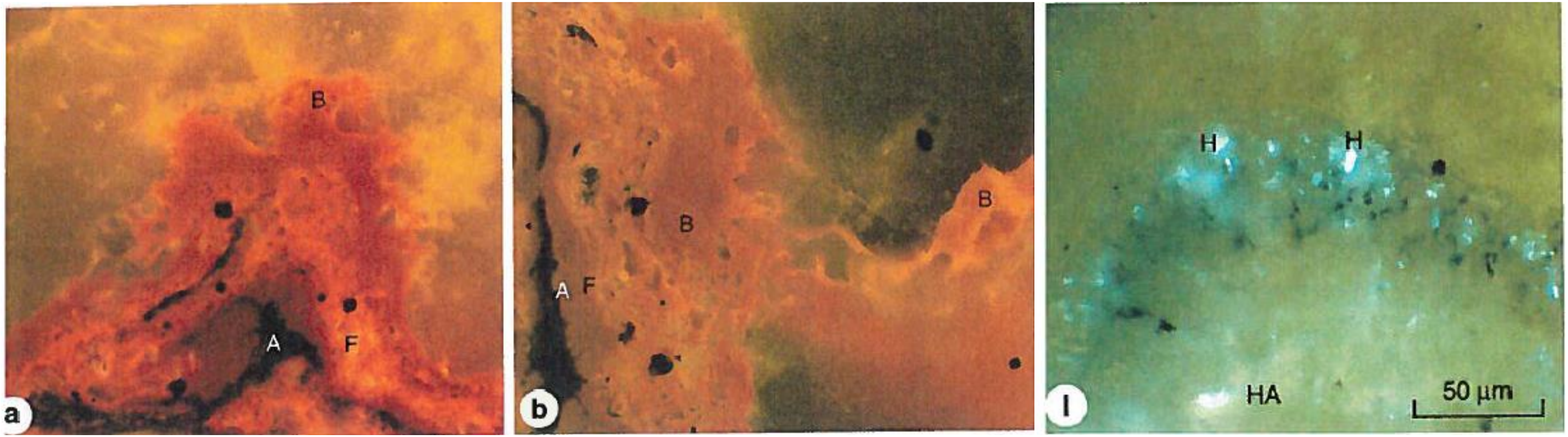
Tissot and Welte (1984)

Evolution of OM



Tissot and Welte (1984)

Bitumen



fluorescing **primary bitumen** (B) and **oily bitumen** within primary pores and microfractures of platformal carbonate source rock; the bitumen was generated directly from associated thermally immature (0.50%R_or, vitrinite equivalent), sulphur-rich fluoramorphinite (F) and filamentous alginite (A) stromatolites; viewed perpendicular to bedding plane; Middle Devonian Winnipegosis Formation, Manitoba

blue-fluorescing, **hydrocarbon fluid inclusions** (H) trapped at the margins and yellow-fluorescing, **hydrocarbon fluid inclusion** (HA) in the core of a rounded, carbonate allochem; Upper Devonian Birdbear Formation, Saskatchewan

Potter et al., 1998

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