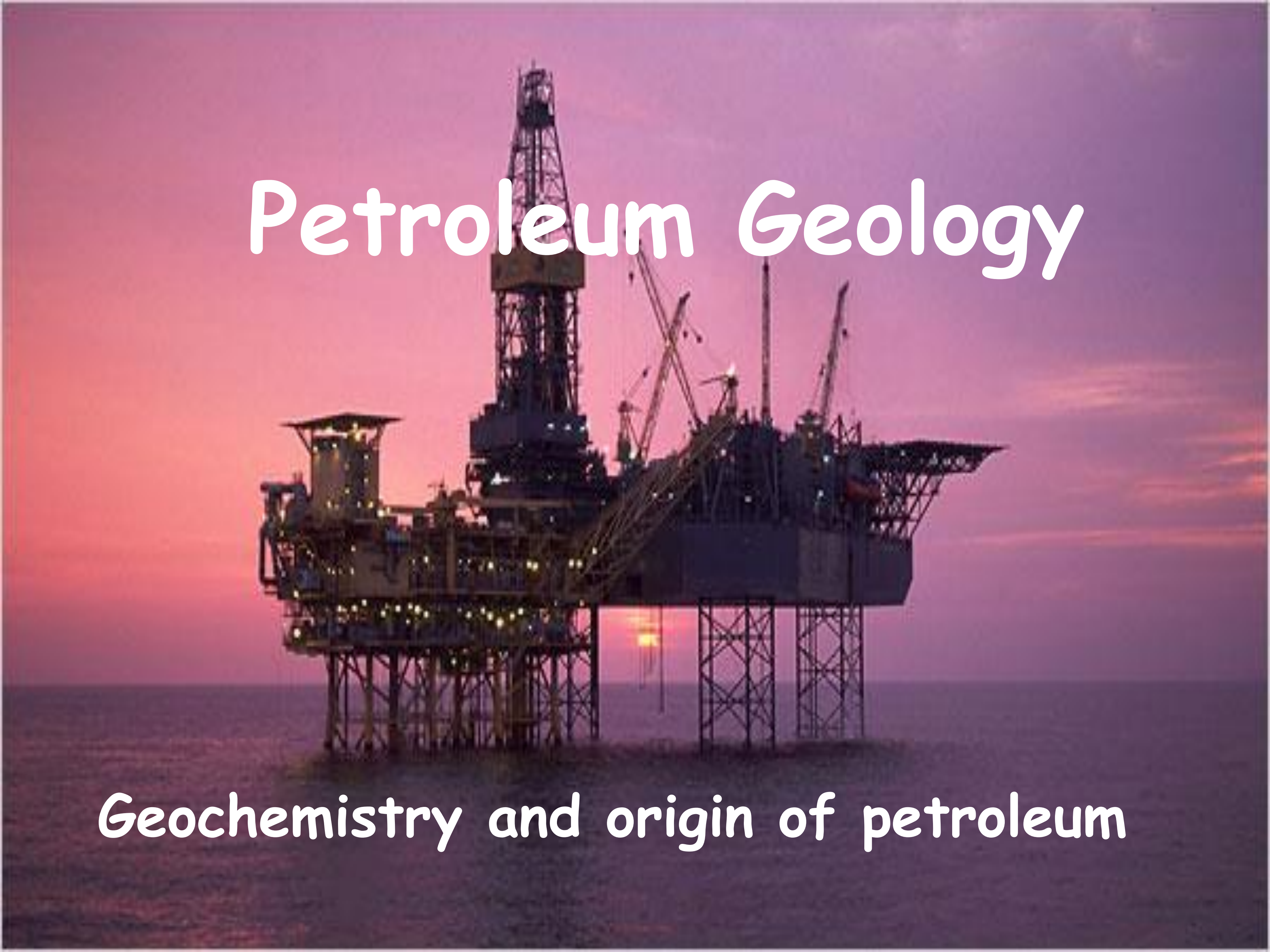


Petroleum Geology

Geochemistry and origin of petroleum

THE CHEMISTRY OF PETROLEUM

Petroleum consists of variable mixtures of the chemical substances known as hydrocarbons and other compouds. Hydrocarbons molecules made predominantly of atoms of carbon and hydrogen in varying abundance arranged and linked together in many different ways

Compounds composed entirely of carbon or hydrogen are referred to as "pure" hydrocarbons, whereas other hydrocarbons with bonded compounds or impurities of sulphur or nitrogen, are referred to as "impure", and remain somewhat erroneously referred to as hydrocarbons.

Others elements that can be present

Oxygen
Nitrogen
Sulphur

Vanadium
Cupper
Nickel

Hydrocarbons grade froms gases via liquid and plastic substances to solid

Gas	Liquid	Plastic	Solids
Natural gas: Dry Wet Condensate (gaseous in sub-surface) Gas hydrates	Oil,crude oil	Asphalt	Coal Kerogen Bitumen

Natural Gases

- "a mixture of hydrocarbons and varying quantities of nonhydrocarbons that exists either in the gaseous phase or in solution with crude oil in natural underground reservoirs".

Major constituents :hydrocarbons of the paraffin series

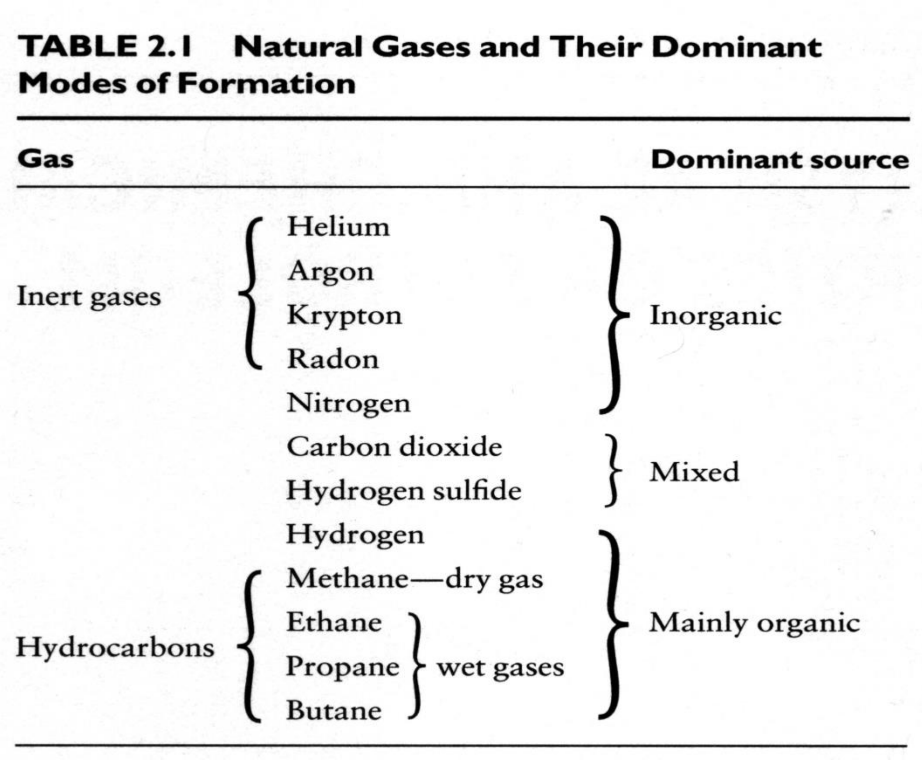


TABLE 2.1 Natural Gases and Their Dominant Modes of Formation

Gas			Dominant source
Inert gases	Helium		Inorganic
	Argon		
	Krypton		
	Radon		
	Nitrogen		
	Carbon dioxide		Mixed
	Hydrogen sulfide		
	Hydrogen		Mainly organic
Hydrocarbons	Methane—dry gas		
	Ethane	wet gases	
	Propane		
	Butane		

- **Dry gas**- contains largely methane, specifically contains less than 0.1 gal/1000ft3 of condensible (at surface T and P) material.
- **Wet gas**- contains ethane propane, butane. Up to the molecular weight where the fluids are always condensed to liquids

Natural Gases

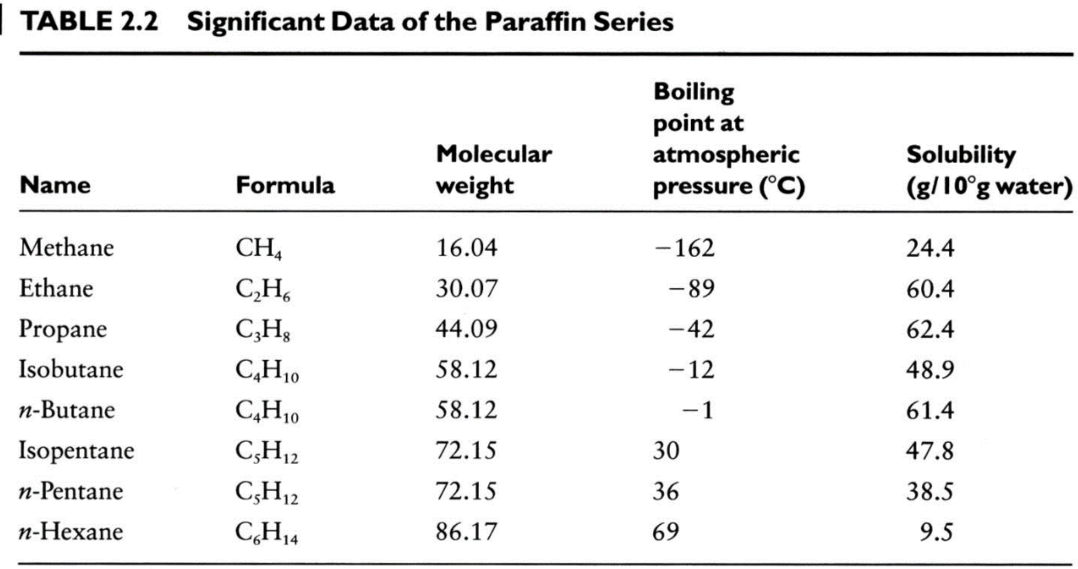
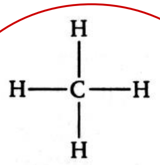


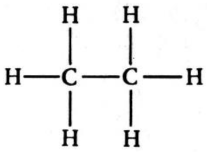
TABLE 2.2 Significant Data of the Paraffin Series

Name	Formula	Molecular weight	Boiling point at atmospheric pressure (°C)	Solubility (g/10°g water)
Methane	CH_4	16.04	−162	24.4
Ethane	C_2H_6	30.07	−89	60.4
Propane	C_3H_8	44.09	−42	62.4
Isobutane	C_4H_{10}	58.12	−12	48.9
n-Butane	C_4H_{10}	58.12	−1	61.4
Isopentane	C_5H_{12}	72.15	30	47.8
n-Pentane	C_5H_{12}	72.15	36	38.5
n-Hexane	C_6H_{14}	86.17	69	9.5

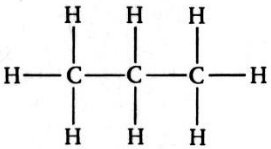


Methane (CH_4)

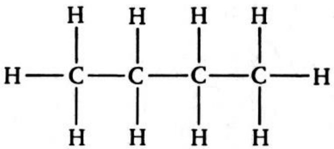
most abundant



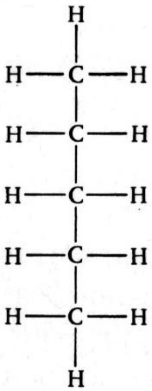
Ethane (C_2H_6)



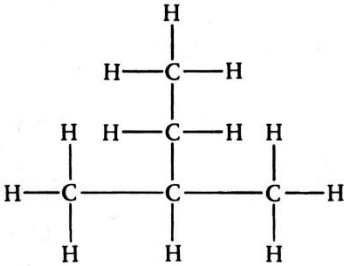
Propane (C_3H_8)



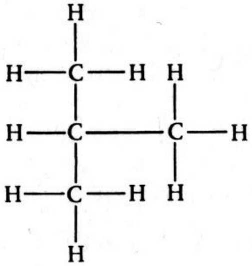
Normal butane (C_4H_{10})



Pentane (C_5H_{12})



Isopentane (C_5H_{12})



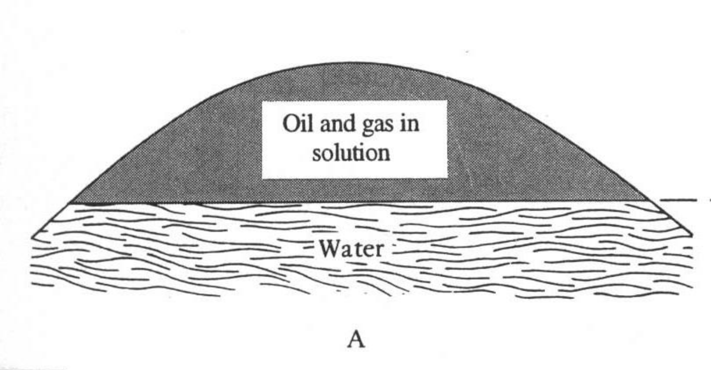
Isobutane (C_4H_{10})

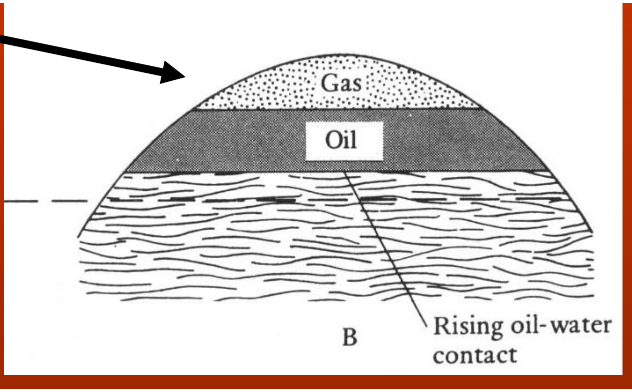
- The gases decrease in abundance up through pentane (C5).
- **(1) Methane** is the largest constituent of natural gas. It can formed in 3 ways:
- **(a) Mantle methane.** Derived from the mantle (presumably primordial methane).
- **(b) Microbial methane** As a reaction product of the bacterial decay of organic matter. Large caused by the reduction of CO2 during oxidation of the organic matter. $4H_2+CO_2 \rightarrow CH_4+2H_2O$
- **(c)Thermogenic methane** Thermal breakdown of heavier hydrocarbons. Appears that the thermal degradation has to be catalyzed for it to occur in nature.

Natural gas occurs in the ground either in its own or together with oil

If together it will be dissolved in the oil

…but if is very abundant it may separate in the reservoi forming a gas cap above the oil

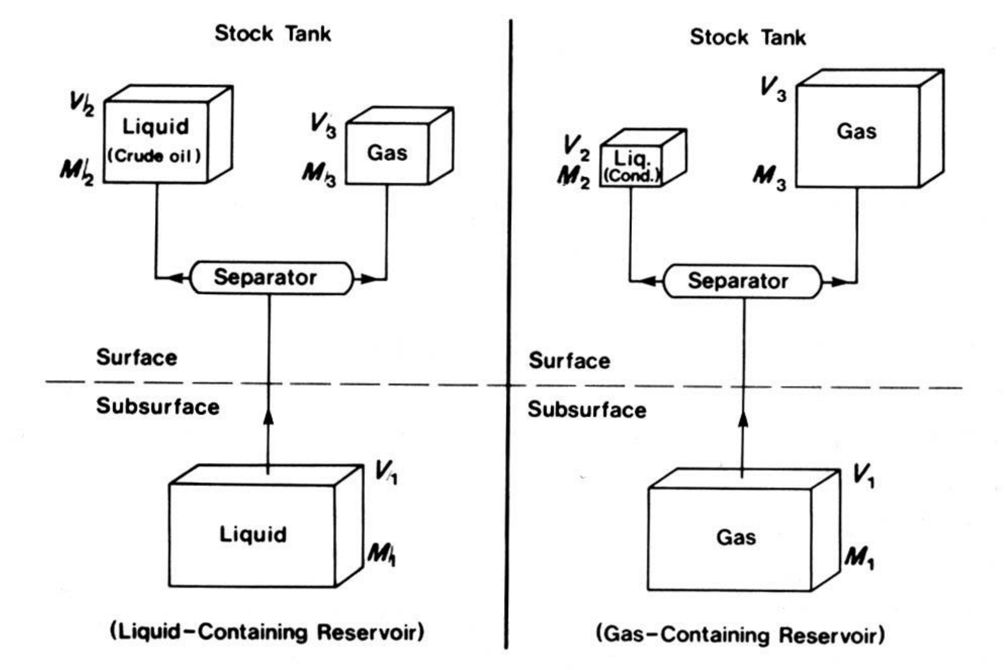




Dissolved gas- That portion of natural gas that is dissolved in liquid phase in the sub- surface. It can be (and usually is) physically separated from the liquid when the fluids are produced.

Associated gas- Also known as the "gas cap" is free gas (not dissolved) that sits on top of, and in contact with, crude oil in the reservoir.

Non-associated gas- Free gas that is trapped without a significant amount of crude oil.



Gas hydrates

Compounds of ice molecules (clathrates) that contain gas molecules (methane, ethane, H_2S, CO_2) in the crystal structure

Source: U.S. DOE

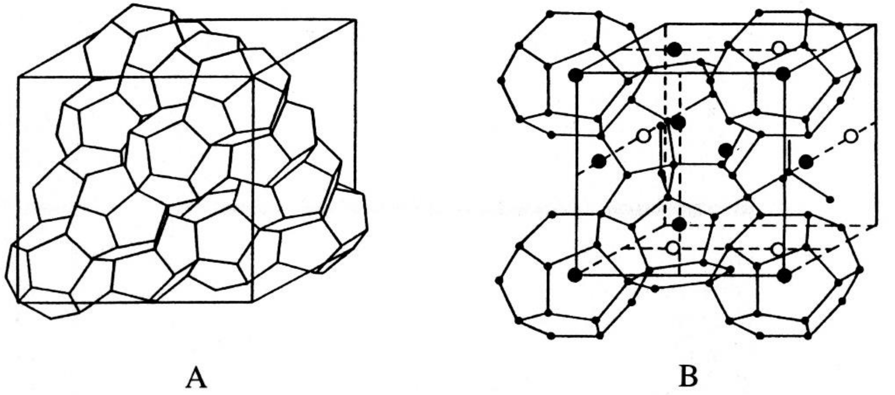
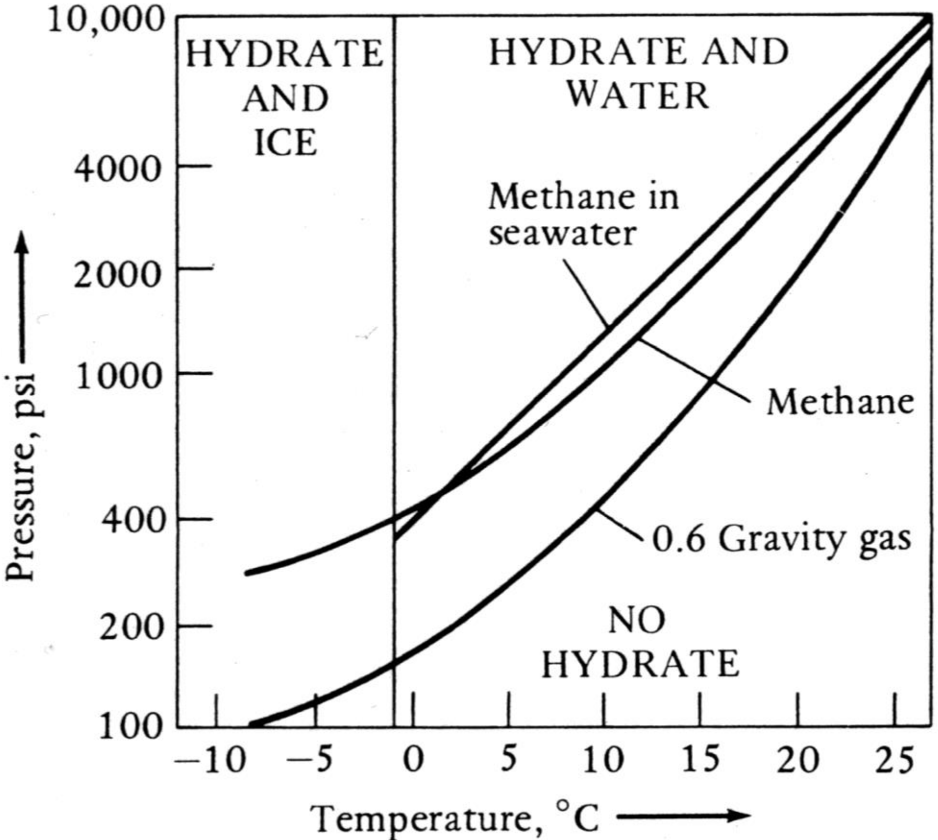


FIGURE 2.4 The two types of lattice structure for gas hydrates: (A) the larger structure with a 17.4-Å lattice and (B) the smaller one with a 12-Å lattice. (From Krason and Ciesnik, 1985.)

Occur only in a very specific P-T conditions.
They are stable at high P and low T

P required for stability increases logarithmically for a linear thermal gradient



Crude oil

Crude oil or crude defined as a mixture of hydrocarbons that existed in the liquid phase in natural underground reservoirs and remain liquid at atmospheric pressure after passing through surface separating facilities (API,AAPG,SPE definition)

Color:range from straw yellow,green brown to dark brown and dark

Crude oil vary enormously depending on the types and relative proportion of the hydrocarbons forming the mixture

1 barrel (bbl) = 42 gallons US =159 liters

Oil production is expressed as barrels/day (bpd, bd, bod, boed)

Also viscosity vary from light (very mobile) to heavy ones (they will scarcely flow)

They vary in both density (or specific gravity) and viscosity

More commonly used scale for oil densities is in degrees (gravity units) API

°API=(141.5/specific gravity)-131.5

Light oils= API gravities >40°

Heavy oils= API gravities <10°

Oil viscosity and API gravity are generally inversely proportional to one another

Variations in oil quality partly reflect its origin,but also what happened to it during the often long period when it was moving around

Crude Oil

Largely consist of carbon and hydrogen with traces of other elements.
There may be an immense number of molecular compounds

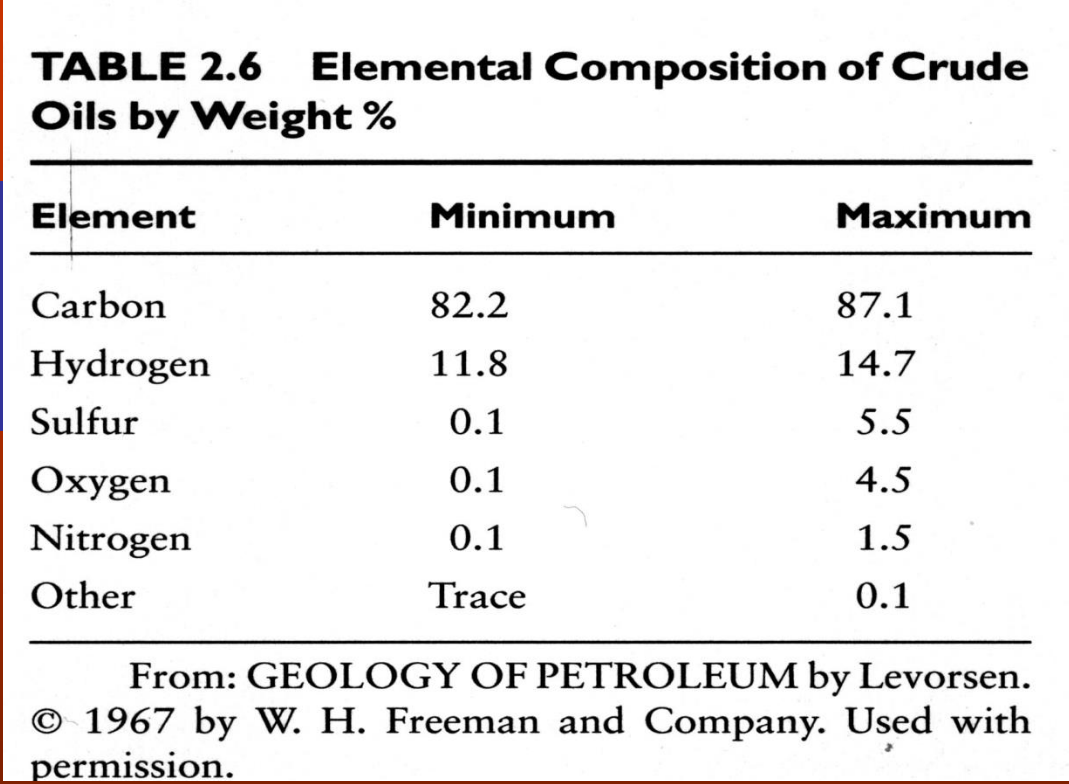


TABLE 2.6 Elemental Composition of Crude Oils by Weight %

Element	Minimum	Maximum
Carbon	82.2	87.1
Hydrogen	11.8	14.7
Sulfur	0.1	5.5
Oxygen	0.1	4.5
Nitrogen	0.1	1.5
Other	Trace	0.1

From: GEOLOGY OF PETROLEUM by Levorsen. © 1967 by W. H. Freeman and Company. Used with permission.

NO TWO OILS ARE IDENTICAL BUT TREND ARE RELATED TO AGE,DEPTH,SOURCE AND GEOG. LOCATION OF THE OIL

For convenience 2 major groups of compounds

Hydrocarbons:

- Paraffins or alkanes
- Naphthenes or cycloalkanes
- aromatics

Heterocompounds **NSO compounds** (resins and asphaltenes)

Paraffins (alkanes)

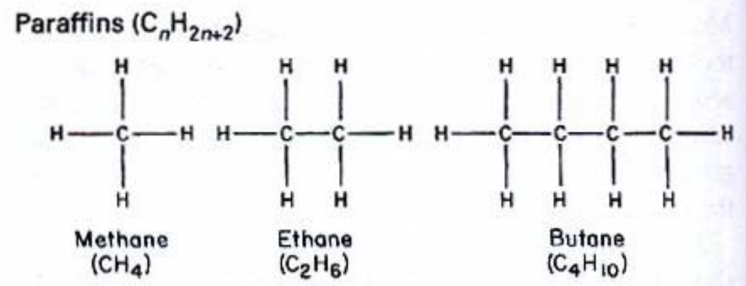
Paraffins or alkanes,are saturated hydrocarbons in wich the carbon atoms are arranged in straight chain, some of them branched.

General formula C_nH_{2n+2}

n<5 paraffins are gaseous (methane,ethan,propane,butane)

N=5 to 15 paraffins are liquid at normal T and P

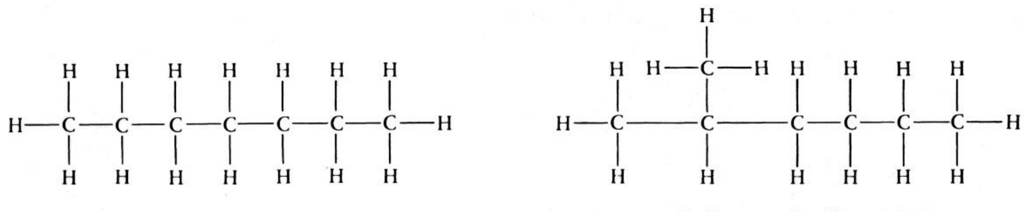
n>15 paraffins grade from viscous liquid to solid waxes



Two type of paraffins

Straight-chain molecules

Branched chain



A Heptane C_7H_{16}

B 2-Methylhexane (isoalkane) C_7H_{16}

FIGURE 2.8 The isomeric structure of the paraffin series. Octane may have a normal chain structure (A) or a branched chain isomer (B).

Naphthenes (cycloalkanes)

General formula C_nH_{2n}

Occur in series consisting of five and six membered carbon rings termed the cyclopentanes and cyclohexanes.

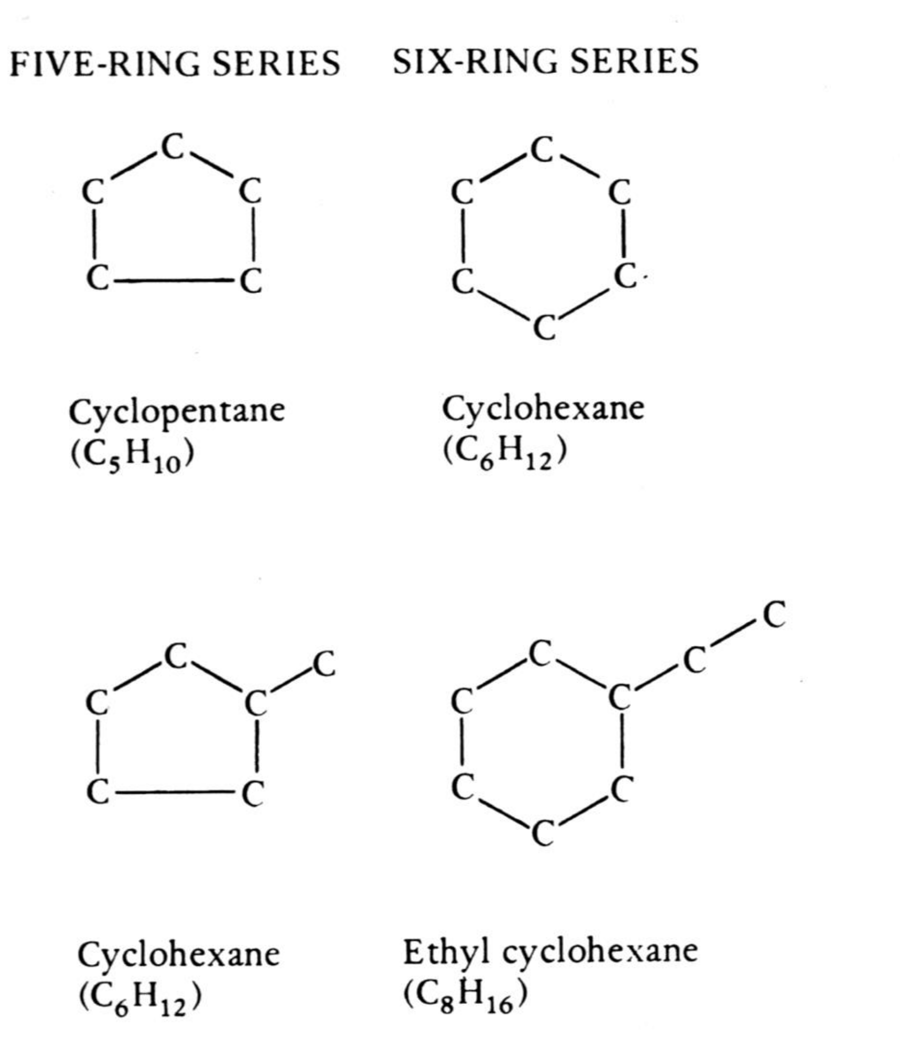
Single bond rings

Most common HC in crude oil (50%)

Reduced number of sites for bonding with hydrogen atoms

Liquid at Normal T and P

Abundant both in light and heavy crude oil



FIVE-RING SERIES

SIX-RING SERIES

Cyclopentane (C_5H_{10})

Cyclohexane (C_6H_{12})

Cyclohexane (C_6H_{12})

Ethyl cyclohexane (C_8H_{16})

Five- and six-ring naphthenes(cycloalkanes

Not shown the accompanying hydrocarbon atoms

Aromatic

Unsuturated hydrocarbons with cyclic structures.

Include several important biomarker that allow oil and source rock to be correlated

No General Formula
Simplest formula C_nH_{2n-6}

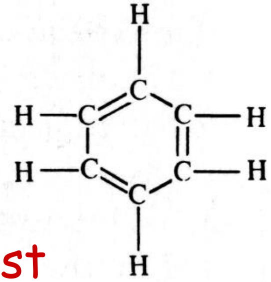
Structure based on a ring of six C atoms

Double bond rings

Liquid at Normal T and P

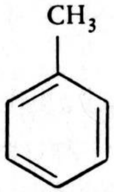
Abundant both in light and heavy crude oil

Toluene is the most common aromatic componen of crude oil,followed by the xylenes and benzene

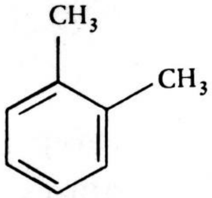


Simplest member Benzene (C_6H_6)

Usual representation of benzene ring



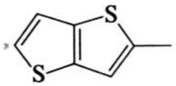
Toluene ($C_6H_5CH_3$)



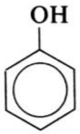
Dimethyl benzene
(one of three isomers of xylene)

Heterocompounds

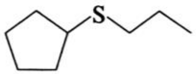
Contain atoms other than carbon and hydrogen,predominantly nitrogen (N), sulfur (S), and oxygen(O). They are divided into resins and asphaltenes



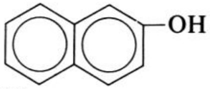
$C_7H_6S_2$ 2-Methylthienothiophene



C_6H_5OH Phenol

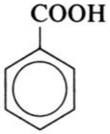


$C_8H_{16}S$ Propylcyclopentylsulfide

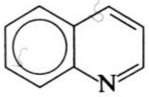


$C_{10}H_7OH$ Naphthol

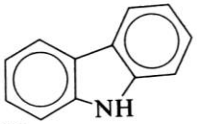
C_4H_4NH Pyrrole



C_6H_5COOH Benzoic acid



C_9H_7N Quinoline



$C_{12}H_8NH$ Carbazole

So… Oil and gas form from organic matter,dead plants and animals. Let's take a look to how and where the OM accumulates to form source rock and the process of maturation of OM into petroleum

A petroleum source rock is generally recognized as a fine-grained sedimentary rock that has naturally generated and released enough hydrocarbons to form a commercial accumulation of oil and/or gas (Tissot and Welte, 1984).

Implicit in this definition is that a source rock meets the following geochemical requirements (Peters and Cassa, 1994):

- the source rock contains sufficient quantity of organic matter
- the organic matter is of sufficient quality to generate oil and/or gas, and
- the source rock attained a level of thermal maturity capable of generating and expelling hydrocarbons

Principal characteristics:quantity,type and degree of maturation of the OM.

A source rock can be

Effective source rock: any sedimentary rock that *has already generated and expelled hydrocarbons.*

Possible source rock: any sedimentary rock whose source potential *has not yet been evaluated*, but which may have generated and expelled hydrocarbons.

Potential source rock: any *immature* sedimentary rock known to be capable of generating and expelling hydrocarbons if its level of thermal maturity were higher.

It follows from these definitions that a particular stratum could be an *effective* source rock in one place; a *potential* source rock in a less-mature area; a *possible* source rock in a nearby unstudied region; and might have no source potential at all in a fourth area where important facies changes had resulted in a drastically lower content of organic matter

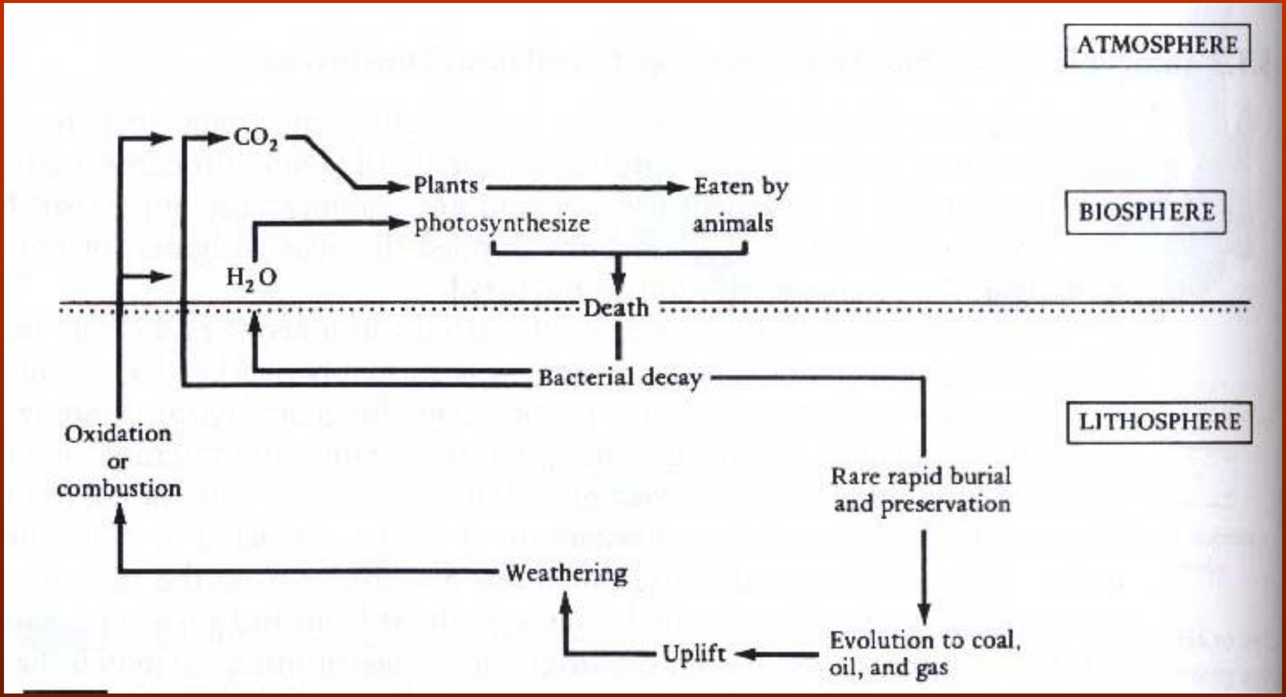
The production and accumulation of organic matter

The Carbon cycle

Total amount of Carbon Earth's crust 2.65×10^{20} g

82% is CO_3 in limestone & dolomites

18% in coal,oil and gas

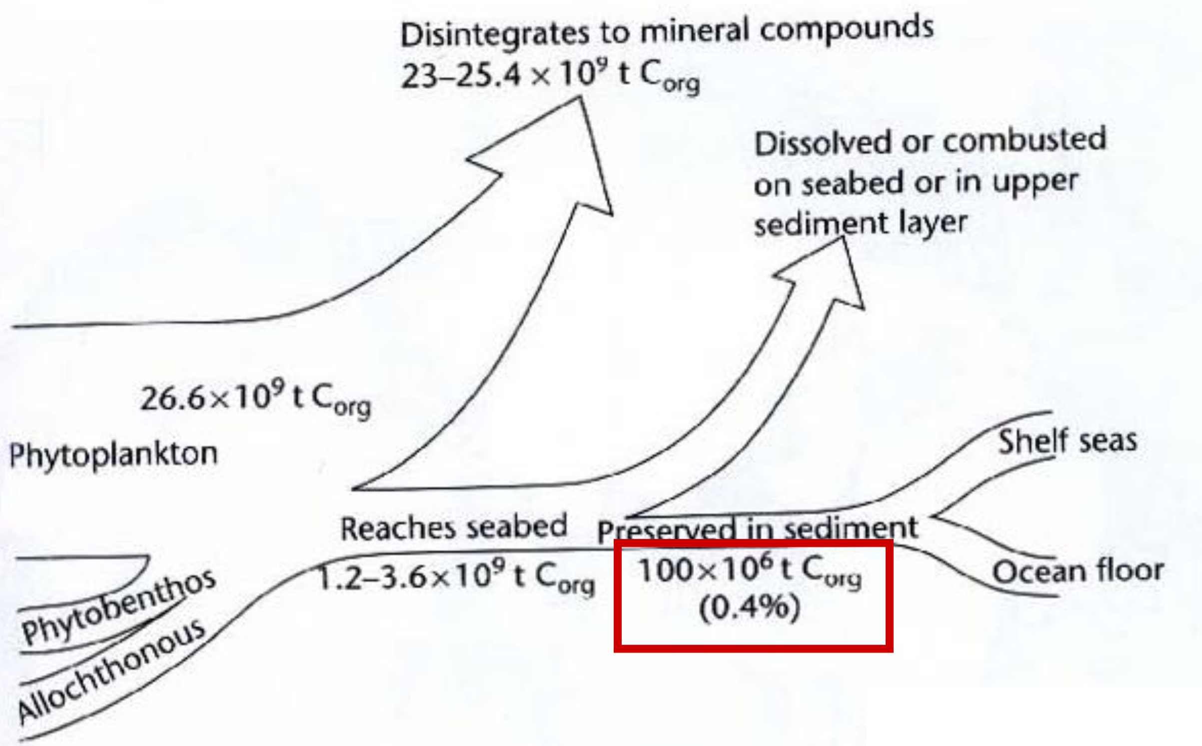


Key reaction is conversion of inorganic carbon into hydrocarbons by

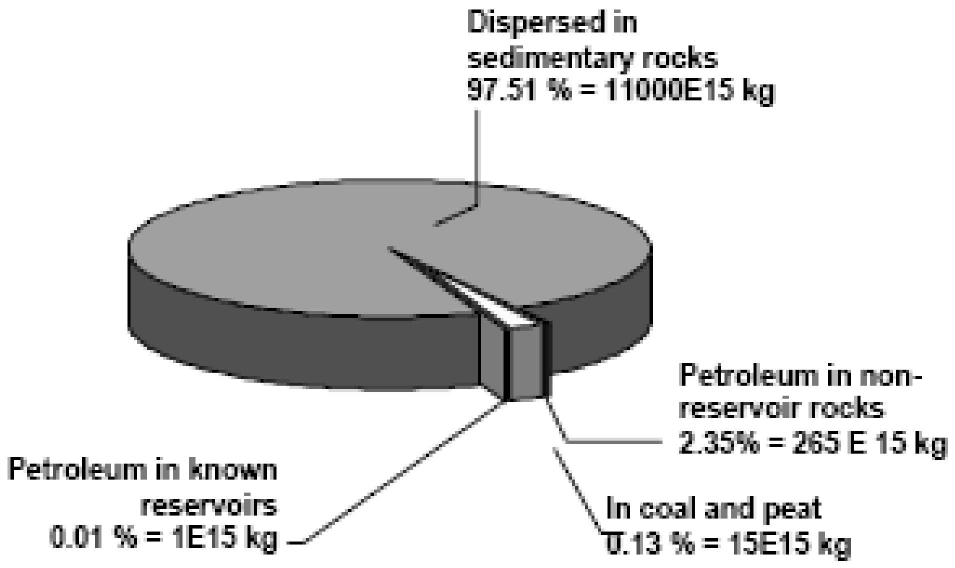
$$6CO_2+12H_2O=C_6H_{12}O_6+6H_2O+6O_2$$

Starting point of more complex Carbon compounds

The Carbon cycle



Petroleum accumulation is an extremely inefficient process: Only about 0.01 % of TOC ends up in known reservoirs !



The major group of chemicals that occur in organic matter are:

Proteins

More abundant in animals less in plants

Carbohydrates

Present both in animals and in plants

Lipids

Present both in animals and in plants. Rich in H.

Lignin

Found only in higher plants

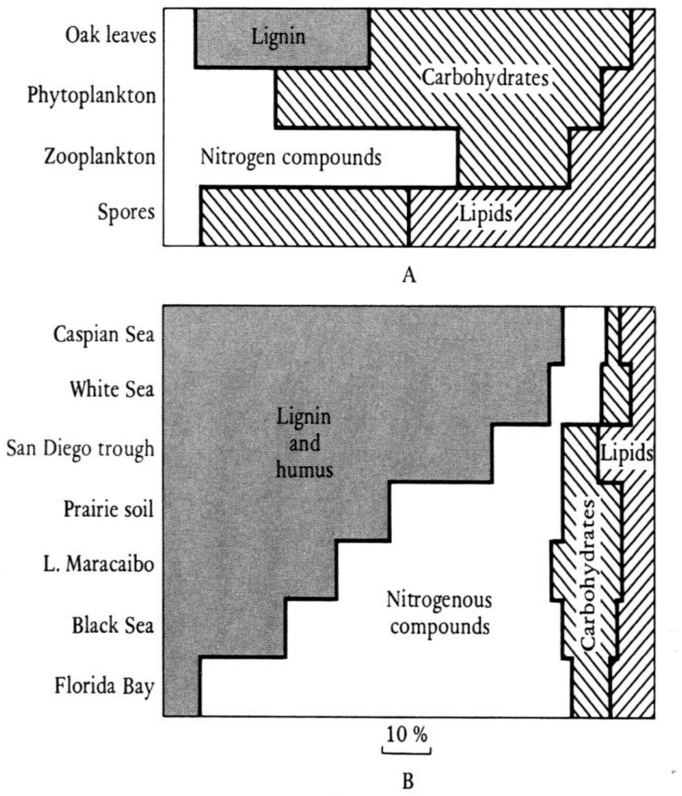
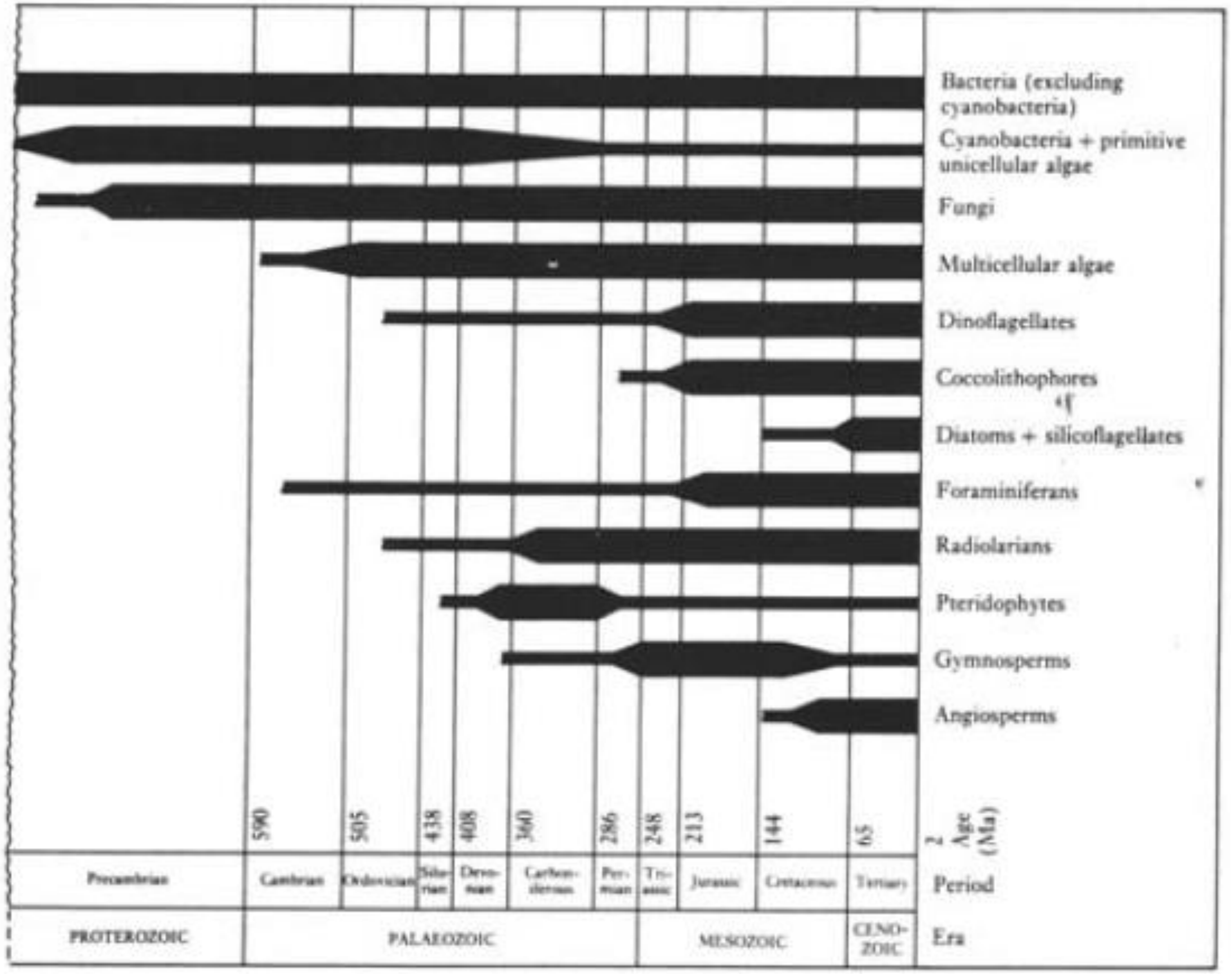


FIGURE 5.5 Composition of organic matter in (A) organisms and (B) shallow Recent sediments. (From: PETROLEUM GEOCHEMISTRY AND GEOLOGY 2/E by Hunt. © 1979 by W. H. Freeman and Company. Used with permission.)

Evolution of important sedimentary organic matter precursors



Important: The amount of organic matter buried is related to the ratio of organic productivity and destruction

High productivity requires:

- Ligth
- T
- Nutrients
- Low turbidity

Sea

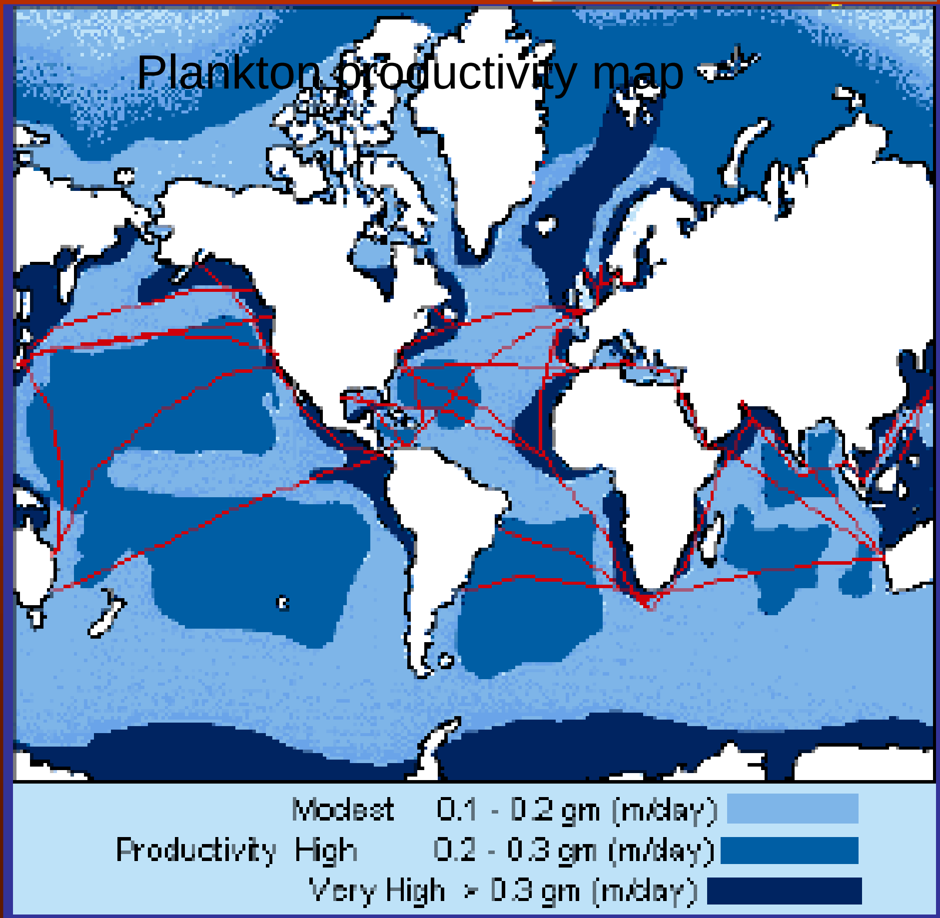
Phytoplankton 90 % OM

+bacteria,zooplankton,fish etc

Land

Plant

Freshwater algae



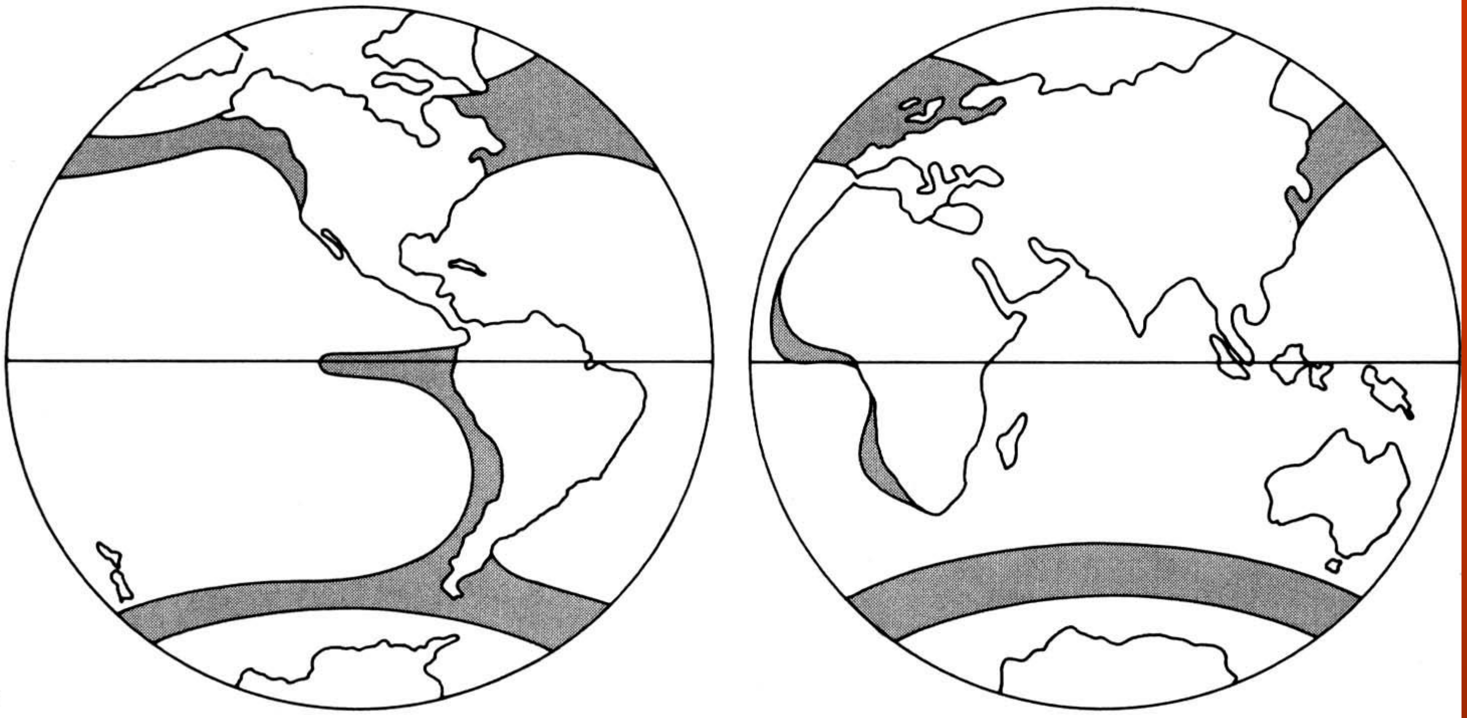


FIGURE 5.6 Production of organic matter in the present-day world oceans. Note the low productivity in polar regions and the high productivity along eastward sides of the oceans. For sources see Debyser

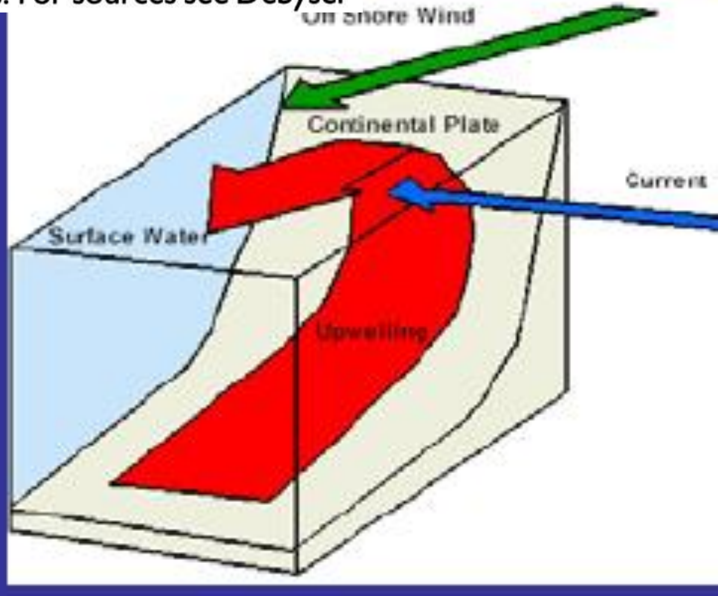
Areas of High productivity

At boundary between polar and temperate regions

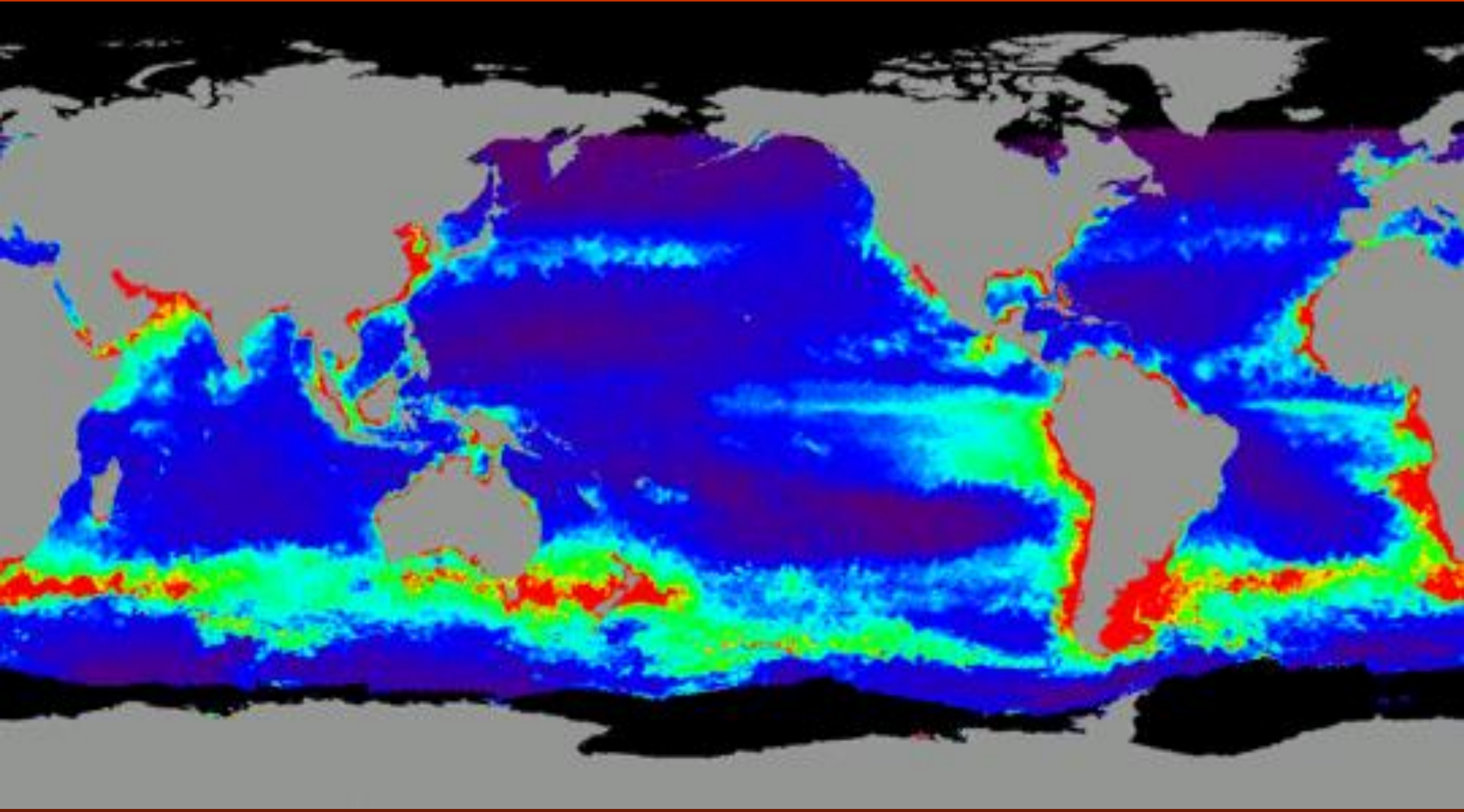
West side of continents

In the Upper 100 m

Upwelling of deep water brings nutrients



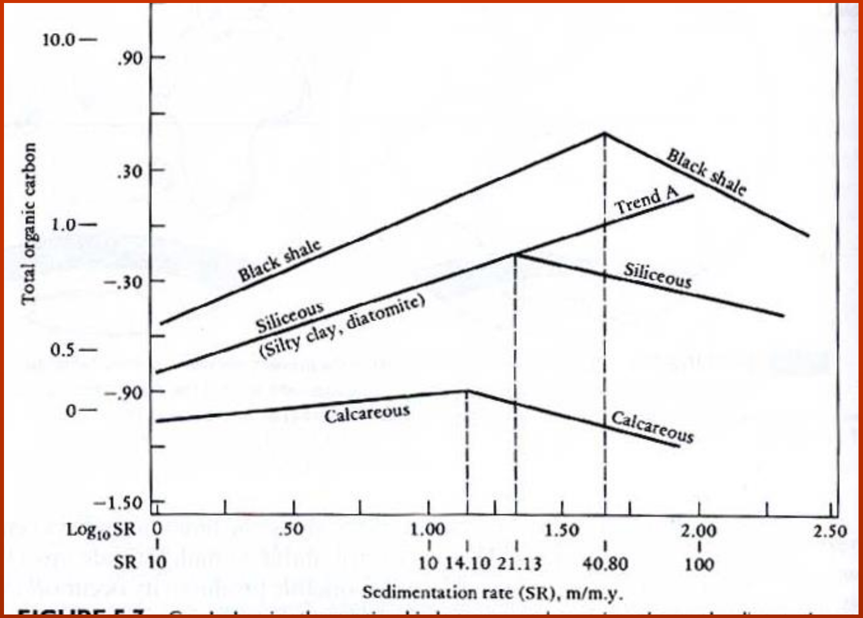
High biological productivity

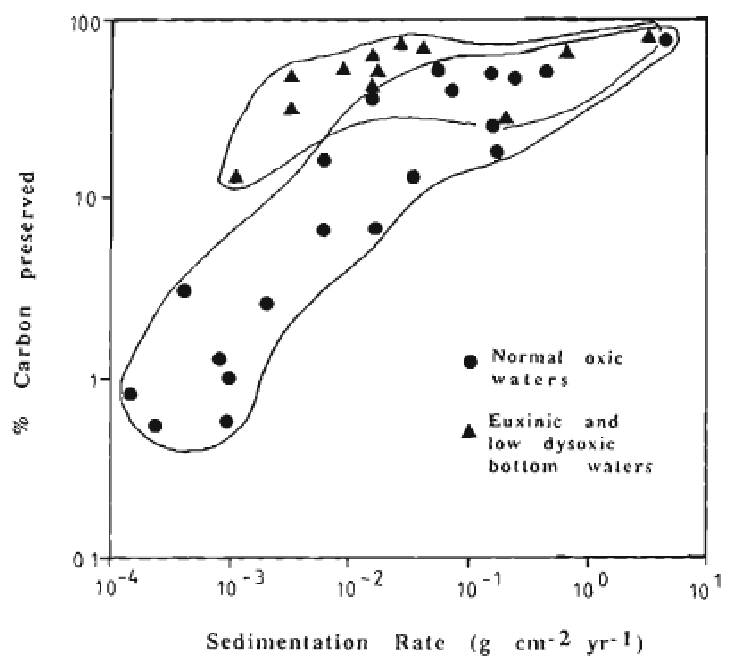


…But Areas of high oceanic productivity are not necessarily the areas where the OM is best preserved

… now we need to preserve the OM

Approximately 80% of all primary organic matter presently produced in the ocean is consumed (Menzel, 1974). The most effective consumers are zooplankton and aerobic microorganisms.





Preservation of OM is favored by anaerobic botton contitions and a rapid (but not too much) sedimenation rate

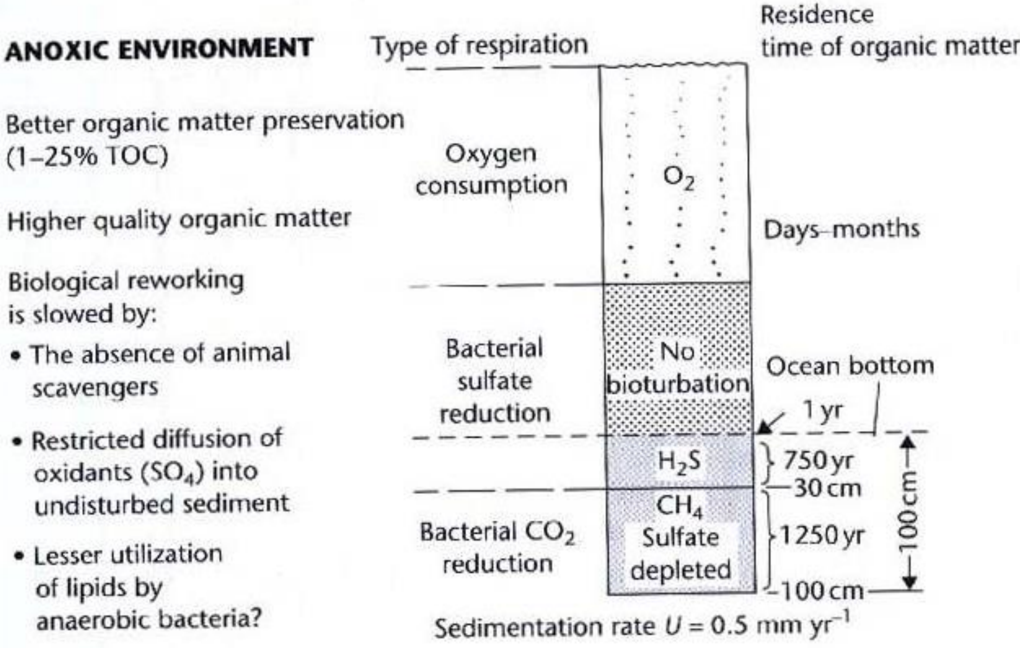
Source rock prediction: Degradation of organic matter

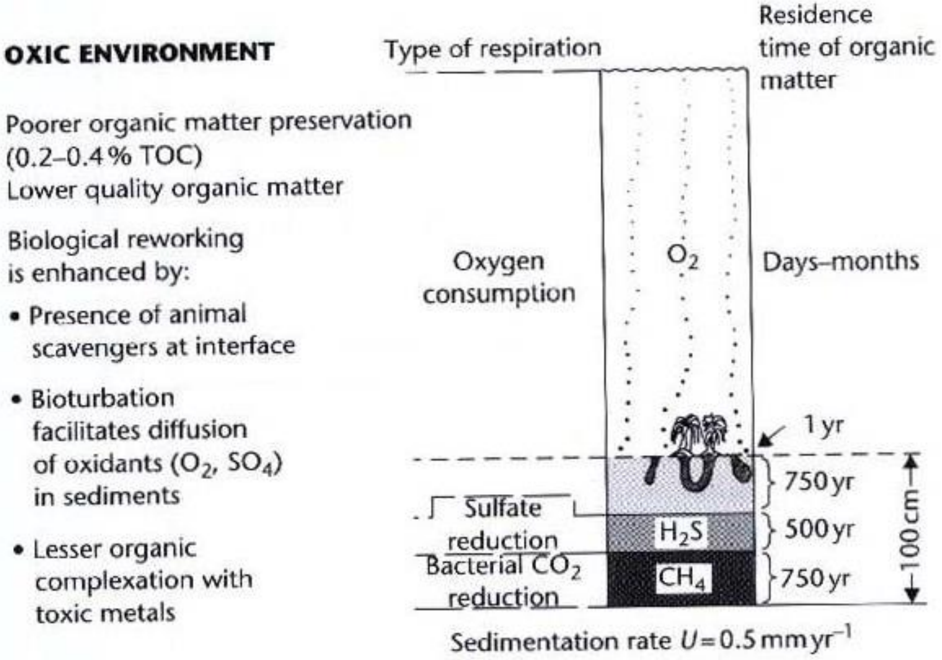
OM is oxided by aerobic bacteria using the available oxygen until there is no more OM or no more oxygen

Anaerobic bacteria derive oxygen first of all from nitrates and then sulfates

BUT

Anaerobic degradation results in a greater preservation of lipid-rich,oil prone material





Mineralogy and Sediment grain size on the preservation of OM

Clay-sized particles can adsorb organic matter and are more readily coated with organic matter than coarse-grained siliciclastics.
clay particles are often and deposited in low-energy environments. Sands are deposited in higher-energy environments ofetn associated with the presence of oxygenated water,higher sedimentation rates, and an abundance of aerobic microand macro-biota.

Sediment particle size is also important because the relative decrease in permeability associated with clay-sized particles restricts the exchange of oxygen-depleted water by oxygen-rich
water .

The existence of fine laminae within a fine-grained sedimentary rock is generally attributed to the presence anoxia within the depositional environment and the
absence of bioturbation (Raiswell and Berner, 1985).

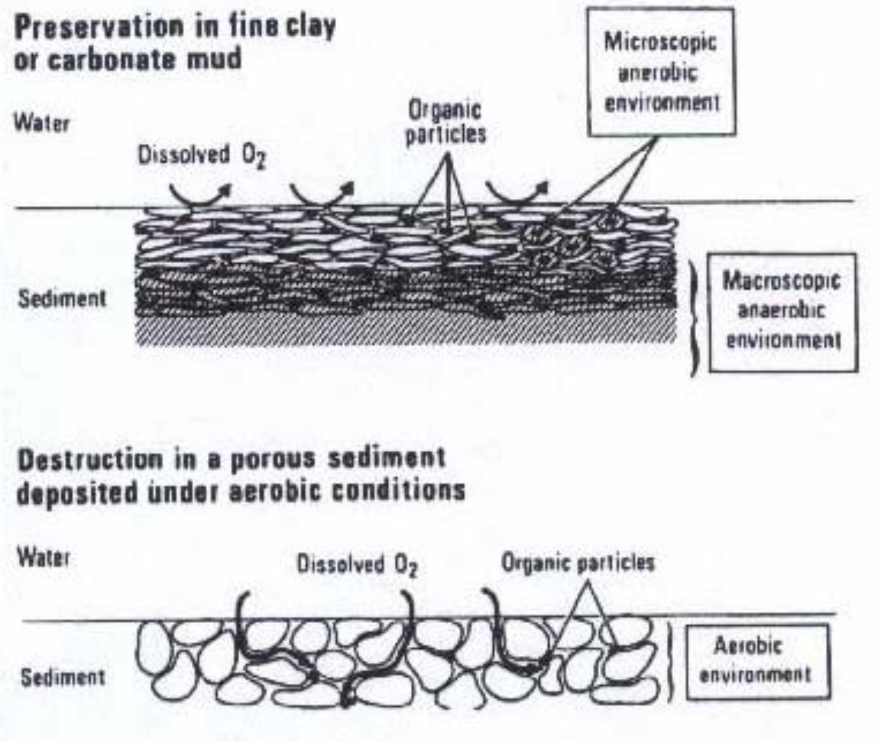


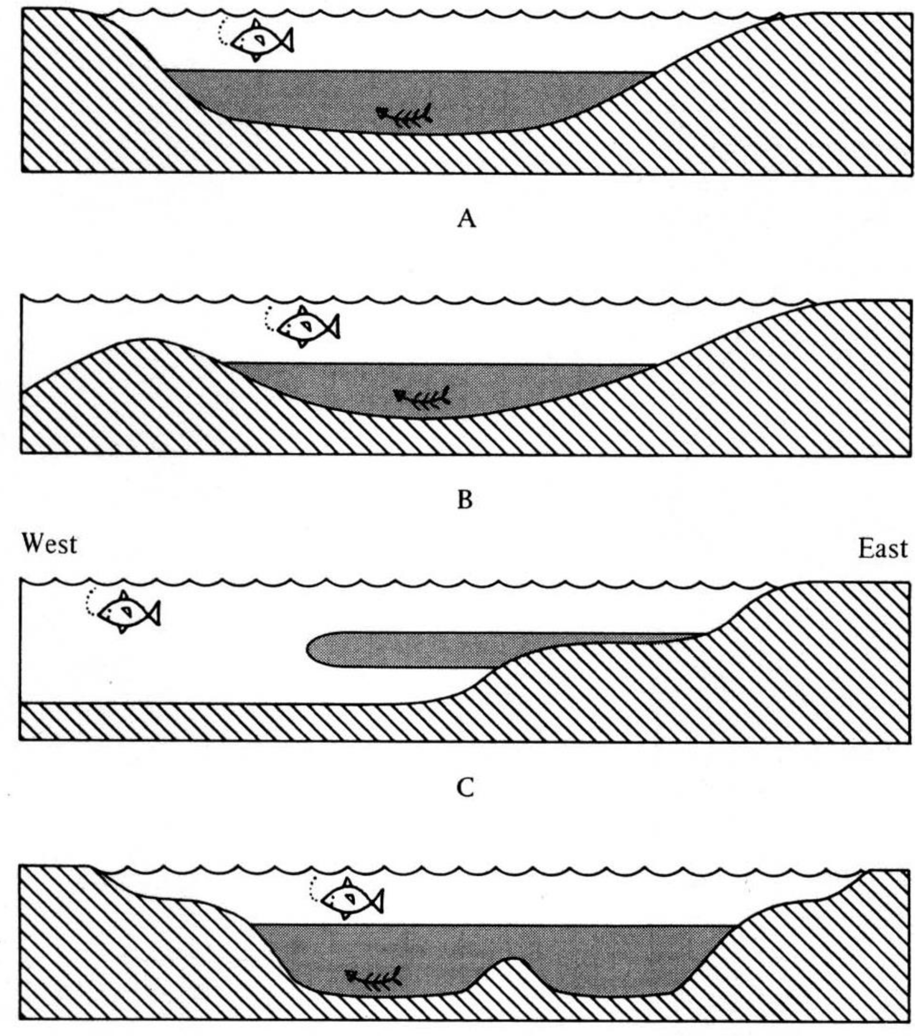
Figure 22. Preservation potential due to lithology. A comparison between an argillite (top) and 'sand' (bottom). Oxygenated water can penetrate the more open pore network of the sand promoting the removal of organic matter (from Tissot and Welte, 1984; reprinted with kind permission of Springer Science and Business Media).

Source rock prediction…Anaerobic or anoxic conditions

Anaerobic means that insufficient oxygen is available for aerobic biological processes

Anoxic= devoid of oxygen,frequently used in the sense of depleted in oxygen-dysaerobic. 0.5 ml/l =oxic/anoxic thereshold

Anoxic conditions are critical to the preservation of organic matter in sediments.



How do you get Anoxia??

- **Water stratification**
  Temperature
  Salinity

- **High organic productivity near surface**

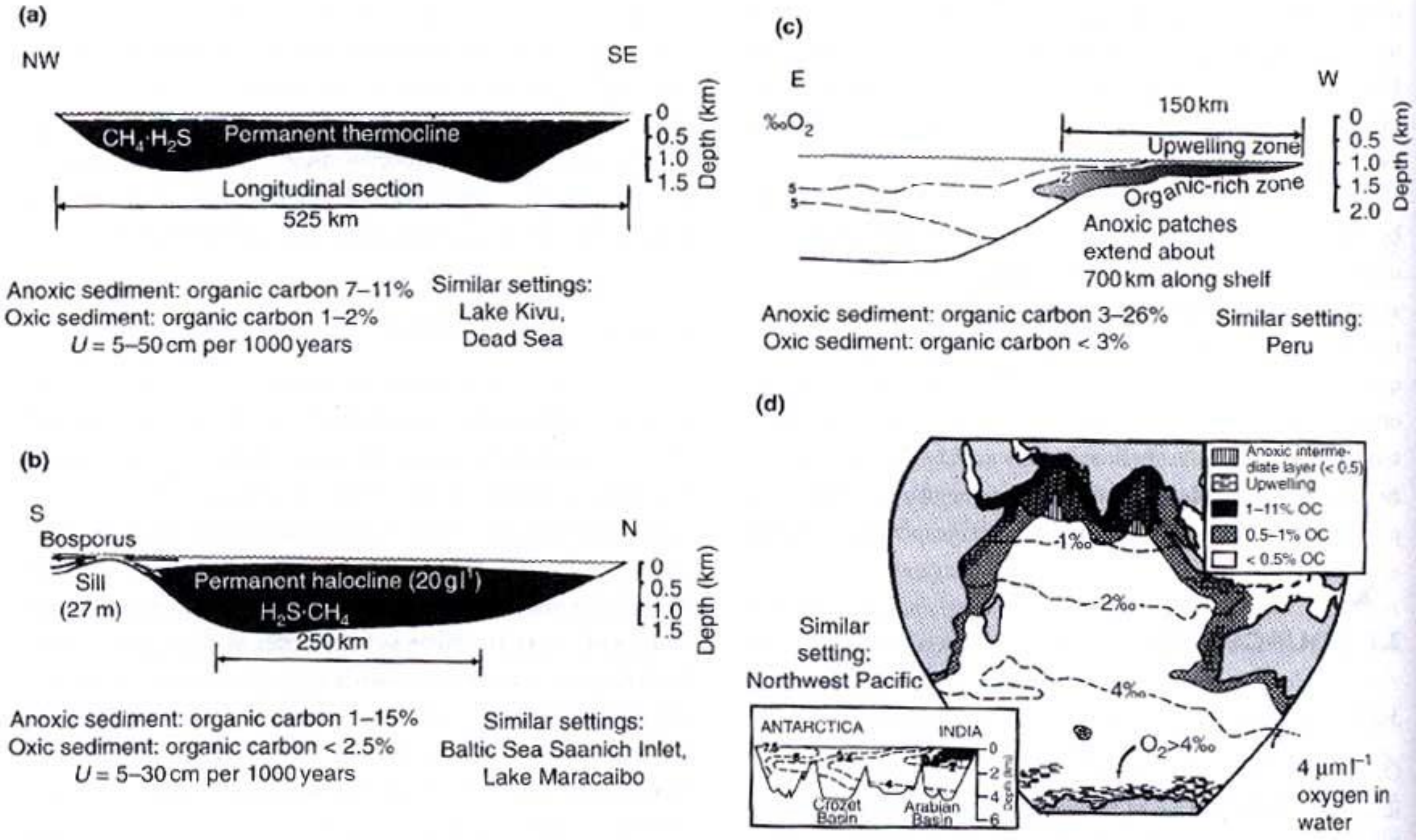
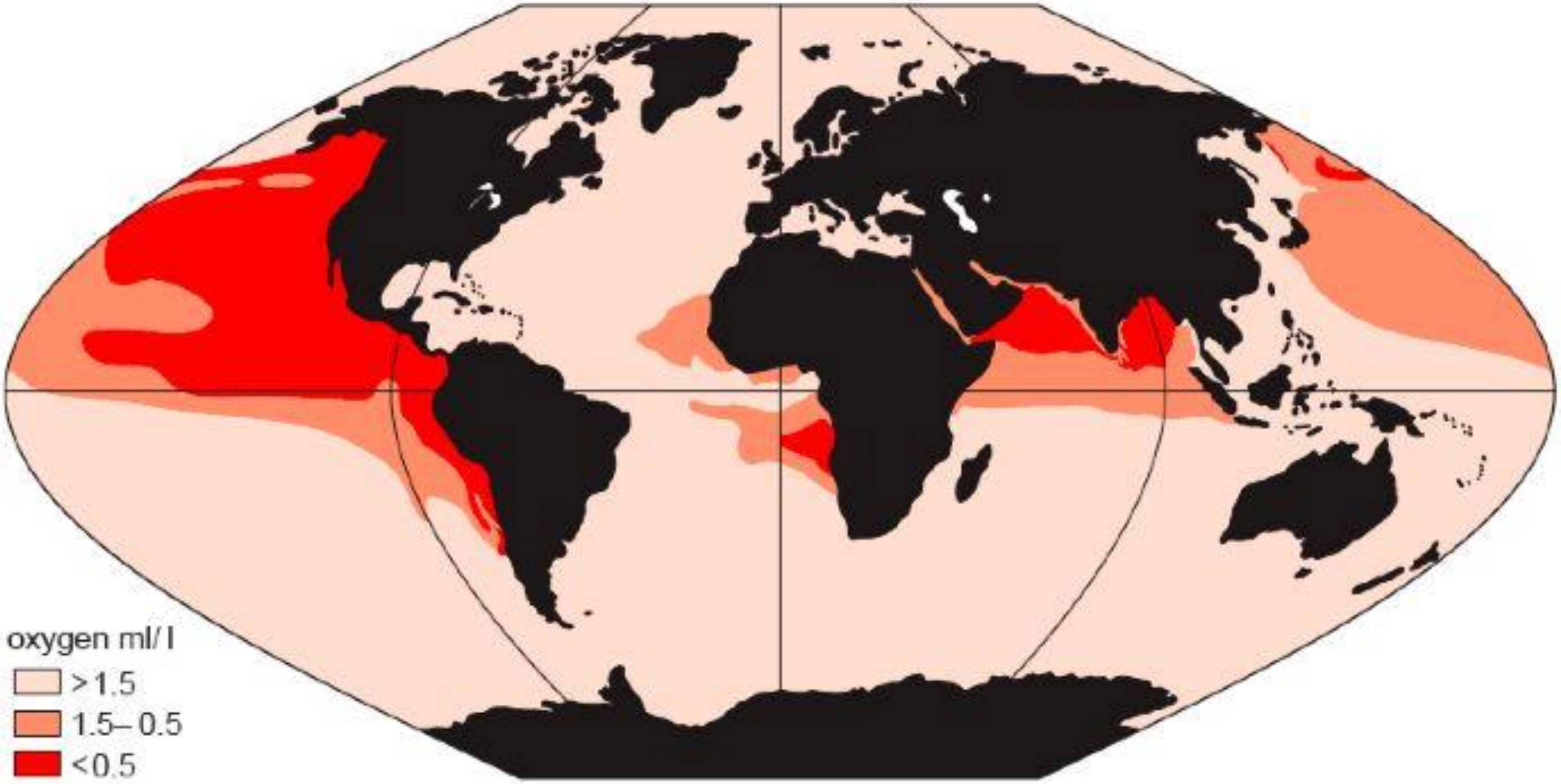


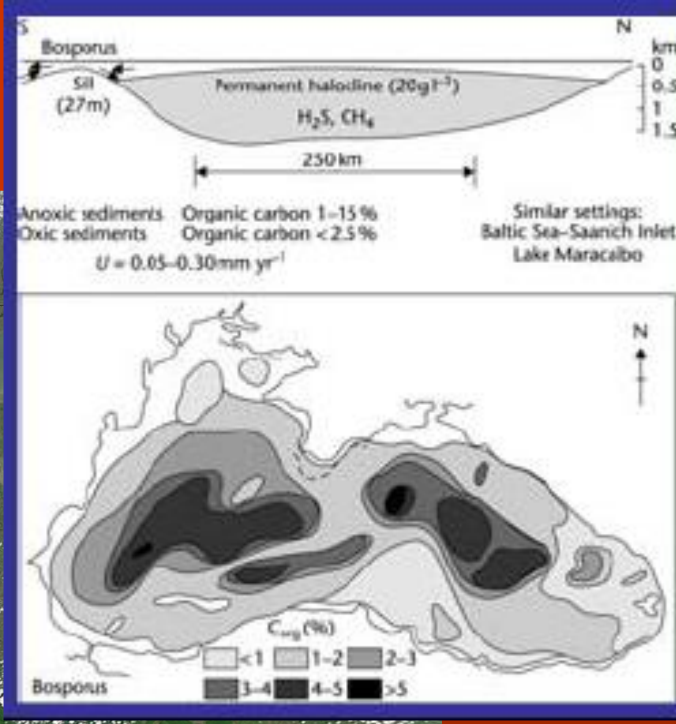
Fig.3.39 The preservation of organic matter in (a) large anoxic lakes such as Lake Tanganyika, (b) anoxic silled basins such as the Black Sea – a "positive water balance" basin, (c) anoxic layers caused by upwelling, such as the South West African shelf, and (d) open ocean anoxic layers, such as in the Indian Ocean. (From Demaison & Moore 1980.)

Distribution of oxygen-depleted waters in the World Ocean



Demaison and Moore, 1980

The Black Sea: the type anoxic basin



When and where do good source rocks formed ?

At times of global *oceanic anoxic events* (OAEs) associated with sea level rises (transgressions)

- Late Devonian transgression(s): Canada (Exshaw Shale and others), Wolga-Ural (Domanik Fm.), North Africa, southern US (Woodford Shale)

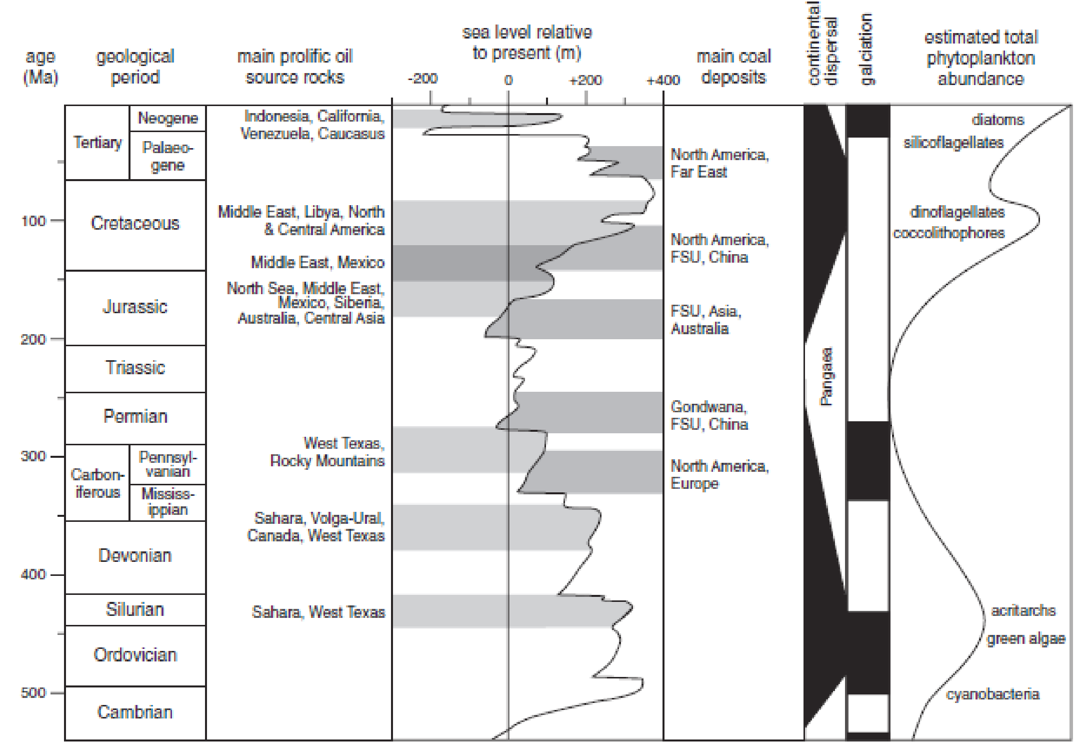


Fig. 4.31 Relationship between eustatic sea level and major depositional periods of coals and petroleum-source rocks (after Tissot 1979; Vail et al. 1978; FSU = former Soviet Union).

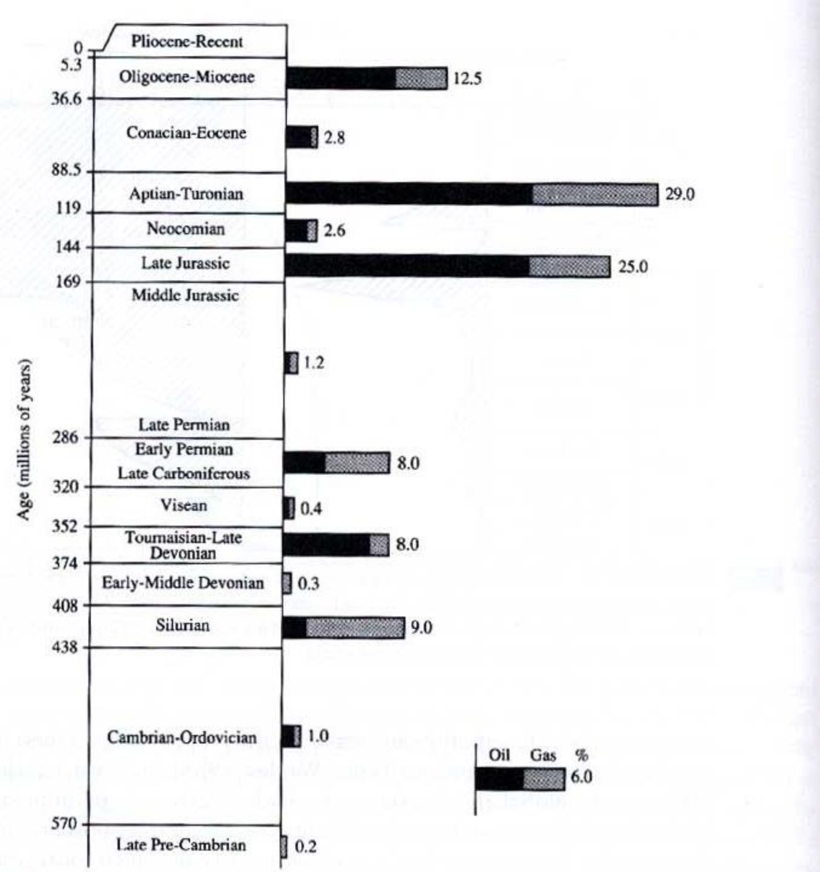


FIGURE 5.11 Histograms showing the distribution of the world's currently discovered oil and gas reserves through geological time. Note the concentration in rocks of Late Jurassic to Early Cretaceous ages, times of known organic-rich sediment deposition. (After Klemme and Ulmishek, 1991.)

- Jurassic and Cretaceous transgression(s):
Principal source rocks in Middle East, Western Siberia, North Sea (Kimmeridgian shale),Venezuela (La Luna Fm.)

- Oligo-Miocene transgression: California (Monterey Fm.), Caucasus, Carpathians, Indonesia

Cenomanian-Turonian black shales

Black Band, South Ferriby, UK

Black shale, Exmouth Plateau

Livello Bonarelli, Furlo, Italy

Niveau Thomel, Vergons, France

…what happens to the OM when buried?

Diagenesis:shallow subsurface normal T & P.Includes biogenic and abiogenic reactions.Loss of CH_4,CO_2 and H_2O from OM leaving a very heavy moleculs called Kerogen.O_2 content reduced. H/C inaltered

Catagenesis: occurs in deeper subsurface with continuous burial and increasing T & P. stages of kerogen decomposition during which oil and wet gas are produced. H/C ratio declines

Metagenesis: high T & P.The last HC (generally CH_4) are expelled.H/C ratio declines until only C in form of graphite is left. represents dry-gas generation

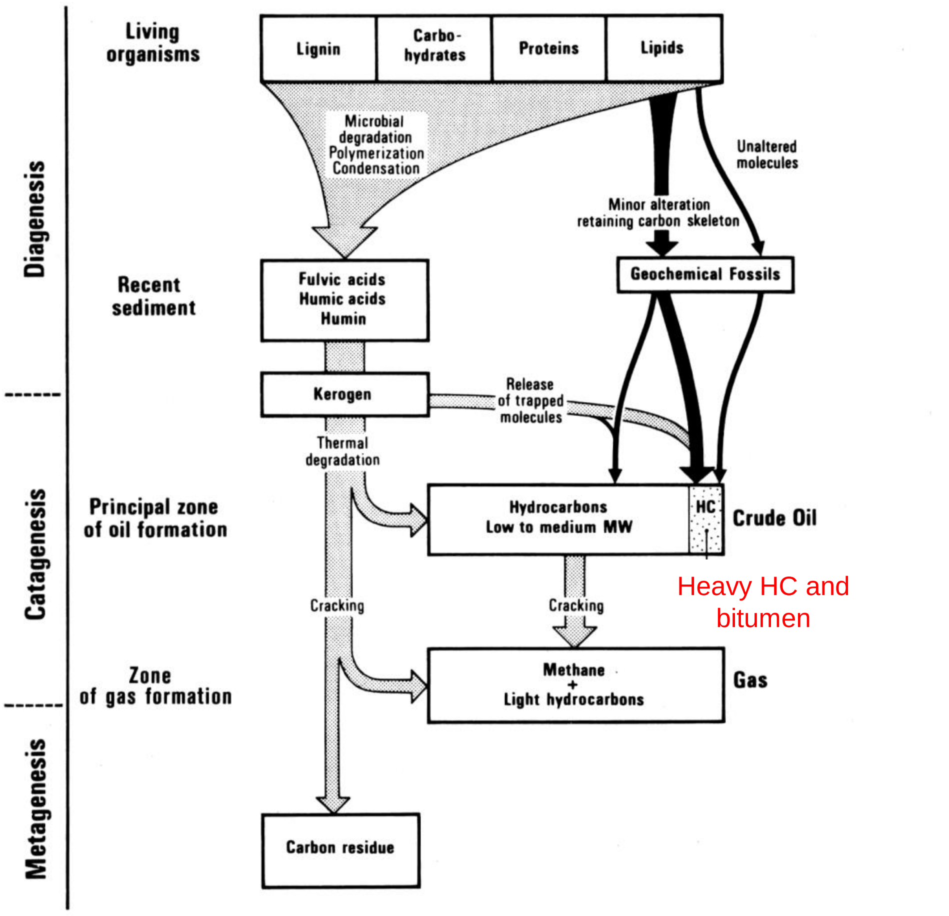


Fig. II.3.1. Sources of hydrocarbons in geological situations, with regard to the evolution of organic matter. Geochemical fossils represent a first source of hydrocarbons in the subsurface *(black solid arrows)*. Degradation of kerogen represents a second source of hydrocarbons *(grey dotted arrows)*

Diagenesis

First stage:oxydation

Second stage:reduction of nitrates and nitrites

Third stage:reduction of sulfate

Methane is a major by product of bacterial decay

$(C_6H_{10}O_5)_n \longrightarrow CO_2+CH_4$ $4H_2+CO_2 \longrightarrow CH_4+2H_2O$

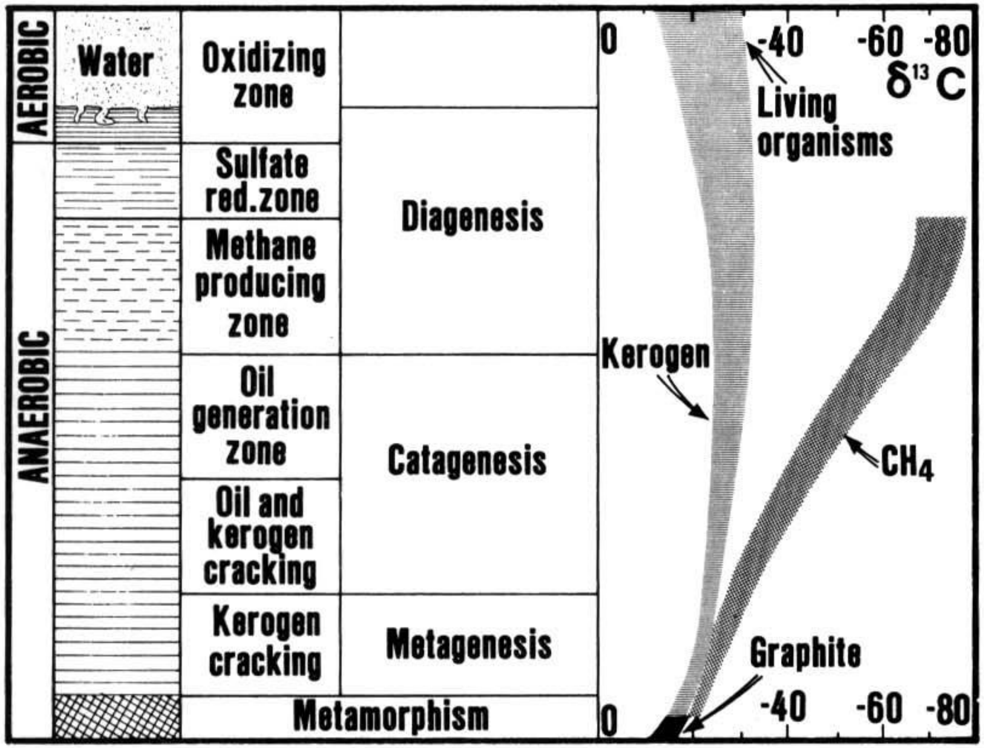


Fig. II.6.2. Successive stages of gas generation in sediments, after Claypool and Kaplan (1974), Demaison and Moore (1980), Galimov (1980) and Rice and Claypool (1981). Isotopic composition of kerogen and methane are shown after Galimov (1980), with minor changes

...Then water and CO_2 continue to be espelled and kerogen formation begins

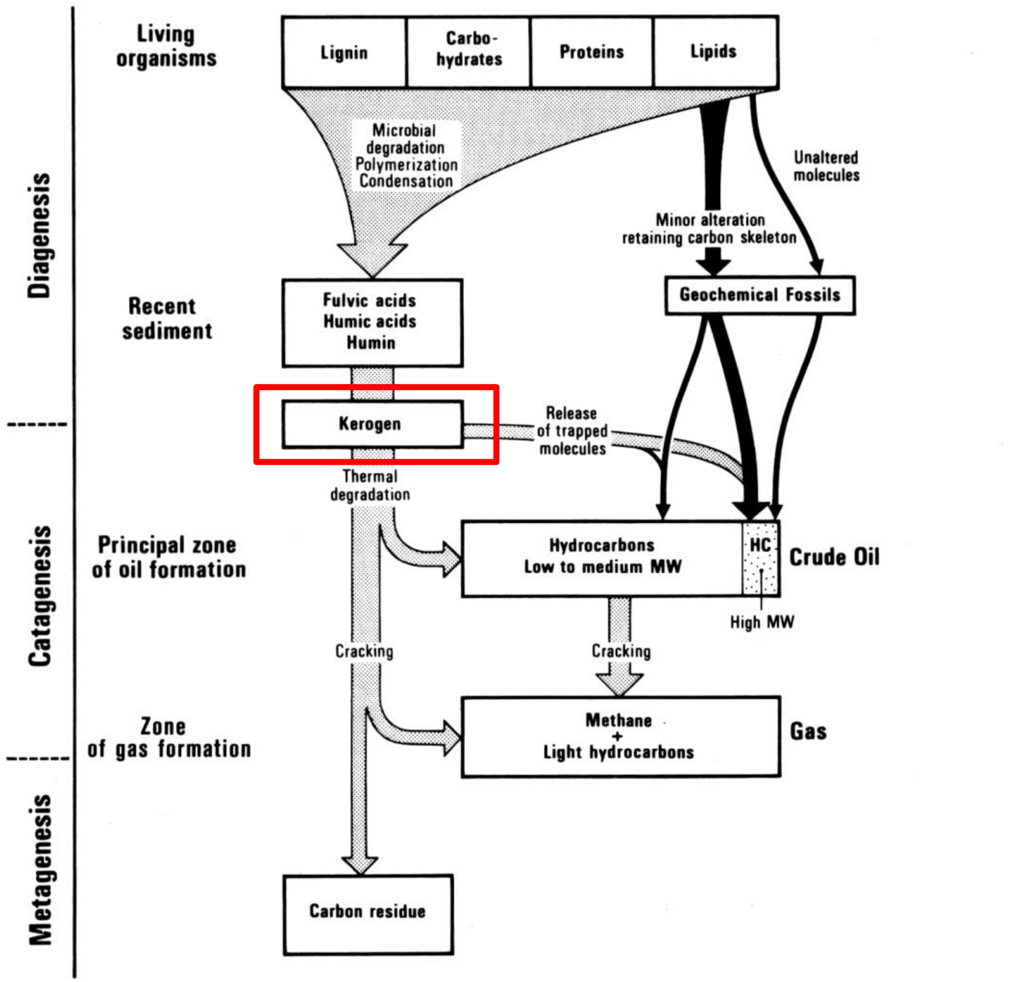
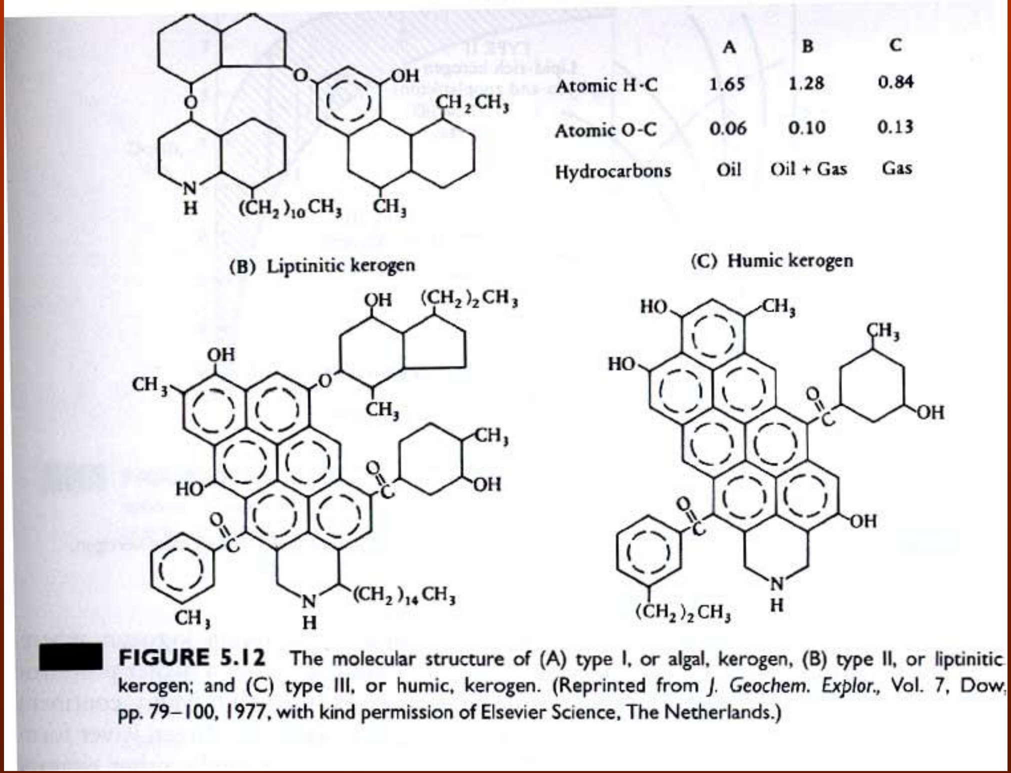


Fig. II.3.1. Sources of hydrocarbons in geological situations, with regard to the evolution of organic matter. Geochemical fossils represent a first source of hydrocarbons in the subsurface *(black solid arrows)*. Degradation of kerogen represents a second source of hydrocarbons *(grey dotted arrows)*

…What are Kerogen and bitumen ???

Kerogen is generally defined as sedimentary organic matter that is insoluble in common organic solvents and aqueous alkaline solvents (Tissot and Welt, 1984).
Bitumen is the organic content of a rock that is extractable whit organic solvents.bitumen forms largely from breaking of chemical bonds in kerogen when T rises

Lack of solubility is a direct result of the large size of kerogen molecules

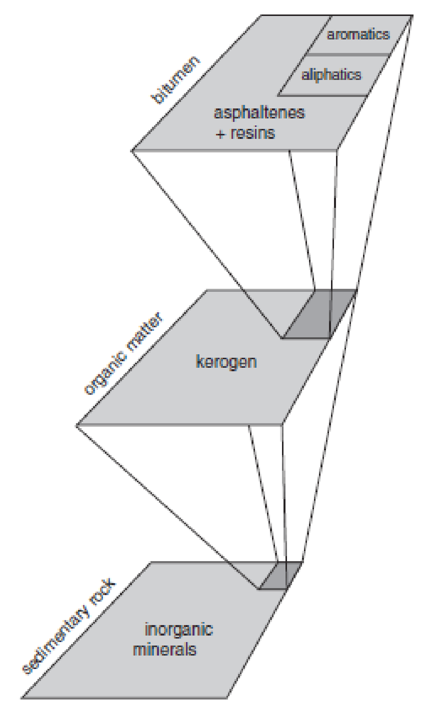


	A	B	C
Atomic H-C	1.65	1.28	0.84
Atomic O-C	0.06	0.10	0.13
Hydrocarbons	Oil	Oil + Gas	Gas

(B) Liptinitic kerogen

(C) Humic kerogen

FIGURE 5.12 The molecular structure of (A) type I, or algal, kerogen, (B) type II, or liptinitic kerogen; and (C) type III, or humic, kerogen. (Reprinted from *J. Geochem. Explor.*, Vol. 7, Dow, pp. 79–100, 1977, with kind permission of Elsevier Science, The Netherlands.)



Formation of Kerogen

Kerogen is the most abundant organic component in the Earth

Kerogen is composed of varying proportions of C,H and O.

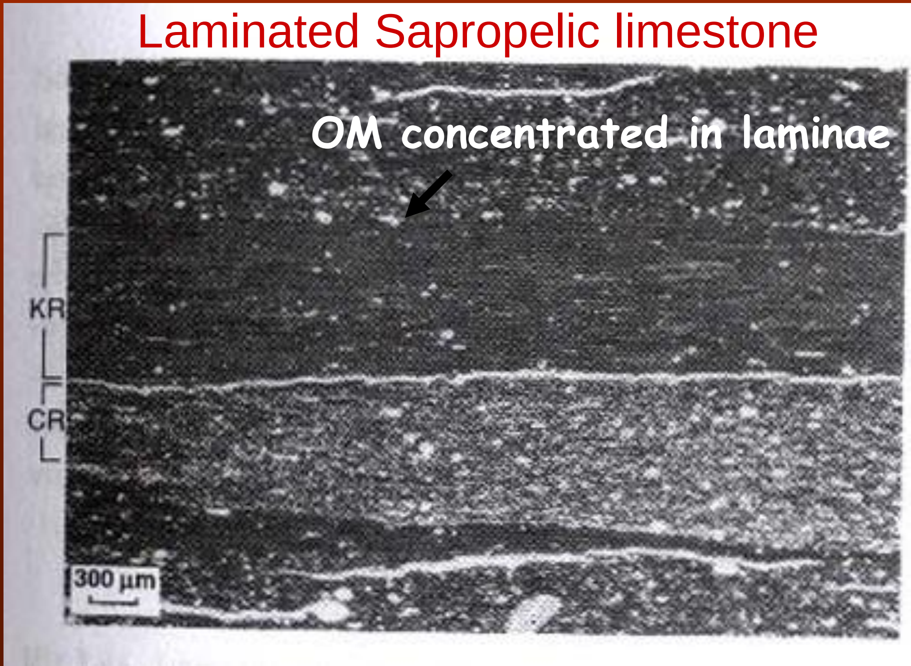
Important1: the type of kerogen is dependent on the types of organic material preserved in each sedimentary environment

Important2: each type of kerogen matures under different burial conditions

The quantity of Kerogen in a rock defines its richness as a source rock which in turn relates to its petroleum potential

- OM-rich source rock=large volume of HC can be generated
- High proportion of organic material in source rock = great efficiency of migration of HC out of source rock

The quantity of kerogen (and bitumen)in a rock is determined from the total organic carbon (TOC)



Laminated Sapropelic limestone

OM concentrated in laminae

PRINCIPLES OF SOURCE-ROCK EVALUATION

QUANTITY OF ORGANIC MATERIAL

The amount of organic material present in sedimentary rocks is almost always measured as the total-organic carbon (TOC) content. This simple, quick, and inexpensive analysis serves as the first and most important screening technique in source-rock analysis.

- rocks containing less than 0.5% TOC negligible hydrocarbon-source potential. The amount of hydrocarbons generated in such rocks is so small that expulsion simply cannot occur..

- Rocks containing between 0.5% and 1.0% TOC are marginal. They will not function as highly effective source rocks, but they may expel small quantities of hydrocarbons and thus should not be discounted completely.

- Rocks containing more than 1% TOC often have substantial source potential. In some rocks TOC values between 1% and 2% are associated with depositional environments intermediate between oxidizing and reducing, where preservation of lipid-rich organic matter with source potential for oil can occur. TOC values above 2% often indicate highly reducing environments with excellent source potential.

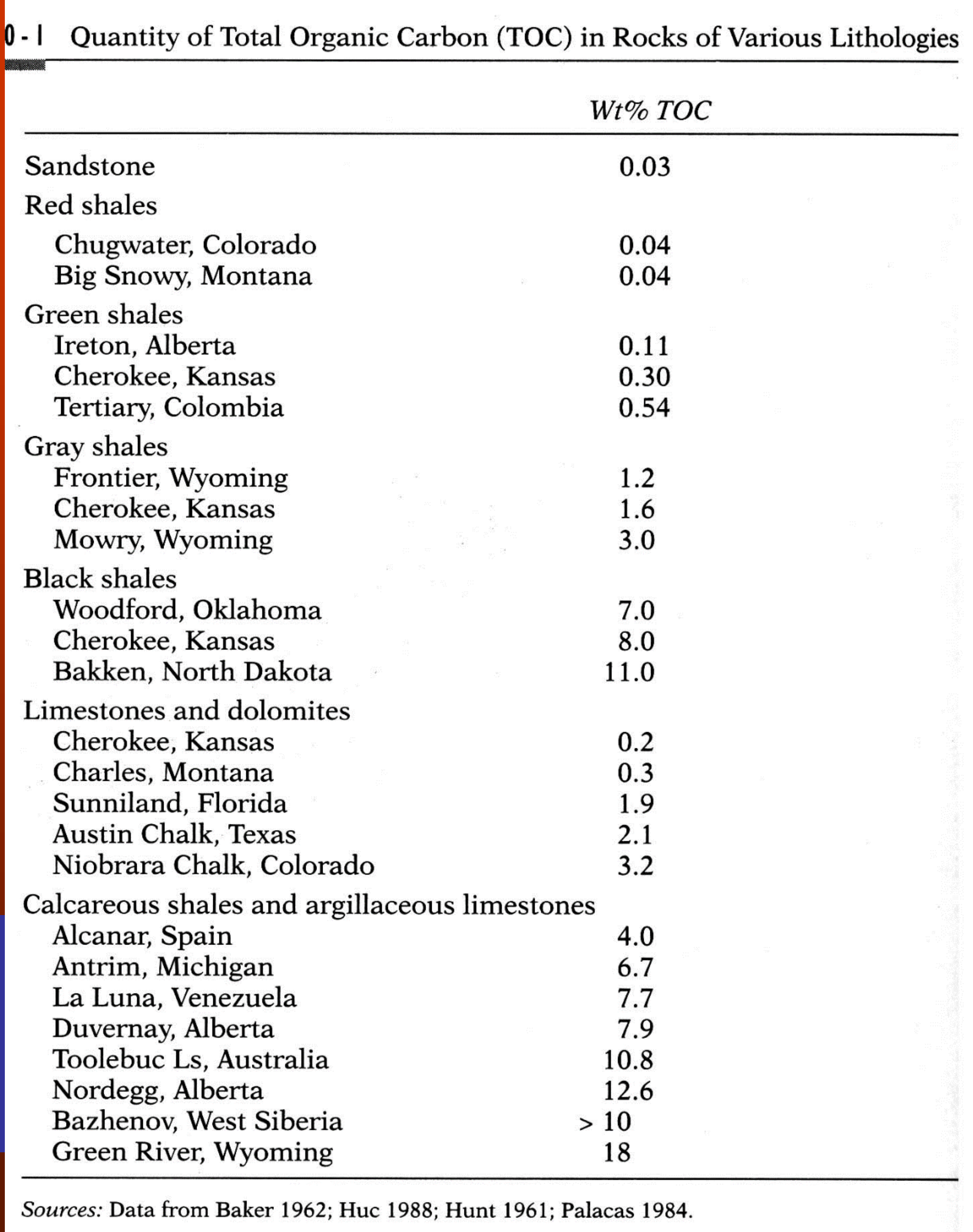
Under normal condition OM is very diluite in the sediments

Global average term

Claystone & shale (excluding oceanic sediments)	0.99 wt%
Carbonates	0.33 wt%
Sandstones	0.28 wt%

BUT

Most source rokc contain in excess of 1 wt%,rich source rock >5wt% and the value can reach 20wt%



0-1 Quantity of Total Organic Carbon (TOC) in Rocks of Various Lithologies

	Wt% TOC
Sandstone	0.03
Red shales	
Chugwater, Colorado	0.04
Big Snowy, Montana	0.04
Green shales	
Ireton, Alberta	0.11
Cherokee, Kansas	0.30
Tertiary, Colombia	0.54
Gray shales	
Frontier, Wyoming	1.2
Cherokee, Kansas	1.6
Mowry, Wyoming	3.0
Black shales	
Woodford, Oklahoma	7.0
Cherokee, Kansas	8.0
Bakken, North Dakota	11.0
Limestones and dolomites	
Cherokee, Kansas	0.2
Charles, Montana	0.3
Sunniland, Florida	1.9
Austin Chalk, Texas	2.1
Niobrara Chalk, Colorado	3.2
Calcareous shales and argillaceous limestones	
Alcanar, Spain	4.0
Antrim, Michigan	6.7
La Luna, Venezuela	7.7
Duvernay, Alberta	7.9
Toolebuc Ls, Australia	10.8
Nordegg, Alberta	12.6
Bazhenov, West Siberia	> 10
Green River, Wyoming	18

Sources: Data from Baker 1962; Huc 1988; Hunt 1961; Palacas 1984.

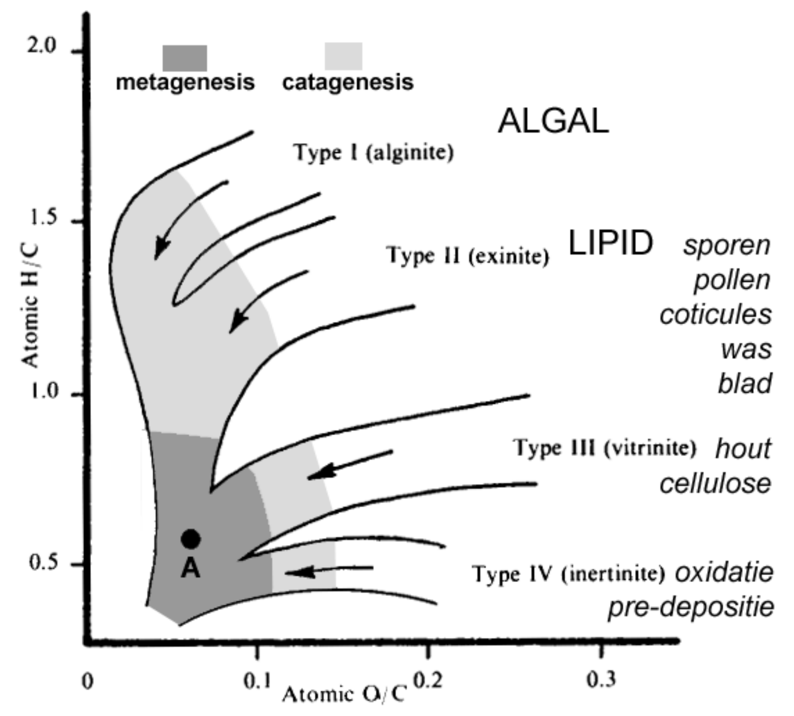
4-(3) types of Kerogen

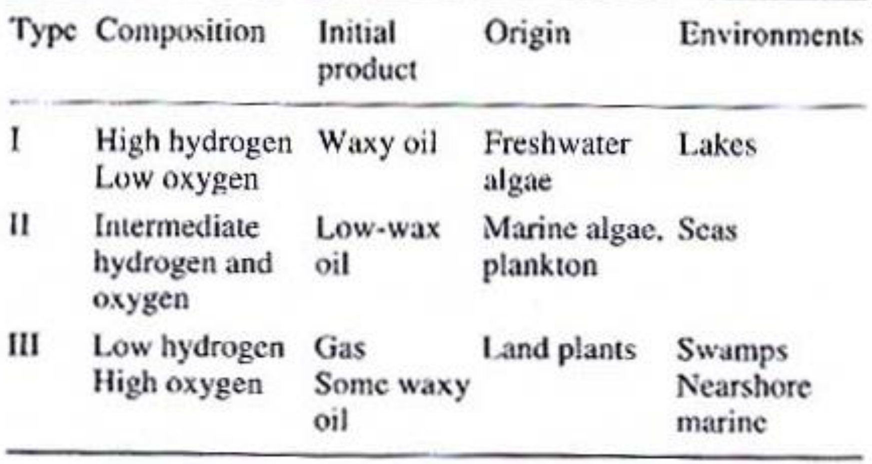
I-Alginite: High H/C ratio Low O/C.Oil prone.mainly algal source.Lacustrine and/or lagoonal environment.Relatively rare

II-Exinite-liptinite: Intermediate H/C ratio and O/C. Oil and gas prone. The source is mainly membranous plants debris and phytoplankton and bacterial organism in marine sediments.This type of kerogens are the most abundant

III-Vitrinite: Low H/C ratio and high O/C. Principally generates gas. The primary source is higher plants debris.

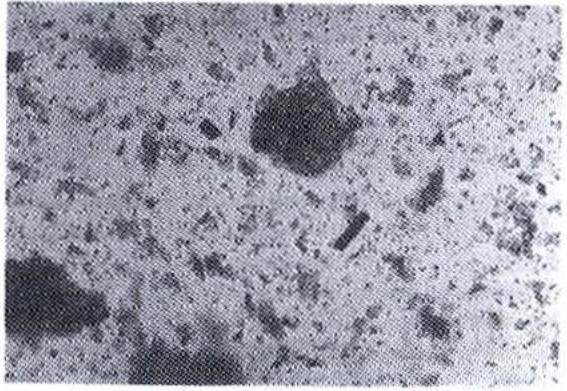
IV-Inertinite:High in C and very low in H.Ofted termed dead-carbon having no effective potential to yield oil and gas



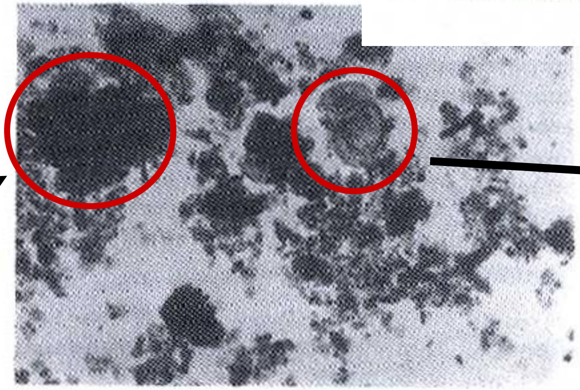


Type	Composition	Initial product	Origin	Environments
I	High hydrogen Low oxygen	Waxy oil	Freshwater algae	Lakes
II	Intermediate hydrogen and oxygen	Low-wax oil	Marine algae, plankton	Seas
III	Low hydrogen High oxygen	Gas Some waxy oil	Land plants	Swamps Nearshore marine

type II



(b)



Bit of land plants

Pollen

(a)

type II

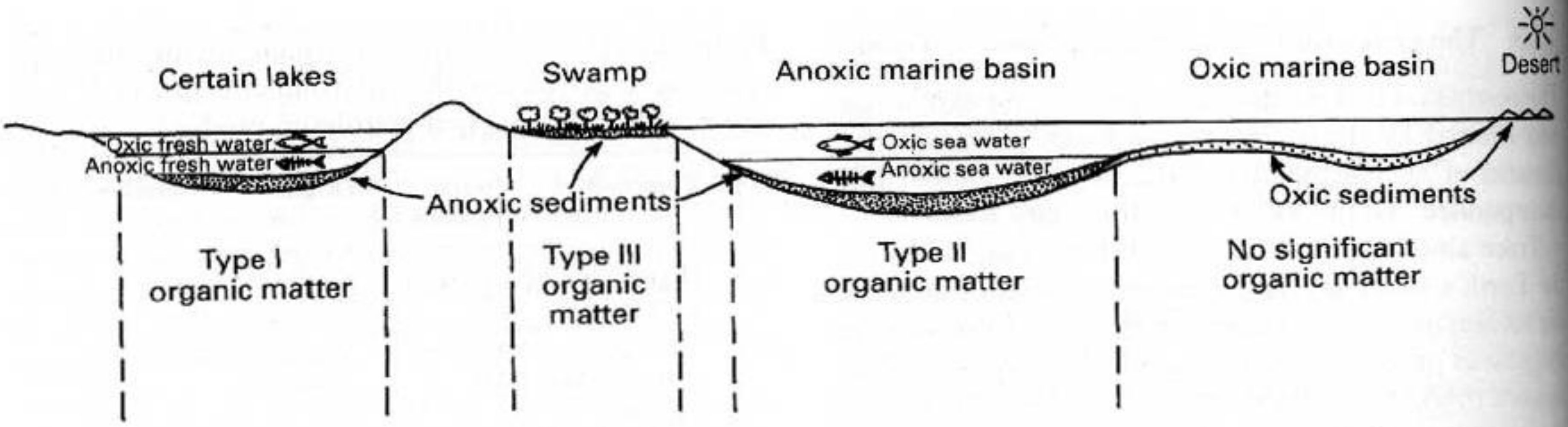


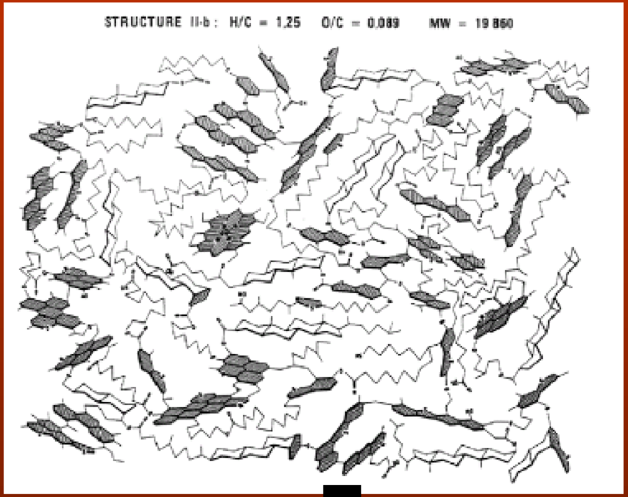
Fig. 2.5 The nature and environments of deposition of the types of organic matter that give rise to petroleum.

Maturation of Kerogen

Kerogen is composed of large hydrocarbon molecules that are stable at low T but will break down into smaller molecules of liquid and gaseous hydrocarbon compounds with progressive exposure to higher T.

This trasformation to smaller and ligher compounds is controlled by the reaction kinetics

The energy required to break the bonds between the atoms



Kerogen

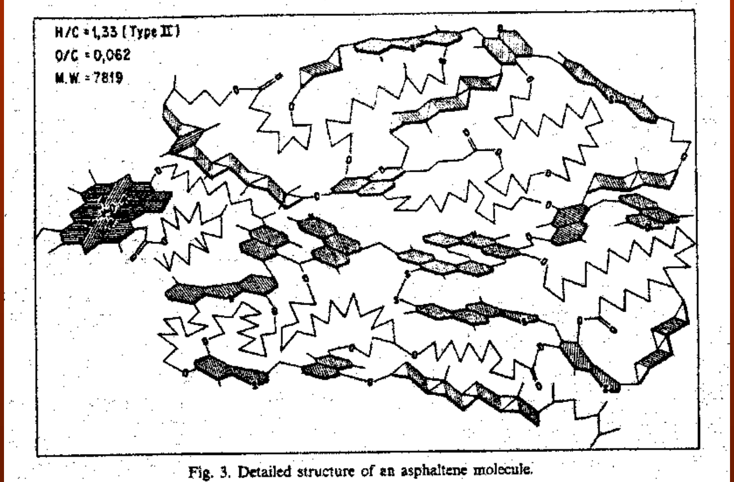
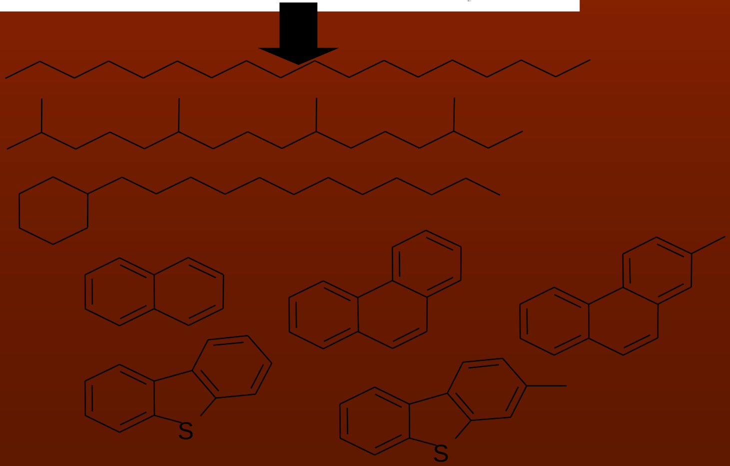
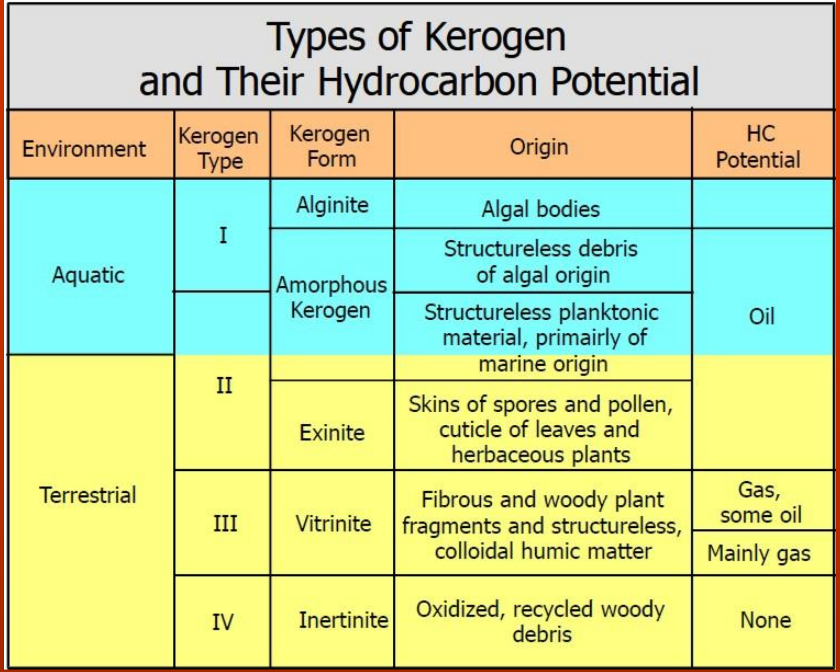


Fig. 3. Detailed structure of an asphaltene molecule.



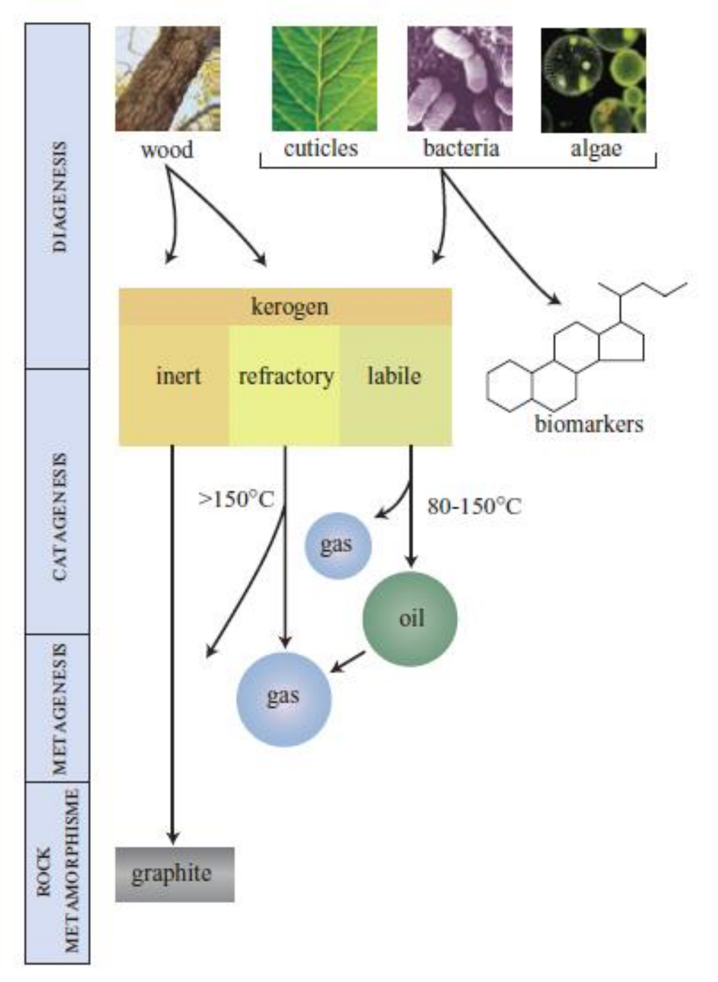
Hydrocarbons

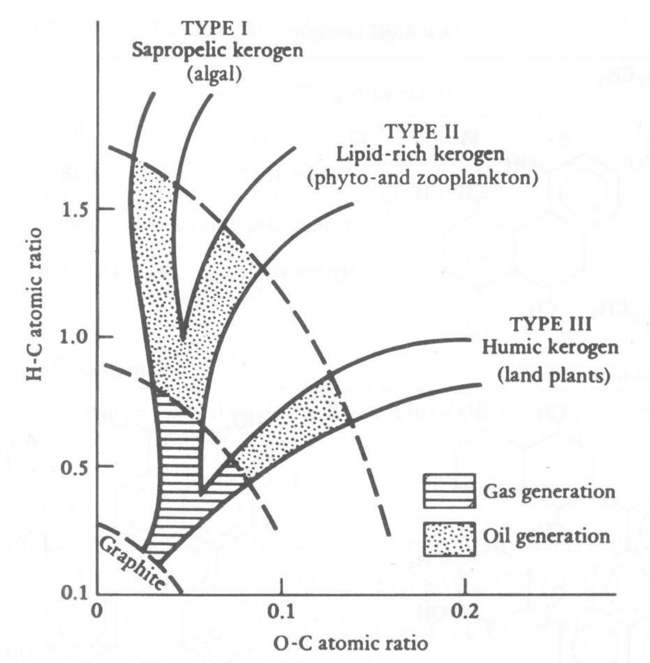
Asphaltenes and Resins /NSO



Types of Kerogen and Their Hydrocarbon Potential

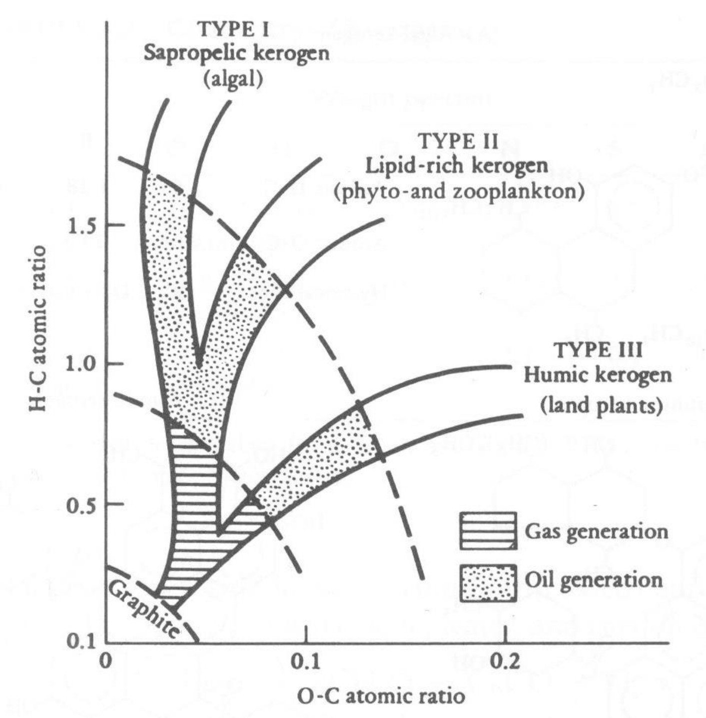
Environment	Kerogen Type	Kerogen Form	Origin	HC Potential
Aquatic	I	Alginite	Algal bodies	
		Amorphous Kerogen	Structureless debris of algal origin	Oil
	II		Structureless planktonic material, primairly of marine origin	
Terrestrial		Exinite	Skins of spores and pollen, cuticle of leaves and herbaceous plants	
	III	Vitrinite	Fibrous and woody plant fragments and structureless, colloidal humic matter	Gas, some oil Mainly gas
	IV	Inertinite	Oxidized, recycled woody debris	None

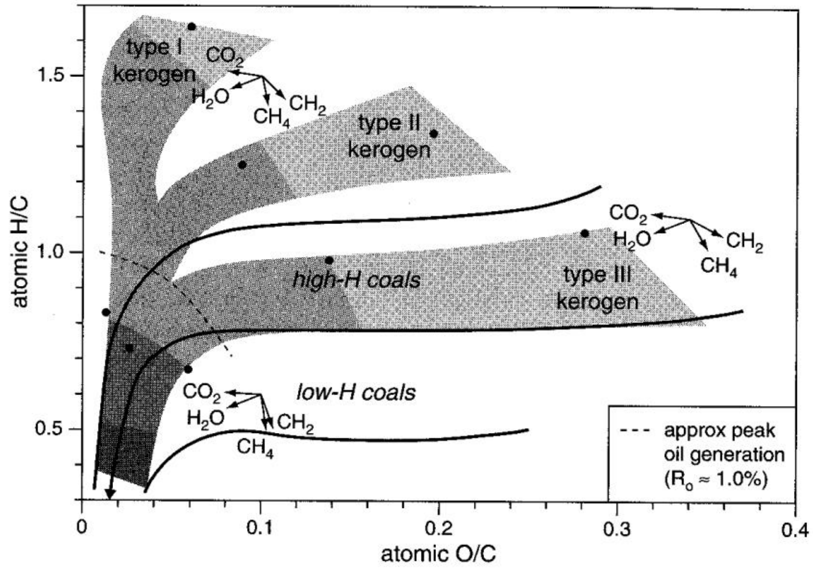




Reactive Kerogen:
Labile : algae,bacteria- lipids
Refractory : vascular parts of land plants
The amount of initial oil are determined by precursory organisms and depositional setting of SR

Van krevelen´s diagram showing the maturation paths of the different types of kerogen

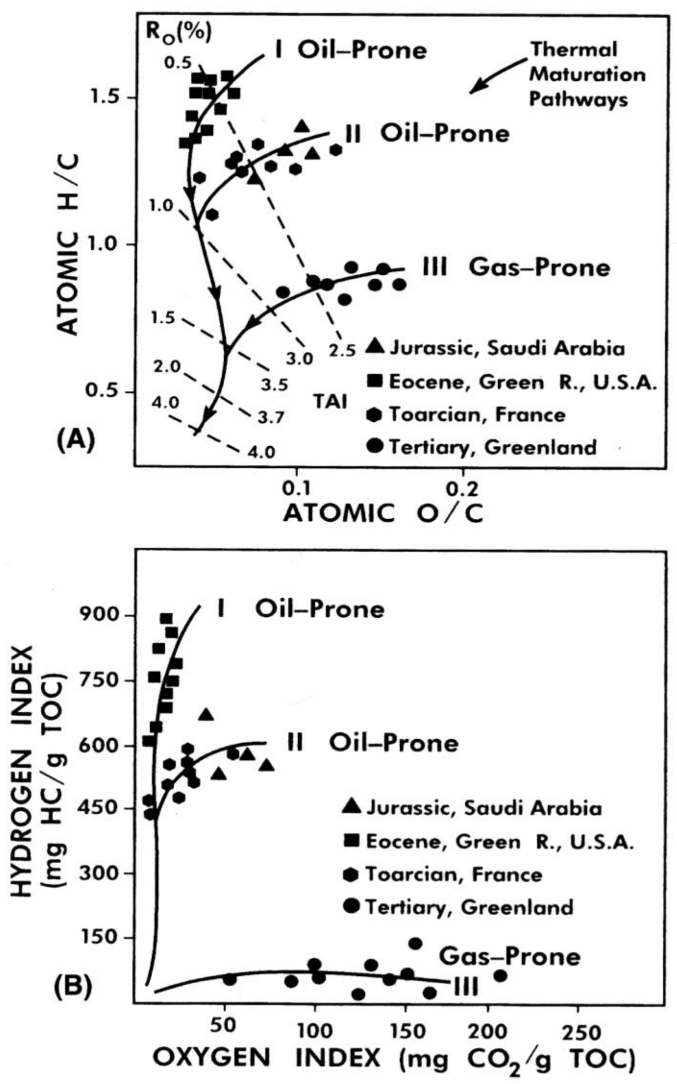




stage	zone		main fluids evolved	approx vitrinite reflectance (R_o)
diagenesis	immature	░	carbon dioxide & water	
catagenesis	oil	▒	liquid hydrocarbons	0.5–0.6%
	wet gas	▓	gaseous hydrocarbons	1.3%
metagenesis	dry gas	█	methane	2.0%

H/C ratio and O/C ratio helps us characterize the origin of organic matter. Marine organisms and algae, in general, are composed of lipid- and protein-rich organic matter, where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants.

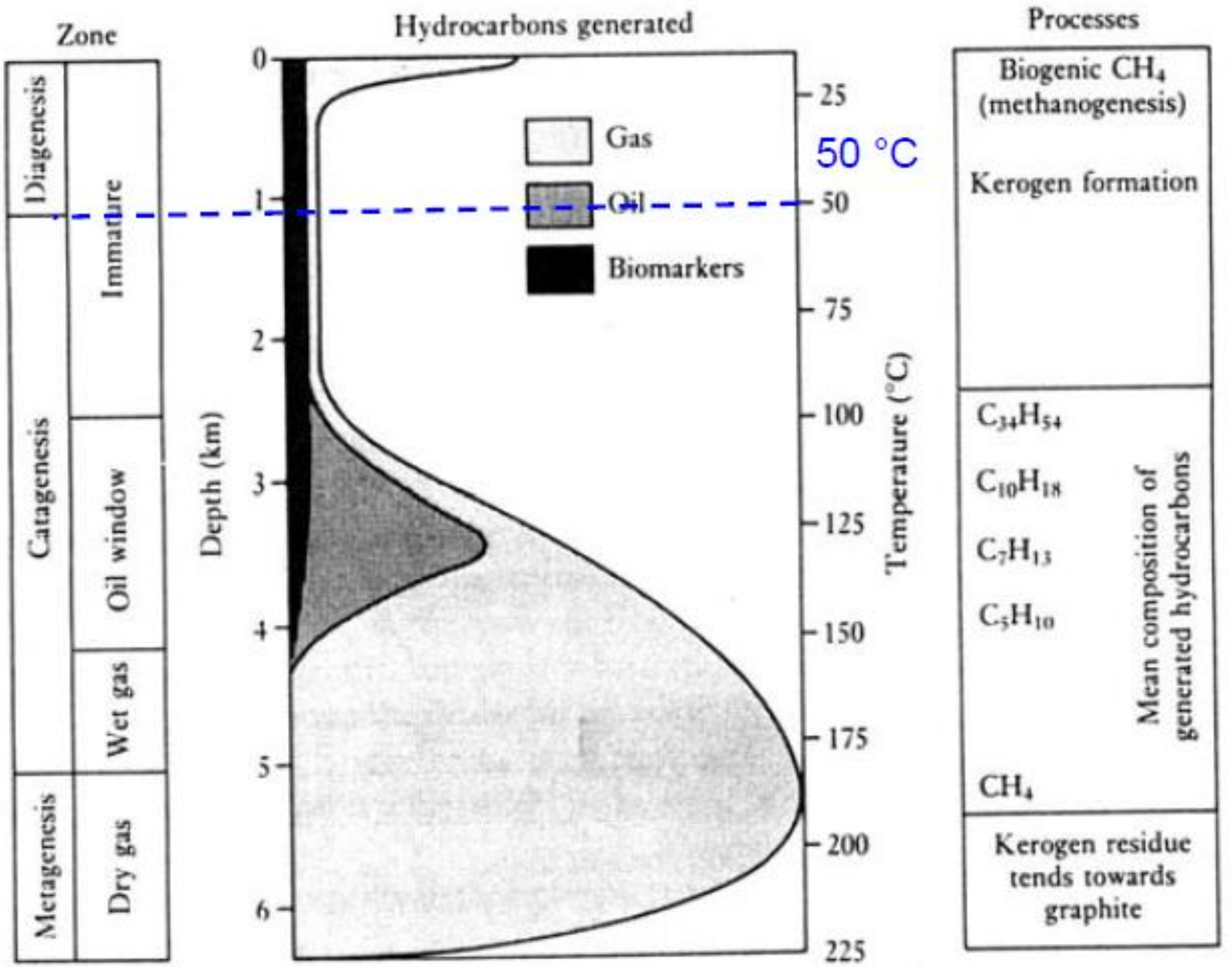
O/C ratio is high for polysacharride-rich remains of land plants and inert organic material (residual organic matter) encountered as background in marine sediments.



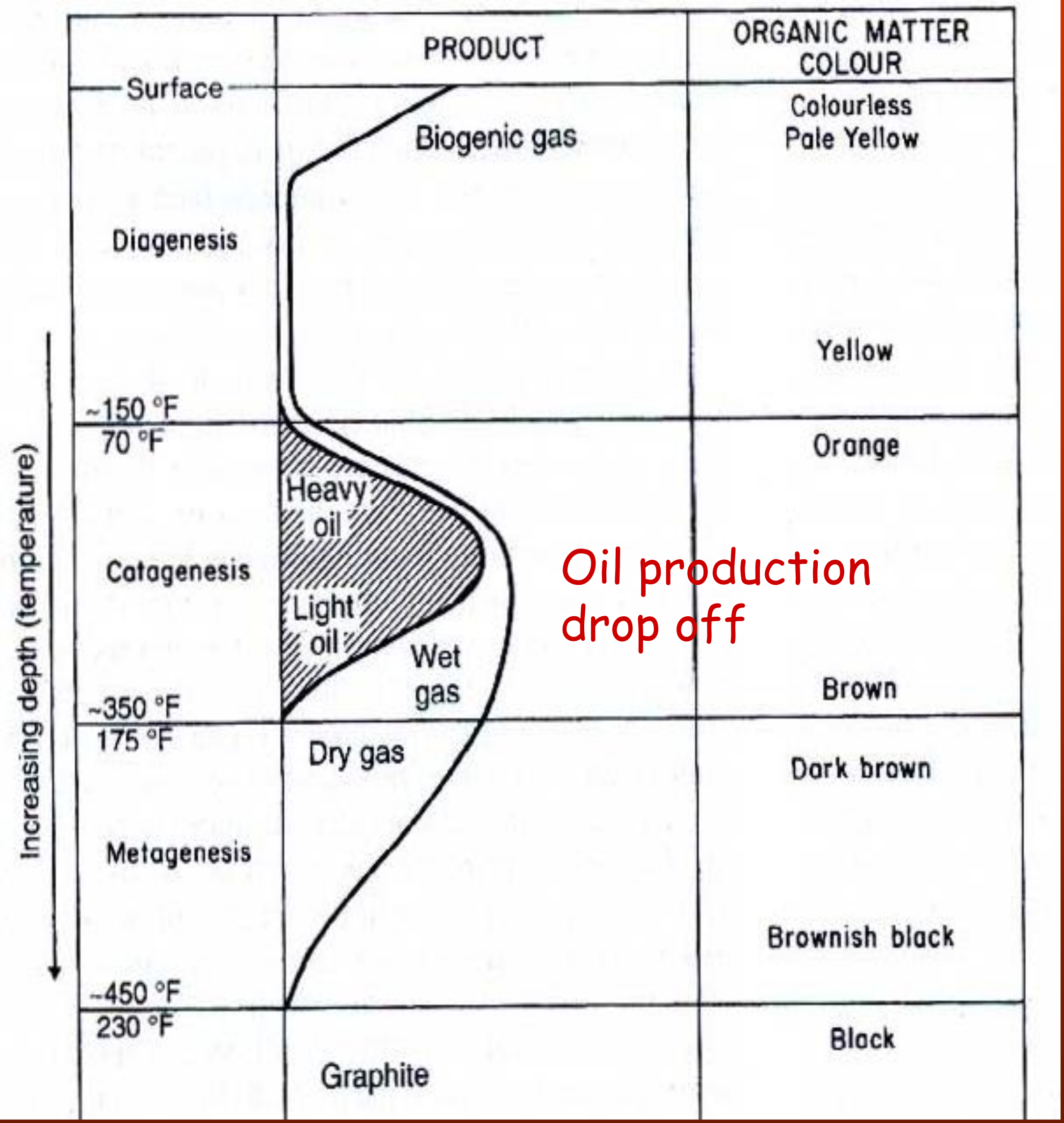
With respect to the generation of petroleum,the most fundamental characteristic of kerogen is hydrogen content,because under optimal conditions a hydrogen-rich kerogen will generate more oil than a hydrogen clean kerogen

Determining the elemental composition of kerogen it is possible to differentiate and classify kerogen and broadly predict the type of petroleum a given kerogen will generate in the subsurface under the right conditions

General scheme of hydrocarbon generation from source rock

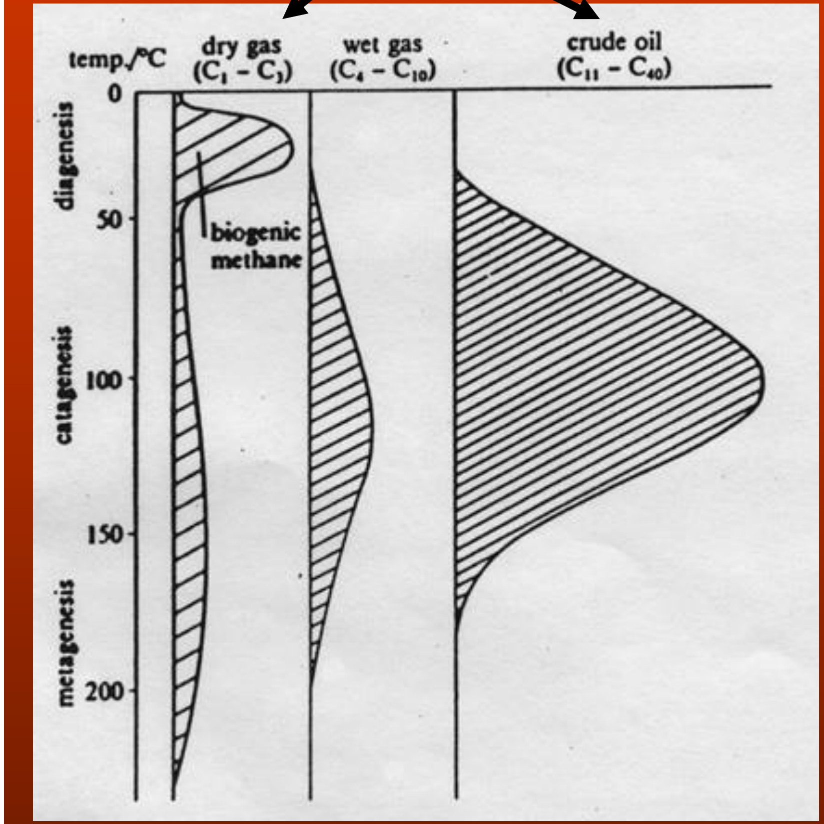


Thermal Maturation



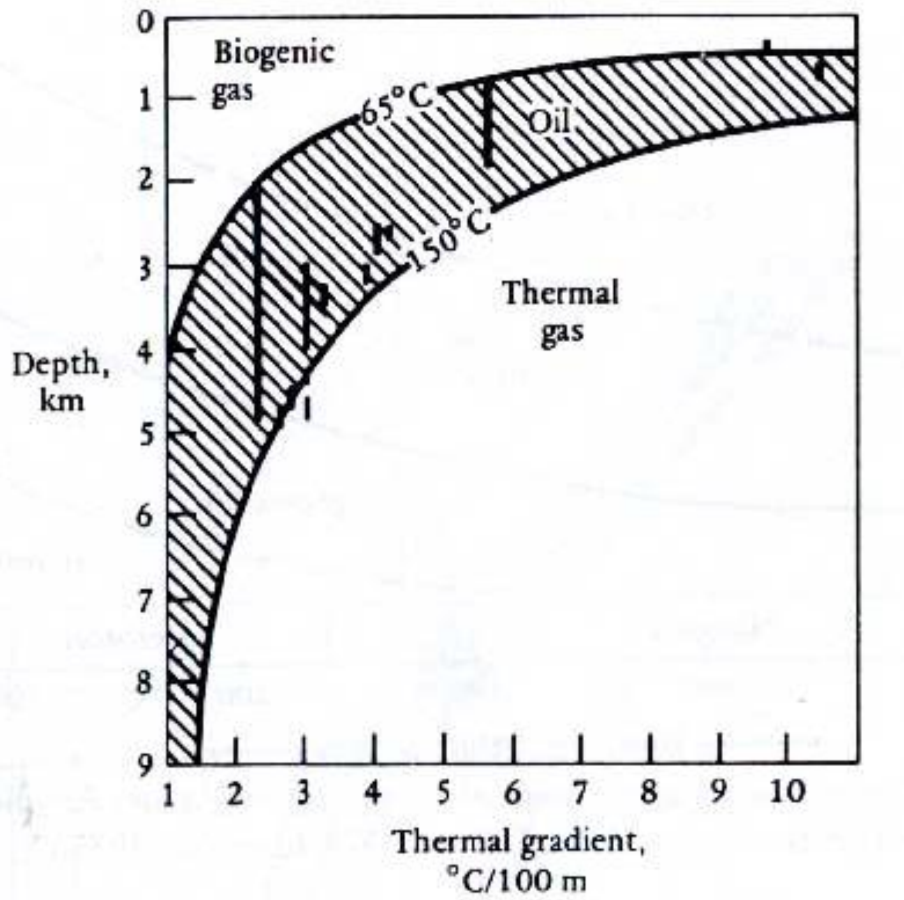
Oil production drop off

Range of number of C atoms in each of maturation products



Significant oil generation: 60-120°C (Oil Window)
Significant gas generation: 120-225 °C

Thermal Maturation



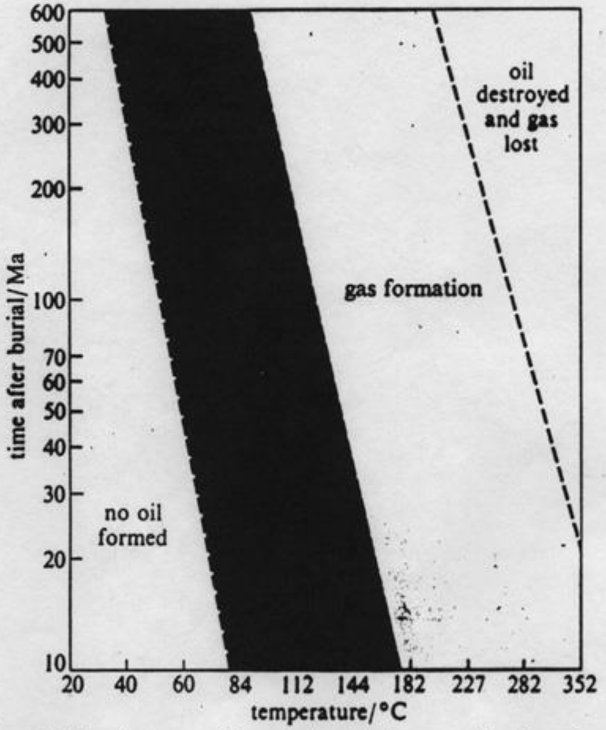
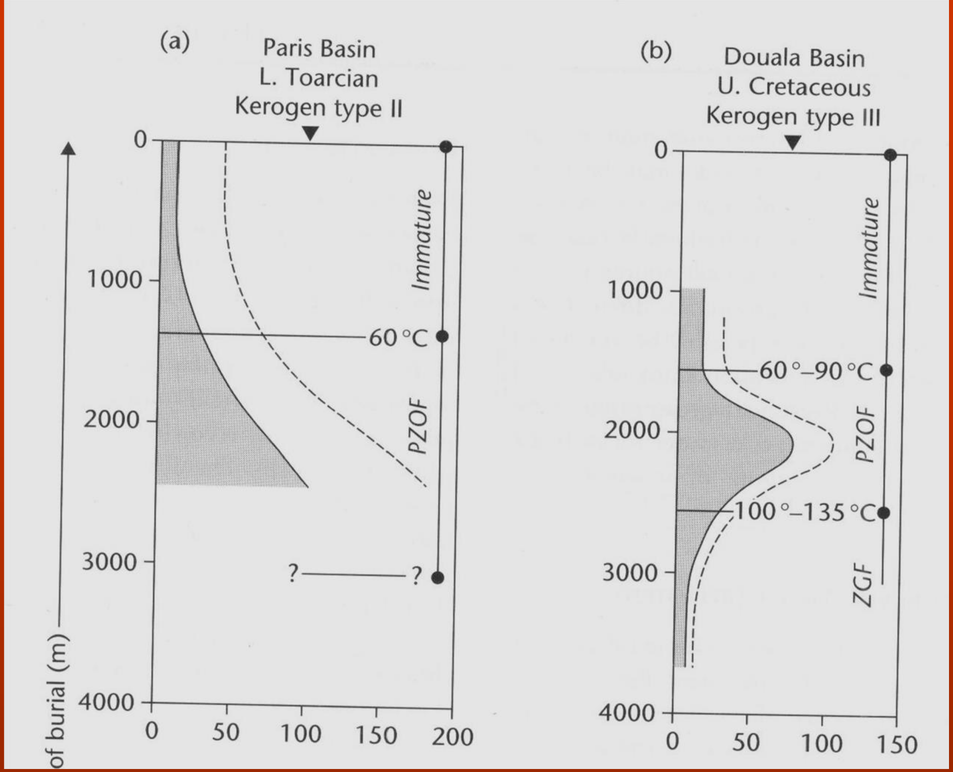
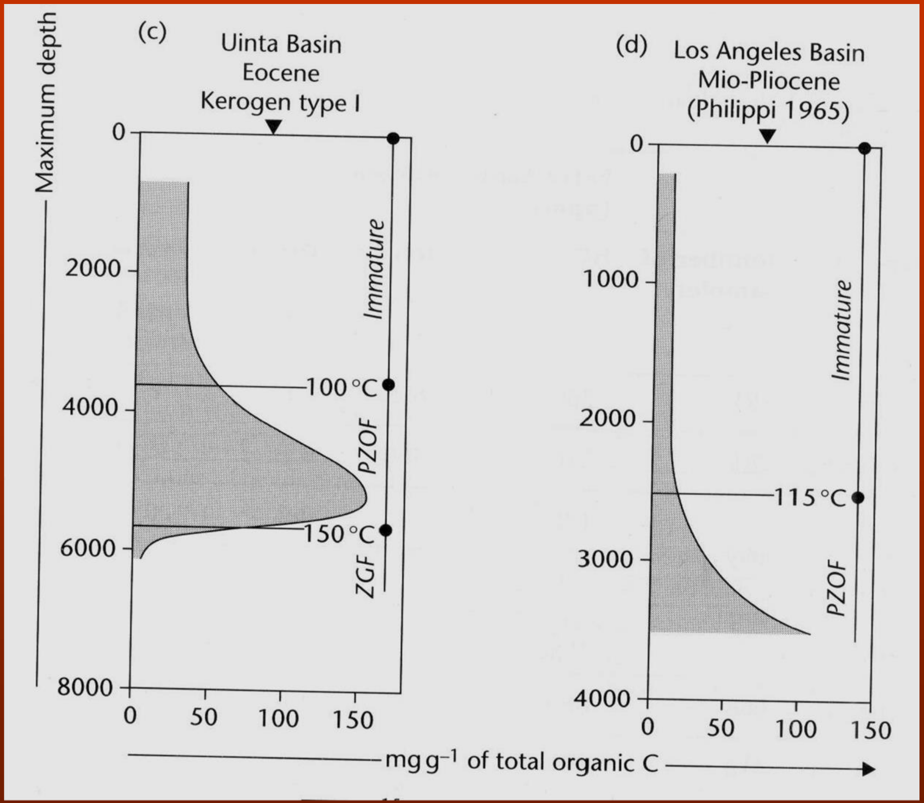


Figure 32 A model showing a possible relationship between the time after burial of source rocks and the temperature for oil and gas formation.

Formation of HC as function of depth in different basins





Paleothermometers

- Chemical
    - Organic
        - Carbon ratio
        - Electron spin resonance
        - Pyrolisis
        - Gas chromatography
    - Inorganic
        - Clay mineral diagenesis
        - Fluid inclusions
- Biological
    - Pollen coloration
    - Vitrinite reflectance

Vitrinite Reflectance

Vitrinite reflectance has world wide acceptance as a basin analysis technique that provides information on Time, temperature and pressure

Applicable over a wide range of temperatures

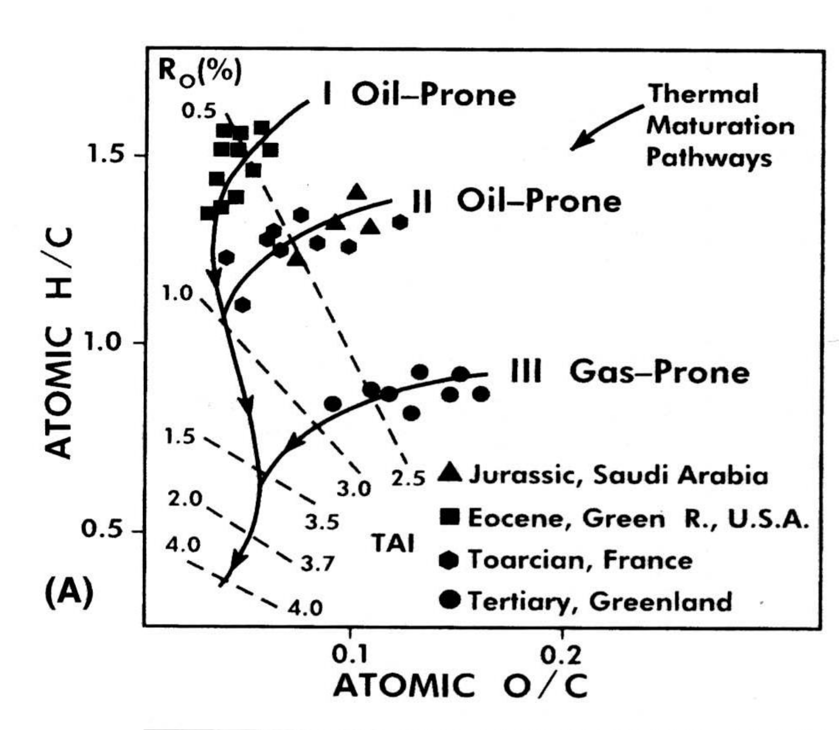
Cheap, and simple relative to other methods

Vitrinite reflectance is a measure of the reflectance of fossil wood. This increases as the physical structure of vitrinite becomes more crystalline and chemically less complex.

Empirical relationship between vitritite reflectance and Hydrocarbon generation

The measurement is given in units of reflectance, % Ro, with typical values ranging from 0% Ro to 3% Ro.

Ro< 0.55 Immature
0.5< Ro <0.8% Onset of oil generation
0.8< Ro <1% cracking of oil to gas
1< Ro <2.5% Dry gas generation



Increasing maturity

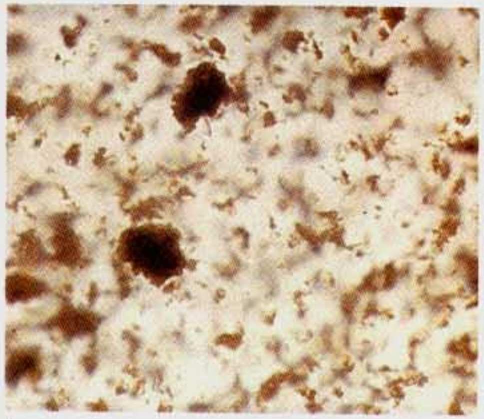
Immature

Mature

Supermature


1


2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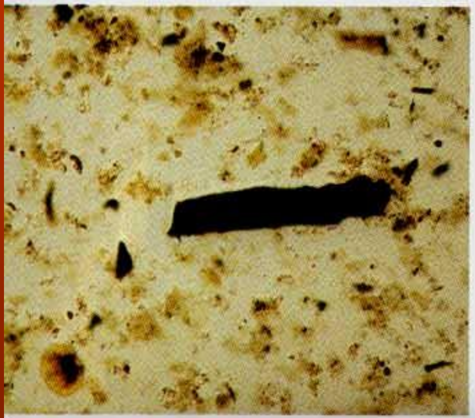
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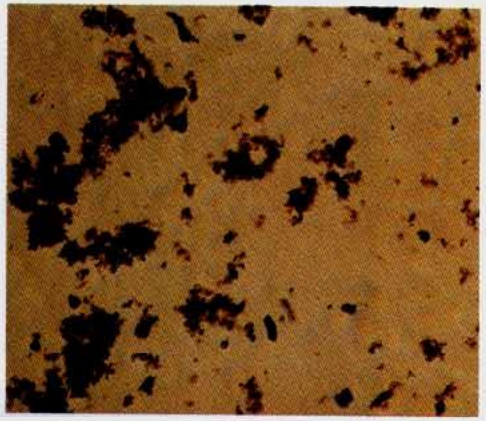
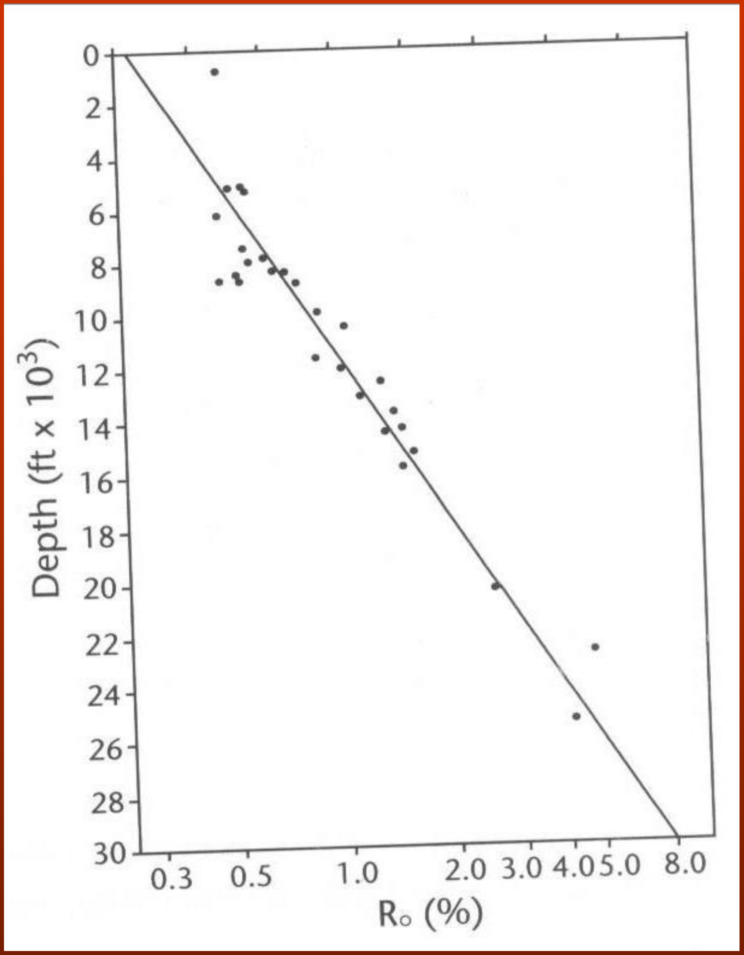
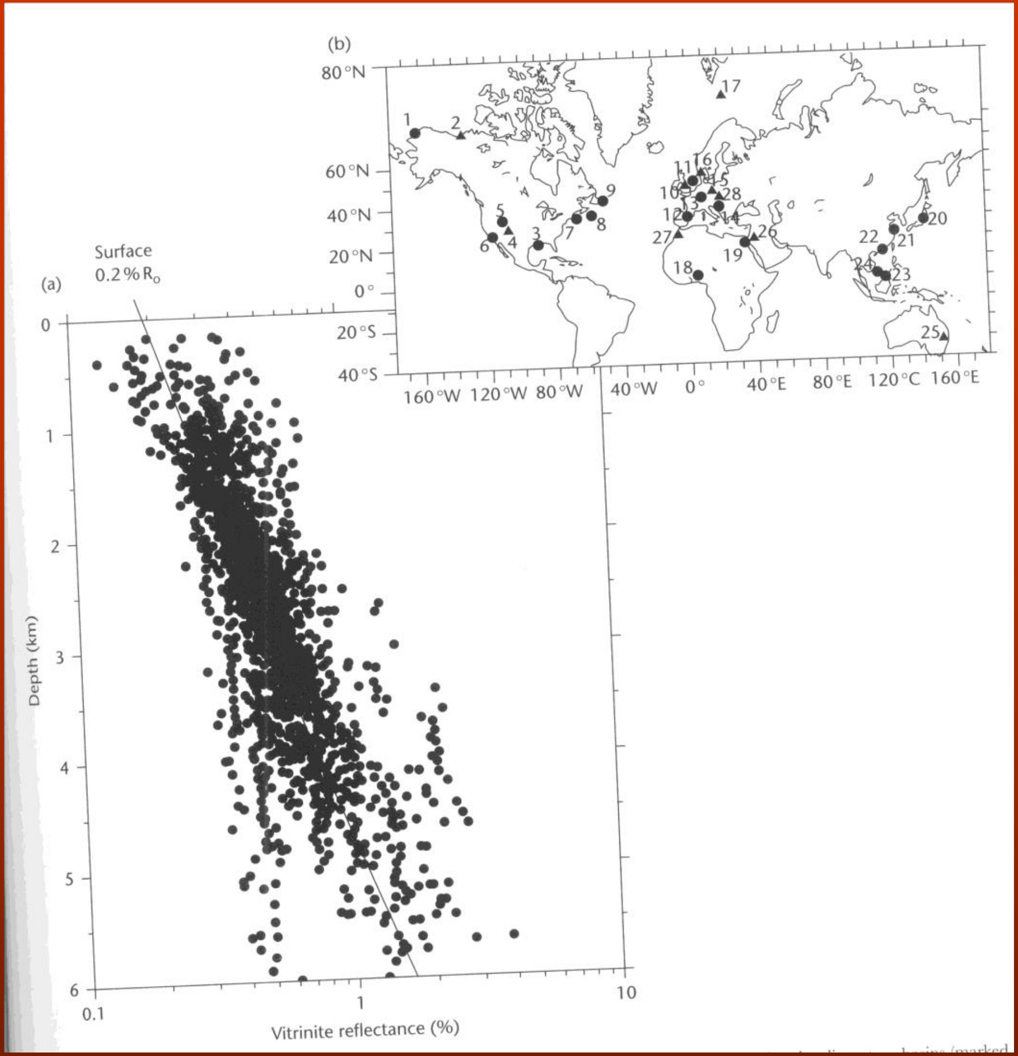


hotograph umber	1	2	3	4	5	6
ocality	Gurpi Fm. Zagros, Iran	Kazdumi Fm. Zagros, Iran	Garan Fm. Zagros, Iran	Kimmeridge Clay Dorest, UK	Kimmeridge Clay Dorset, UK	Sembar Fm. Lower Indus, Pakistan
ype of erogen	I	I	I	II	II	II
laturation evel	Immature	Mature	Supermature	Immature	Mature (just)	Supermature
$_o$(%)	0.4	0.9	2.0	0.4	0.5	2.0
lagnifi-ation	X25	X25	X62	X25	X25	X62

Vitrinite Reflectance





VR in geological simple settings starts at about 0.2-0.3% and increase steadily with depth.the slope of the curve gives an indication of the geothermal gradient in the history of the basin

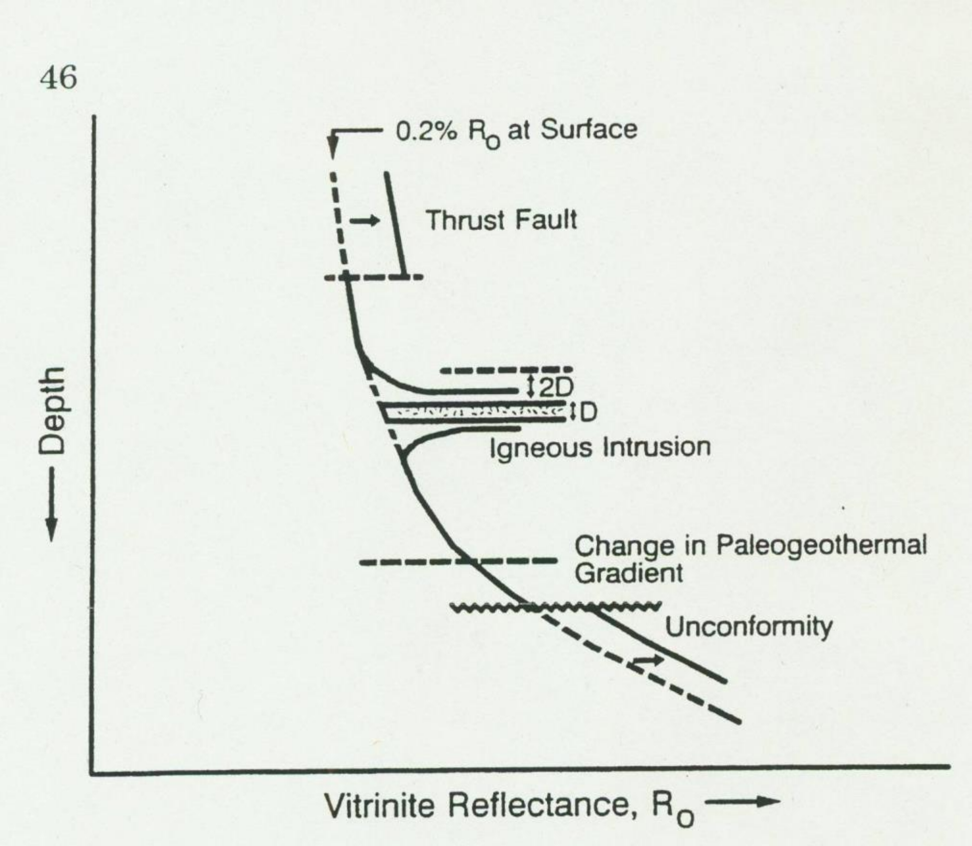
But.....

The sample must contain vitrinite

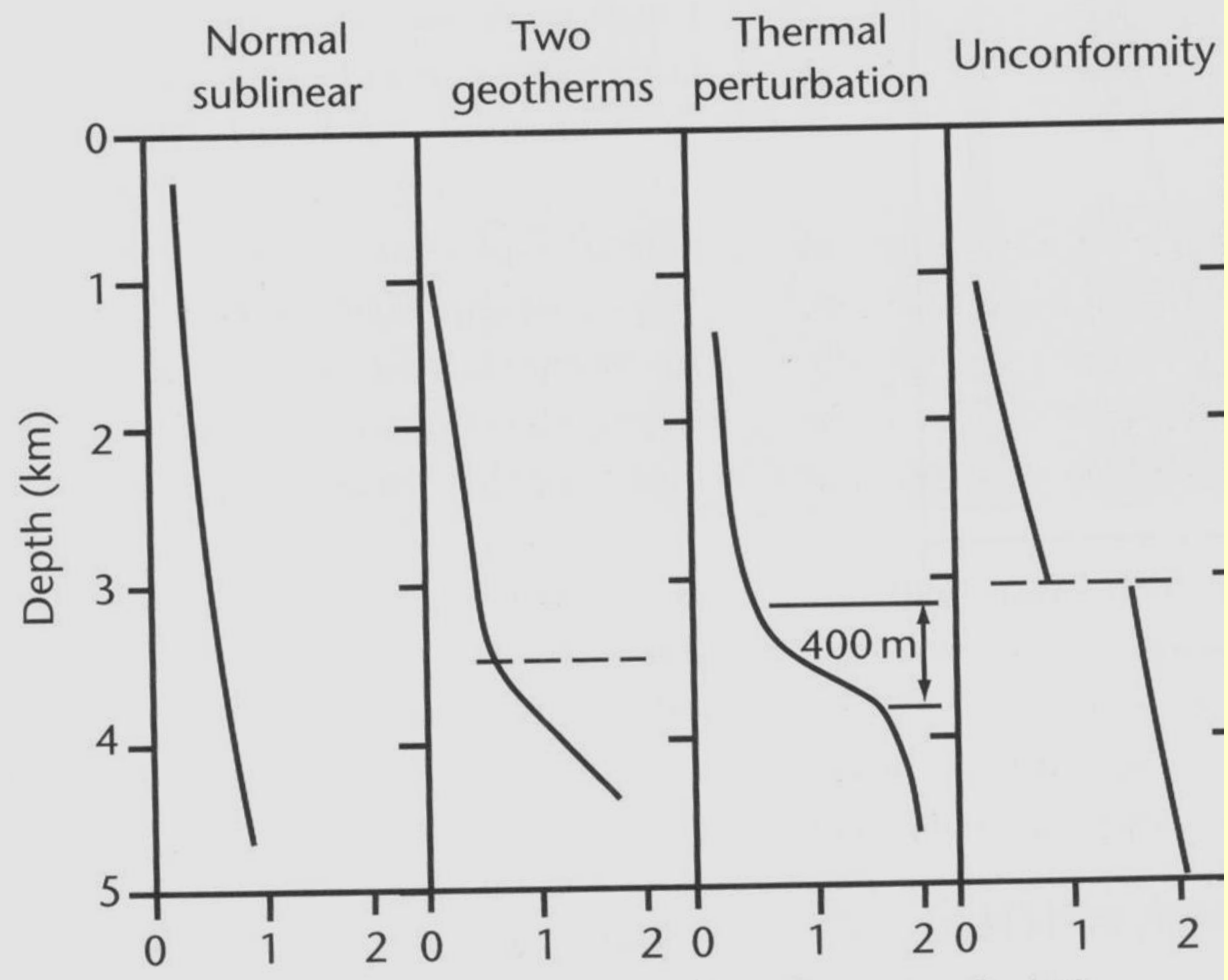
It is a poor measure of thermal maturity below about 0.4%

Simple Ro profiles can be modified by several geological processes

Thrust faulting
Erosional unconformities
Ingneous intrusions
Caving of materials



Vitrinite Reflectance



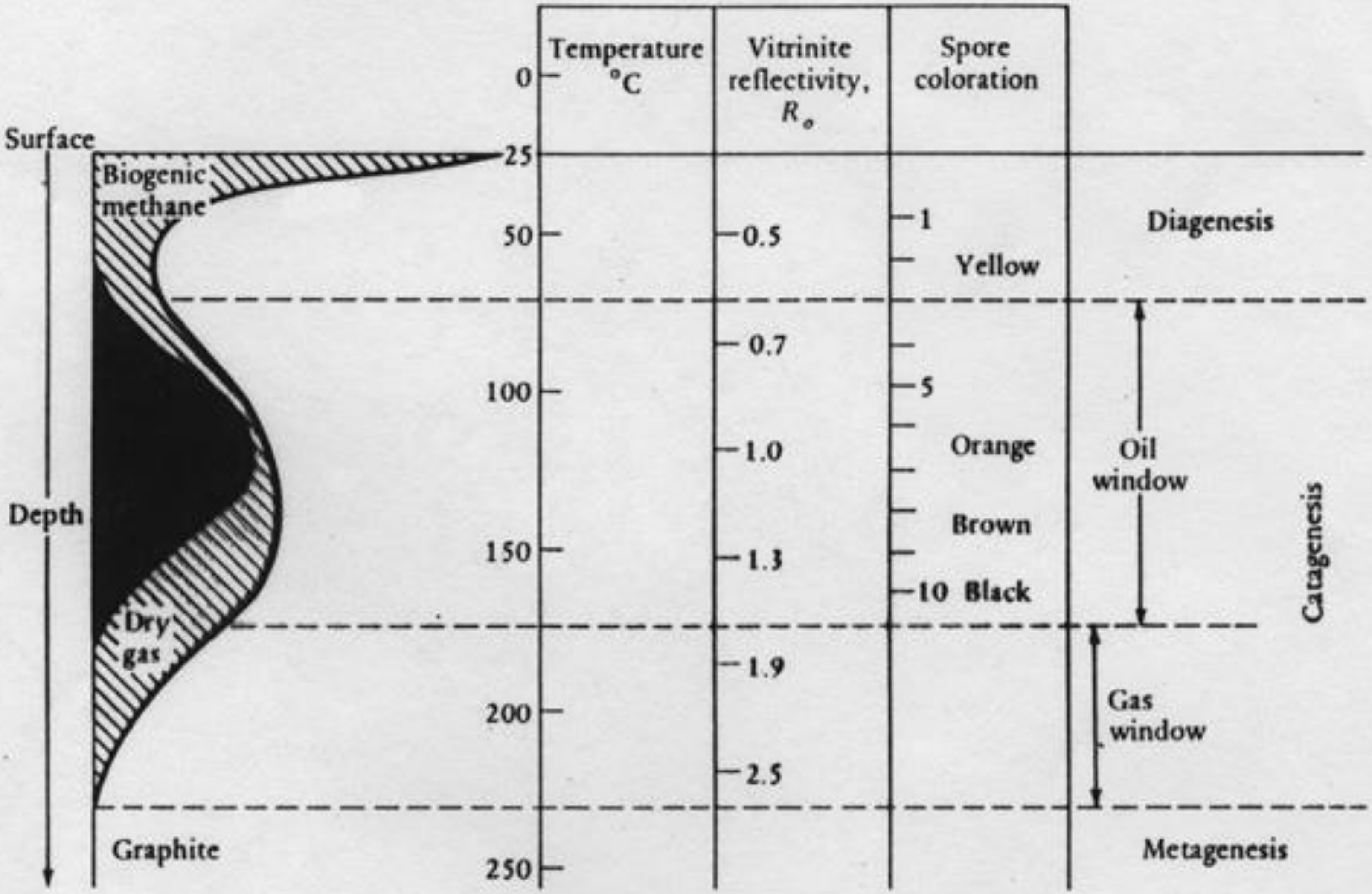


FIGURE 5.14 *Correlation between hydrocarbon generation, temperature, and some paleothermometers.*

Detection and measurement of source rock

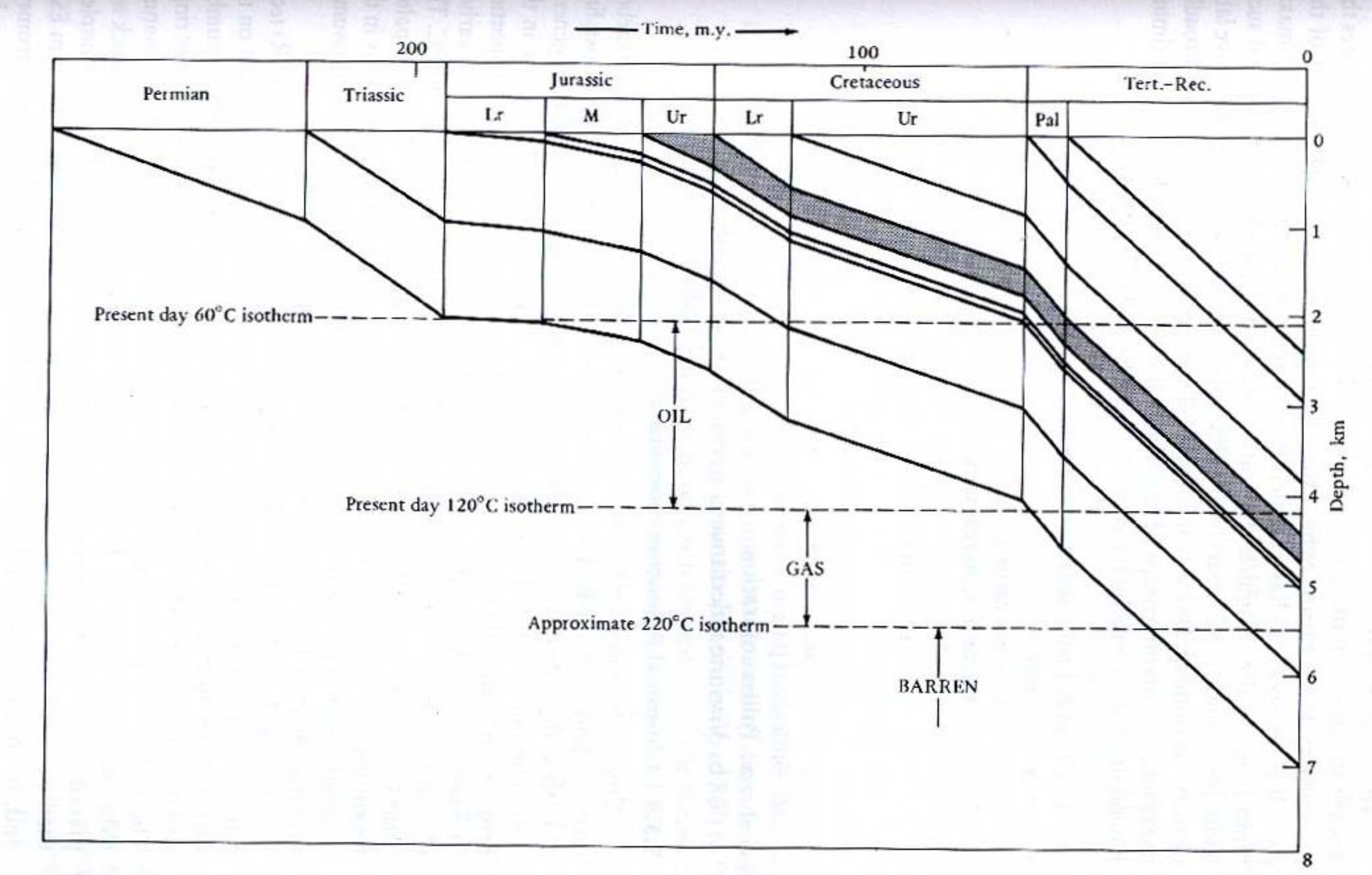
A Range of geochemical analysis areavailable to identify and measure source rocks and petroleum fluids

What we whant to know other that simply establishing where a source rock exist?

the richness of the source rock
the petroleum type and composition
the thermal maturity of the source rock
its geochemical composition in order to assess migration routes

Because it is not enough to answer to these questions:
Are OM rich source rock in the basin?
Are they present in large volume?
Are they gas or oil prone?

It is fundamental to know wheter or not the source rocks have maturated sufficiently to generate petroleum



T is not the only parameter to take into account for oil generation

Never forget TIME

Rock Eval pyrolysis

Rock Eval pyrolysis is one of the most commonly techniques used to identify the type and maturity of organic matter and to detect petroleum potential in sediments.

The Rock Eval (RE) pyrolysis method consists of a programmed temperature heating in an inert atmosphere (helium) of a small sample

The pyrolysis oven temperature program is as follows: for 3 min, the oven is kept isothermally at 300°C and the free hydrocarbons are volatilized and measured as the S_1 peak .

The temperature is then increased from 300° to 550°C (at 25°C/min). This is the phase of volatilization of the very heavy hydrocarbons compounds ($>C_{40}$) as well as the cracking of nonvolatile organic matter. The hydrocarbons released from this thermal cracking are measured as the S_2 peak .
The temperature at which S_2 reaches its maximum depends on the nature and maturity of the kerogen and is called T_{max}.

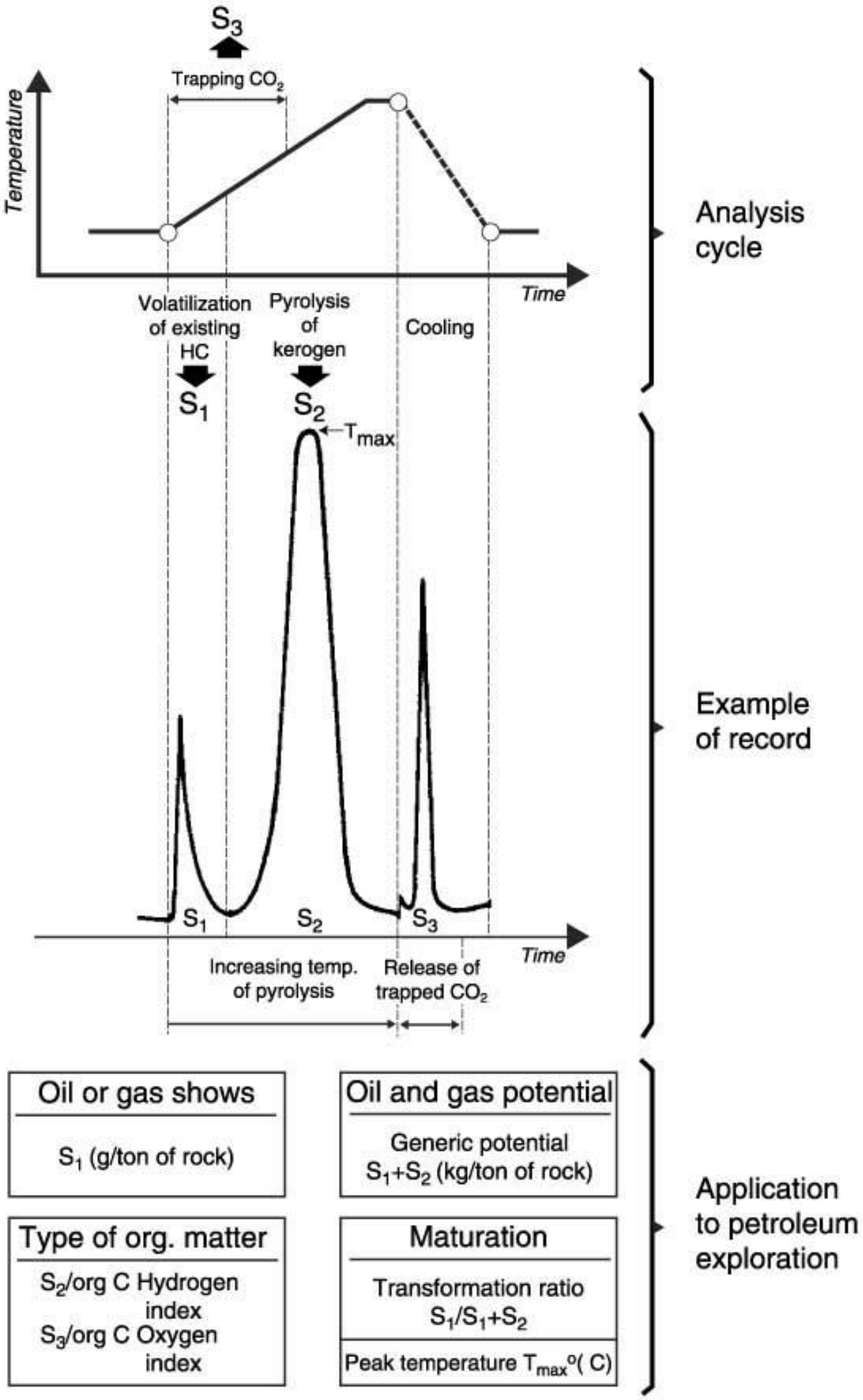
The CO_2 issued from kerogen cracking is trapped in the 300°-390°C range. The trap is heated, and CO_2 is released and detected on a TCD during the cooling of the pyrolysis oven (S_3 peak).

S1 : the already generated oil in the rock. These are the free hydrocarbons (oil and gas) already present in the sample, and they are distilled out of the sample at initial heating of the sample to a temperature of 350 ° C. Free hydrocarbons increase with depth. S1 = 1.0 mg HC/g dry rock -- Minimum value for good source rocks.

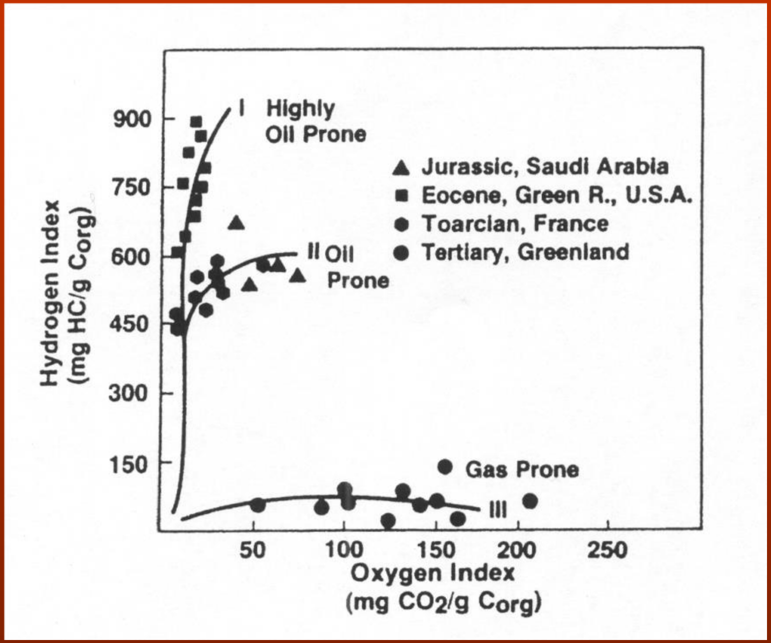
S2 : the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter (kerogen) when the sample temperature is increased to 550 ° C. S2 is an indication of the quantity of hydrocarbons that the rock may potentially produce should burial and maturation continue. This parameter normally decreases with burial depths >1 km.
S2 >= 5.0 mg HC/dry rock -- Minimum value for good source rocks.

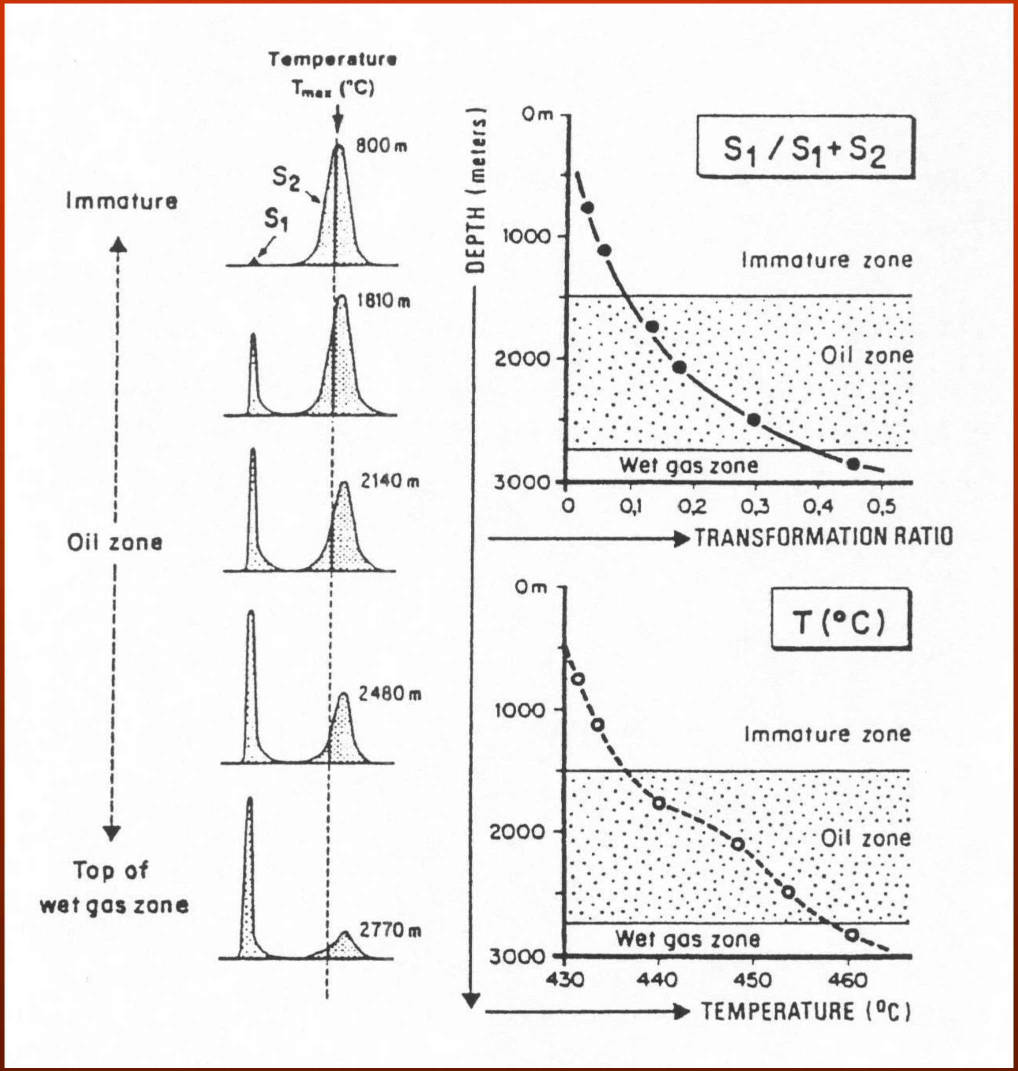
S3 : The trapped CO 2 released during pyrolysis up to a temperature of 390 ° C. This value is proportional to the oxygen present in the kerogen. Carbonate rocks may increase S3 values.

T max : The temperature at maximum release of hydrocarbons occurs during Rock-Eval pyrolysis. This occurs at the top of the S2 peak. T max is dependent on the type of kerogen present in the source rock. Plotting T max versus the Hydrogen Index (HI) shows the different maturation paths of different kerogen types. .



Rock Eval pyrolysis






Hydrogen Index (HI) = S_2/TOC

Oxygen Index (OI) = S_3/TOC

Production Index (PI) = $S_1/(S_1 + S_2)$

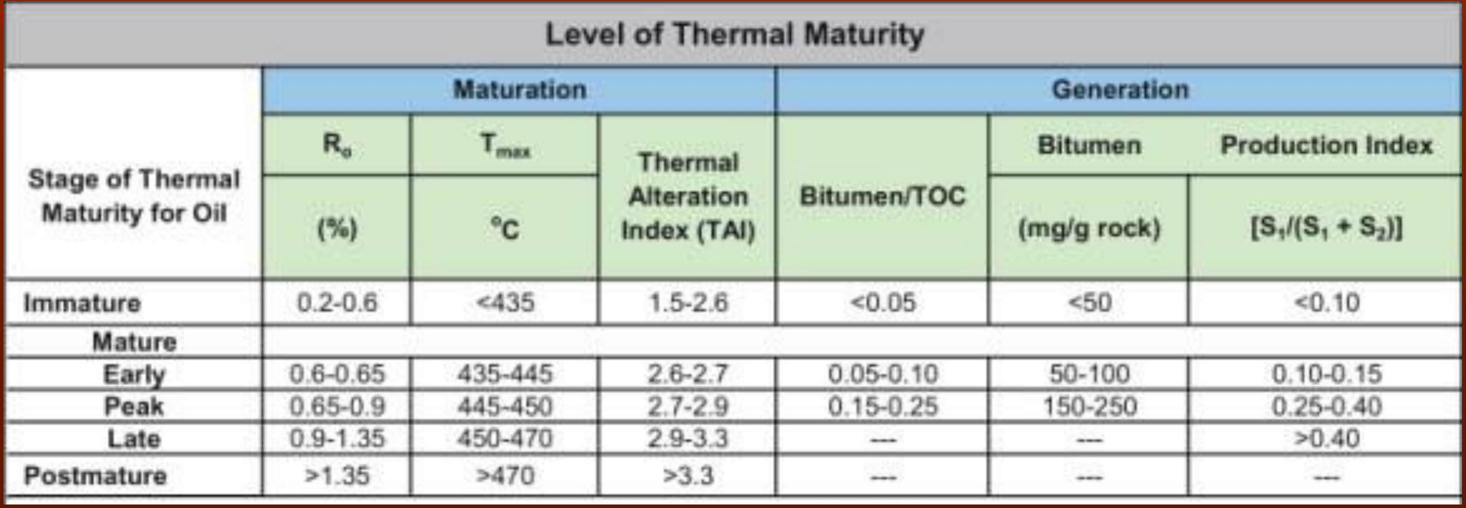
Transformation Index (TI) = S_1/TOC

Potential Yield (PY) = $S_1 + S_2$

HI : Hydrogen index [HI = (S2/TOC) x 100]. The ratio of S2 hydrogen (in mg HC/g dry rock) to total organic carbon (TOC), in grams. The hydrogen index is a measure of the hydrogen richness of the source rock, and when the kerogen type is known it can be used to estimate the thermal maturity of the rock. When plotted against the oxygen index (OI), the HI can be used to provide a crude assesement of the petroleum generative potential in a source rock (Peters and Moldowan, 1993).

OI : Oygen index [OI = (S3/TOC) x 100]. The ratio of S3 (mg CO2/g dry rock) to TOC (in grams). This parameter measures the oxygen richness of a source rock and can be used in conjunction with the hydrogen index to estimate the quality and thermal maturity of source rocks. This index is unreliable in rocks with high carbonate content. High OI values (>50 mg/g) are characteristic of immature hydrocarbons.

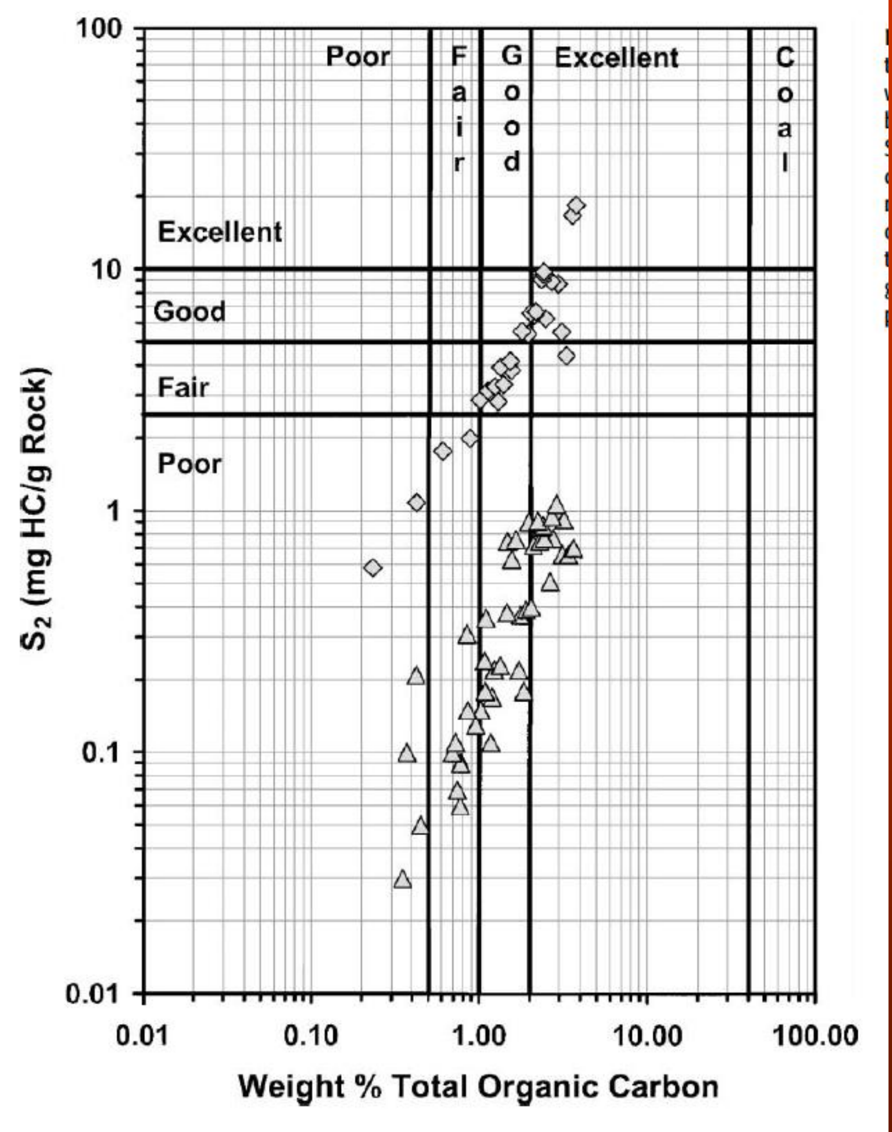
PI : Production index [PI = S 1 /[S 1 + S 2]. The production index is the ratio of already generated hydrocarbon to potential hydrocarbons. Low ratios indicate either immaturity or extreme postmature organic matter. High rations indicate the mature stage or contamination by migrated hydrocarbons or drilling additives. The PI increases steadily with depth and associated hydrocarbon generation. PI values less than 0.01 indicate the immature stage. Early and peak mature stages correspond to PI values of 0.10 to 0.15 and 0.25 to 0.40, respectively. PI values greater than 0.4 indicate the late mature stage.



Level of Thermal Maturity

Stage of Thermal Maturity for Oil	Maturation			Generation		
	R_o	T_{max}	Thermal Alteration Index (TAI)	Bitumen/TOC	Bitumen	Production Index
	(%)	°C			(mg/g rock)	$[S_1/(S_1 + S_2)]$
Immature	0.2-0.6	<435	1.5-2.6	<0.05	<50	<0.10
Mature						
Early	0.6-0.65	435-445	2.6-2.7	0.05-0.10	50-100	0.10-0.15
Peak	0.65-0.9	445-450	2.7-2.9	0.15-0.25	150-250	0.25-0.40
Late	0.9-1.35	450-470	2.9-3.3	---	---	>0.40
Postmature	>1.35	>470	>3.3	---	---	---

TOC and Source rock



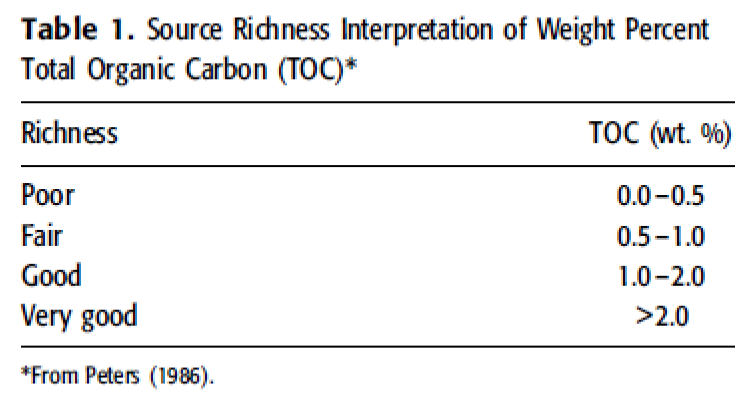


Table 1. Source Richness Interpretation of Weight Percent Total Organic Carbon (TOC)*

Richness	TOC (wt. %)
Poor	0.0–0.5
Fair	0.5–1.0
Good	1.0–2.0
Very good	>2.0

*From Peters (1986).

Good source rock should have high TOC BUT not all organic matter are equal (oil,gas, oil+gas generation)
TOC by itself is NOT necessarily a good indicator of how much HC a sediment can generate

The more H associated with the C the more HC can be generated (S2)

TOC and Source rock

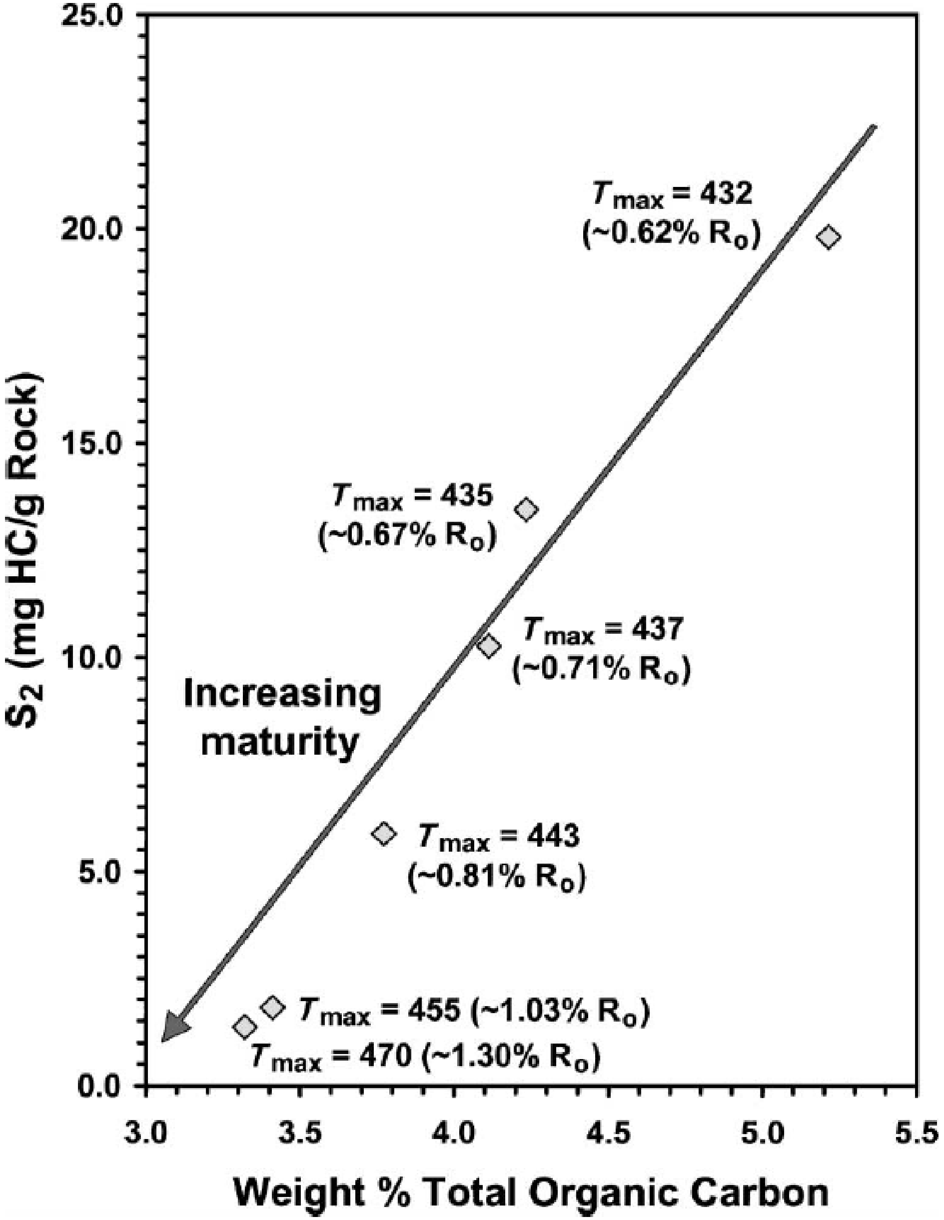


Figure 2. As a source rock generates and hydrocarbon migrates off, the amount of organic matter in the source rock will decrease with a corresponding decrease in total organic carbon (TOC), and the amount of reactive kerogen will decrease (the amount of hydrogen will decrease) resulting in a decrease in Rock-Eval S_2 (the amount of hydrocarbon formed during the thermal decomposition of the kerogen) (from data described by Jarvie and Lundell, 1991). The T_{max} is a Rock-Eval maturity indicator (temperature at the maximum of the S_2 peak, in degrees Celsius) and the % R_o values are the estimated equivalent vitrinite reflectance values of the T_{max}.