The Carbon Cycle, Organic Matter and Maturation

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Why is Carbon so Important in the Life Cycle?

Carbon has numerous ways of bonding with many other elements, particularly oxygen and hydrogen

It forms "organic" and "inorganic" compounds. Organic compounds are considered unstable in the biosphere because they are in the reduced state. Inorganic compounds, principally calcite and dolomite, are stable because they are in the oxydized state.

Carbon is contained in most substances that are vital for the development of life ("biomolecules"): Proteins, lipids, sacharides, etc.

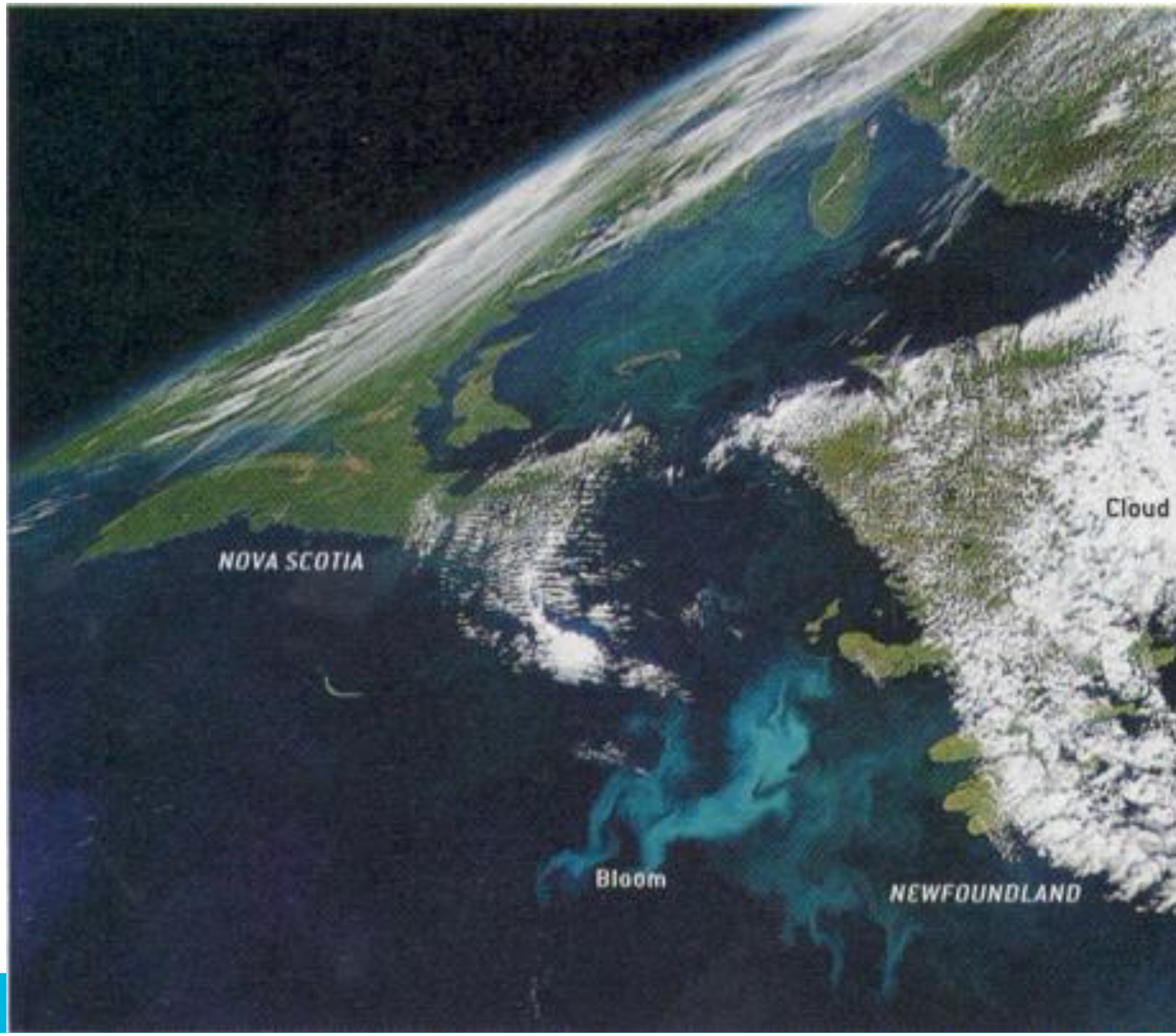
Plankton is Main Source of Oil and Gas

Diatoms are an important group of phytoplankton. They contain a silica skeleton and may reach 1 mm in diameter (right). Other phytoplankton organisms have a carbonate skeleton.

Zooplankton includes planktonic foraminifera, radiolaria, and planktonic crustacea.

Source: www.imagequestmarine.com

Planktonic Bloom in the Atlantic



Source: Scientific American, June 2002

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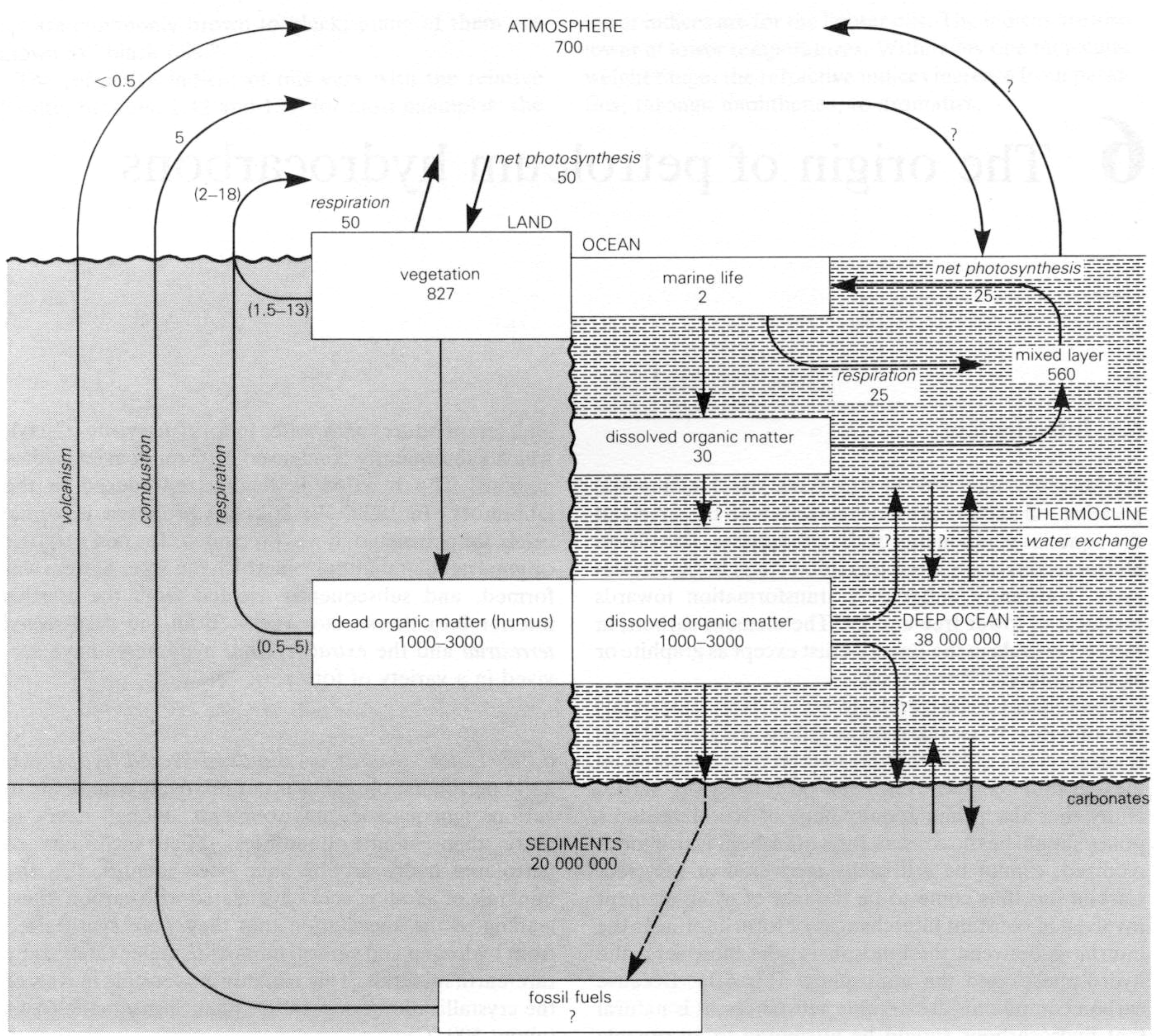
The Carbon Cycle

Source:
Scientific American

The red arrow indicates fertilizing of the ocean with iron-rich dust, leading to increased algal growth and an acceleration of the carbon cycle

Mass Balance of Carbon in Nature

THE ORIGIN OF PETROLEUM HYDROCARBONS



Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

Where Most Carbon Resides

Mt. Dinara, Croatia

A Side Note on the Origin of Petroleum

Many researchers have proposed non-organic origins of petroleum. Among these, the most popular is the inorganic origin theory. Russian geochemists proposed that telluric currents deep in the Earth's crust combine water, graphite, iron and sulfur as a giant battery that were "cooked" into hydrocarbons. Porfirev (1974) even postulated that all known oilfields were formed in this way during the Neogene.

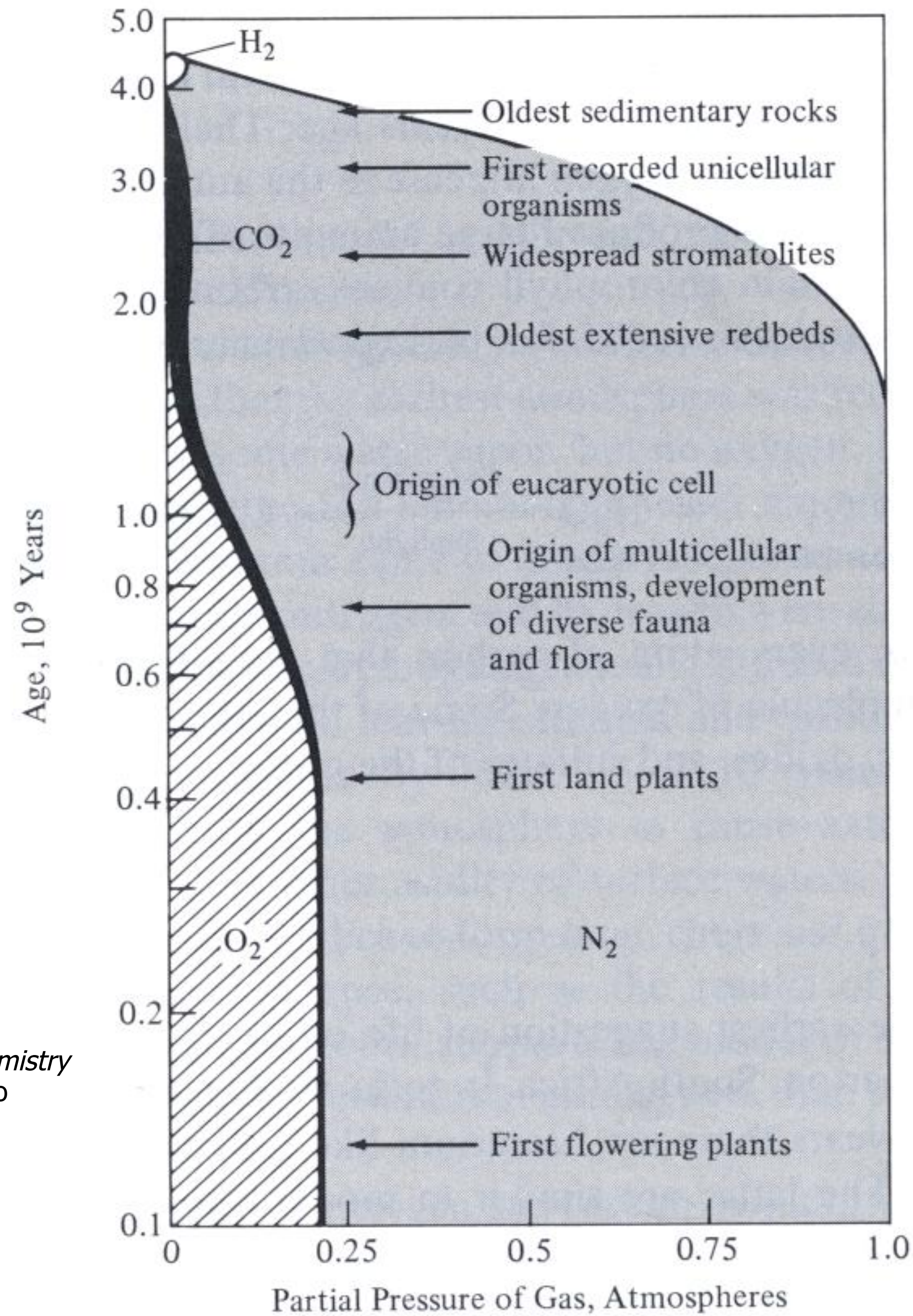
Another hypothesis was formulated by T. Gold. In his view, the components of the early atmosphere are still stored in and slowly degassed from the Earth's mantle, mostly in the wake of earthquakes.

A Side Note on the Origin of Petroleum ctd.

Geochemical evidence points strongly towards an organic origin of petroleum, as we shall see later in this course. Theories of an inorganic origin mostly come from regions where oil is found in igneous and metamorphic rocks, or where no organic source rock is evident. One should not discard these theories too lightly. After all, carbon is common in many igneous rocks, and the early atmosphere was reducing and probably rich in methane, in addition to water vapor, ammonia, hydrogen and other hydrocarbons. It is possible that photochemical reactions could modify it to form a heavy oil slick on the Earth's surface that formed a breeding ground for more complex compounds including prebiotic forms.

Evolution of Atmosphere and Life on Earth

Notice logarithmic scale of age!



Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

A Side Note on the Origin of Petroleum ctd.

Meteorites have been found with up to 6% organic matter including paraffins, aromatics, and heavy NSO compounds (later to be discussed).

Their isotope composition, however, is different from terrestrial compounds, and they were probably formed through irradiation of light elements in a primeval dust cloud.

We will assume in the following that MOST petroleum is of biogenic, terrestrial origin.

Hoba meteorite, Namibia
Largest preserved on Earth

Biomolecules in Living Organisms

Lipids, mostly fats, oils and waxes, have the greatest potential to be hydrocarbon sources. They are combinations of the fatty acids of the general formula $C_nH_{2n}O_2$ with glycerol, $C_3H_5(OH)_3$. An important example is glyceride $C_{17}H_{35}COOCH_3$ formed from the stearic acid.

Proteins are giant molecules that make up the solid constituents of animal tissues and plant cells. They are rich in carbon but contain substantial amounts of N, S and O.

Carbohydrates are based on sugars $C_n(H_2O)_n$ and their polymers (cellulose, starch, chitin). They are common in plant tissue.

Lignin is a polymer consisting of numerous aromatic rings. It is a major constituent in land plants and converts to coal through desoxygenation.

Abundances of Biomolecules

	Lipids*	Proteins	Carbohydrates	Lignin
Spruce Wood	4	1	66	29
Oak Leaves	5	6	52	37
Phytoplankton	11	23	66	
Zooplankton	18	60	22	
Invertebrates	10	70	20	
Marine Sediments*	1	40	47	

* Large variations possible

Phytoplankton typically is 10 times more abundant than zooplankton and 100-1000 times more abundant than fish.

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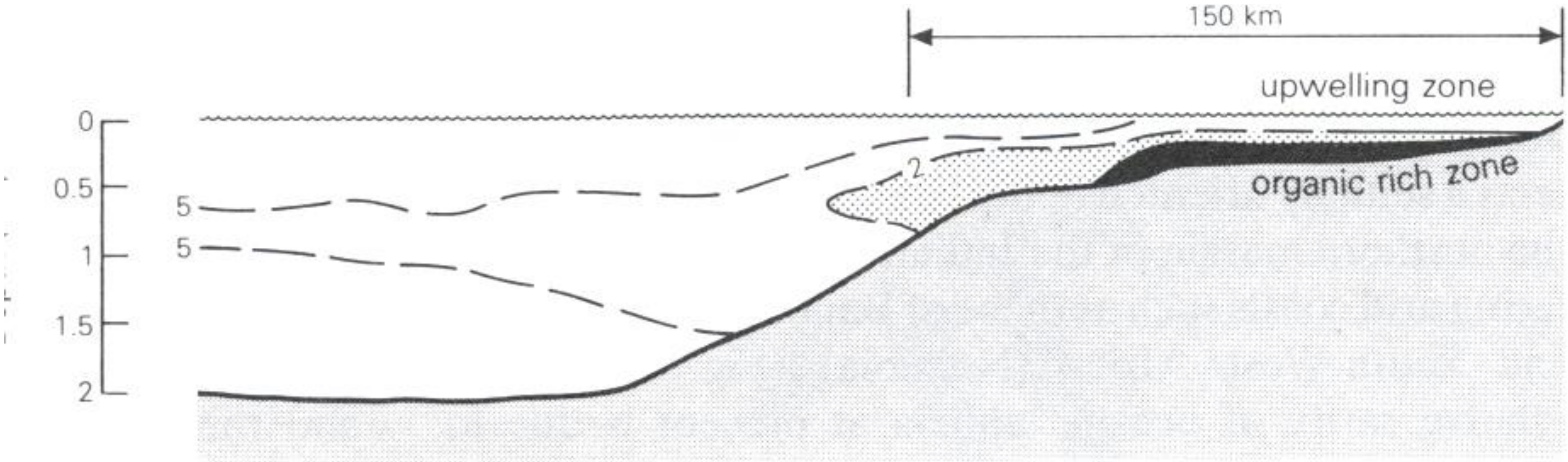
Average Composition of Biomolecules

	C	H	O	S	N
Lipids	76	12	12		
Proteins	53	7	22	1	17
Carbohydrates	44	6	50		
Lignin	63	5	31.6	0.1	0.3
Petroleum	83-87	10-14	0.1-1.5	0.5-6	0.1-1.5

In weight percentages
Notice: Lipids are closest to petroleum composition, but they are richer in oxygen and poorer in carbon.

The Organic Matter Engine



Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

This figure shows oxygen concentrations in a schematic cross-section from the ocean to the continental rise, shelf edge and shelf. The open ocean waters are generally rich in oxygen due to circulation and exchange with the atmosphere. Upwelling of nutrient-rich water leads to high organic productivity in the photic zone on the shelf, but lack of circulation and organic decay may produce anoxic bottom waters there.

Study Questions

What organic biomolecules did your breakfast contain today?

What is the principal difference between your metabolism and that of plants?

Why is the open ocean less favorable for phytoplankton growth than shelf areas?

What happens to the carbon cycle if all the ice caps melt?

Write down the basic chemical formulas for

- the formation of sugar through photosynthesis
- the burning of a simple lipid
- the transformation of carbonates at high temperatures

Preservation of Organic Matter

The biomolecules described before are reduced forms of carbon and hydrogen. Their preservation potential depends crucially on anoxic conditions, i.e. the absence of oxygen that could oxidize them.

Stratified basins that prevent vertical circulation and thus the transport of oxygen to greater depths provide excellent conditions for this. An example is the Black Sea, which is salinity-stratified, but many lakes are also anoxic in their deeper waters because of thermal stratification or abundance of nutrients and lack of circulation.

Preservation of Organic Matter

Access to air (oxygen) rapidly - at geological scales - oxidizes organic matter and converts it into CO_2 and H_2O.

The total carbon content in the Earth's crust is $9 \cdot 10^{19}$ kg (the hydro- and biosphere contain less than 10^{-5} of this). Over 80% of this is in carbonates. Organic carbon amounts to $1.2 \cdot 10^{19}$ kg and is distributed approximately as follows:

Dispersed in sedimentary rocks (~)	97.0 %
Petroleum in non-reservoir rocks	2.0 %
Coal and peat	0.13 %
Petroleum in reservoirs	0.01 %

This illustrates the low efficiency of the preservation process.

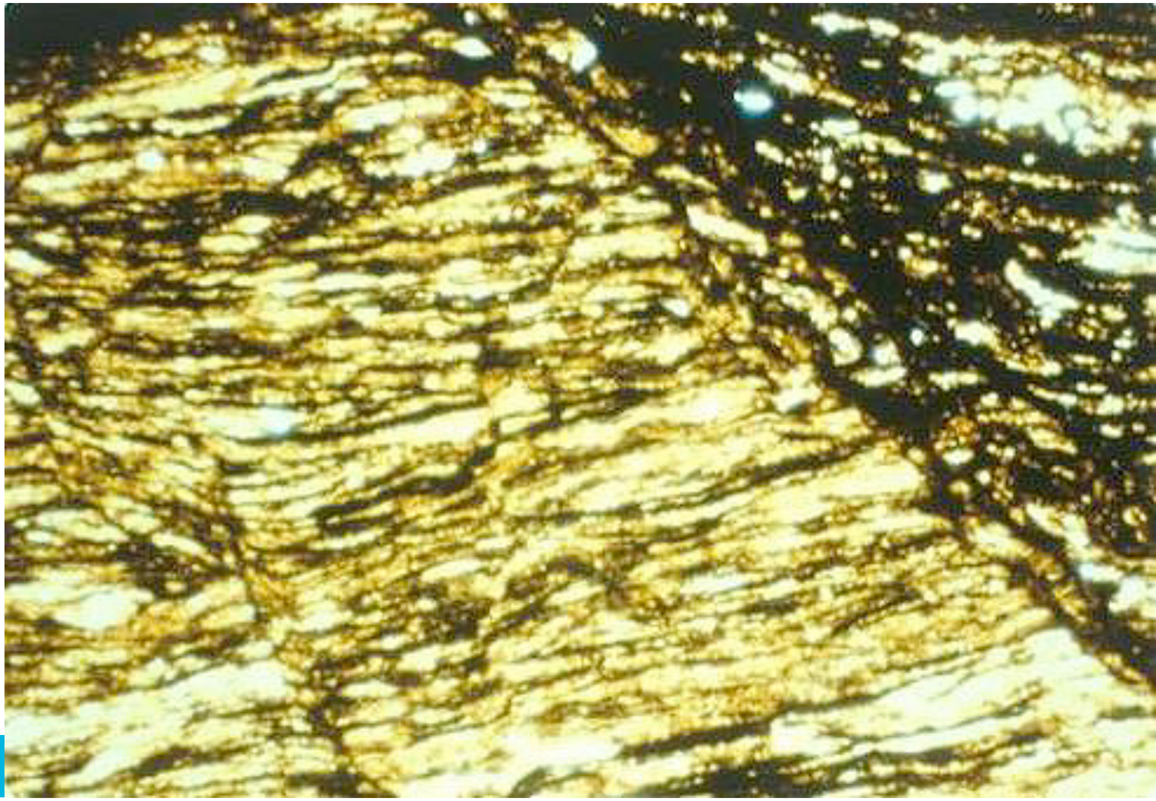
Total Organic Carbon (TOC)

If a rock contains significant amounts of organic carbon, it is a possible source rock for petroleum or gas. The TOC content is a measure of the source rock potential and is measured with total pyrolysis.
The table below shows how TOC (in weight percent) relates to the source rock quality.

TOC	Quality
0.0-0.5	poor
0.5-1.0	fair
1.0-2.0	good
2.0-4.0	very good
>4.0	excellent

Source Rocks

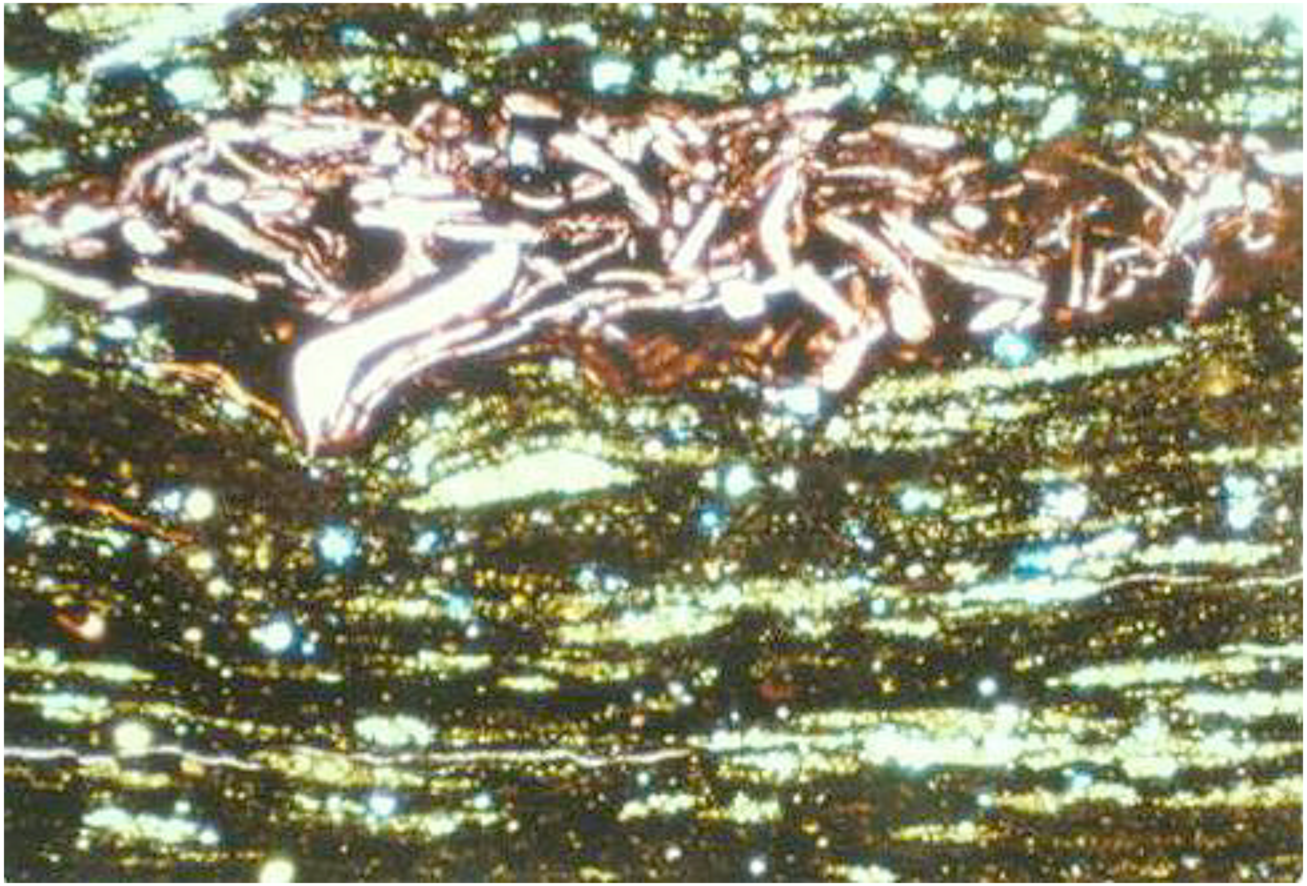
Generally, finer-grained sediments contain more organic matter than coarser-grained ones because of the restricted diffusion and thus the lower amount of oxygen that can get in contact with OM. TOC can reach 20% or more. Coals and oil shales are rich in OM but are called source rocks.



A fine-grained carbonate rock of Jurassic age containing abundant organic matter.

Well Saddam-8, central Iraq.

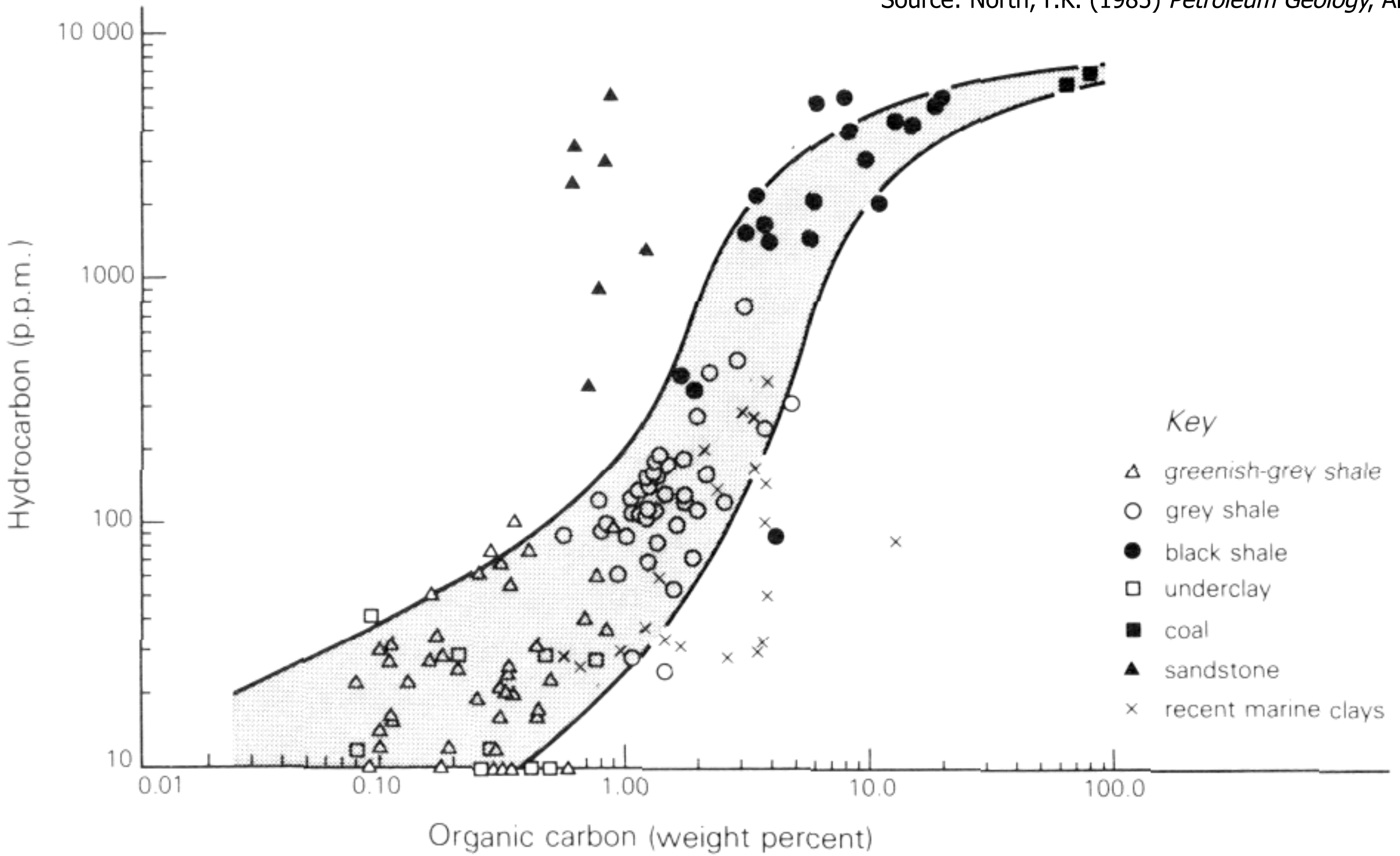
Source Rocks



Phosphatic remains of a vertebrate and organic matter in the same source rock as on the previous slide.

TOC and HC

Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin



The relationship shown on this graph is a major argument for the biogenic origin of fossil hydrocarbons

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TOC Types

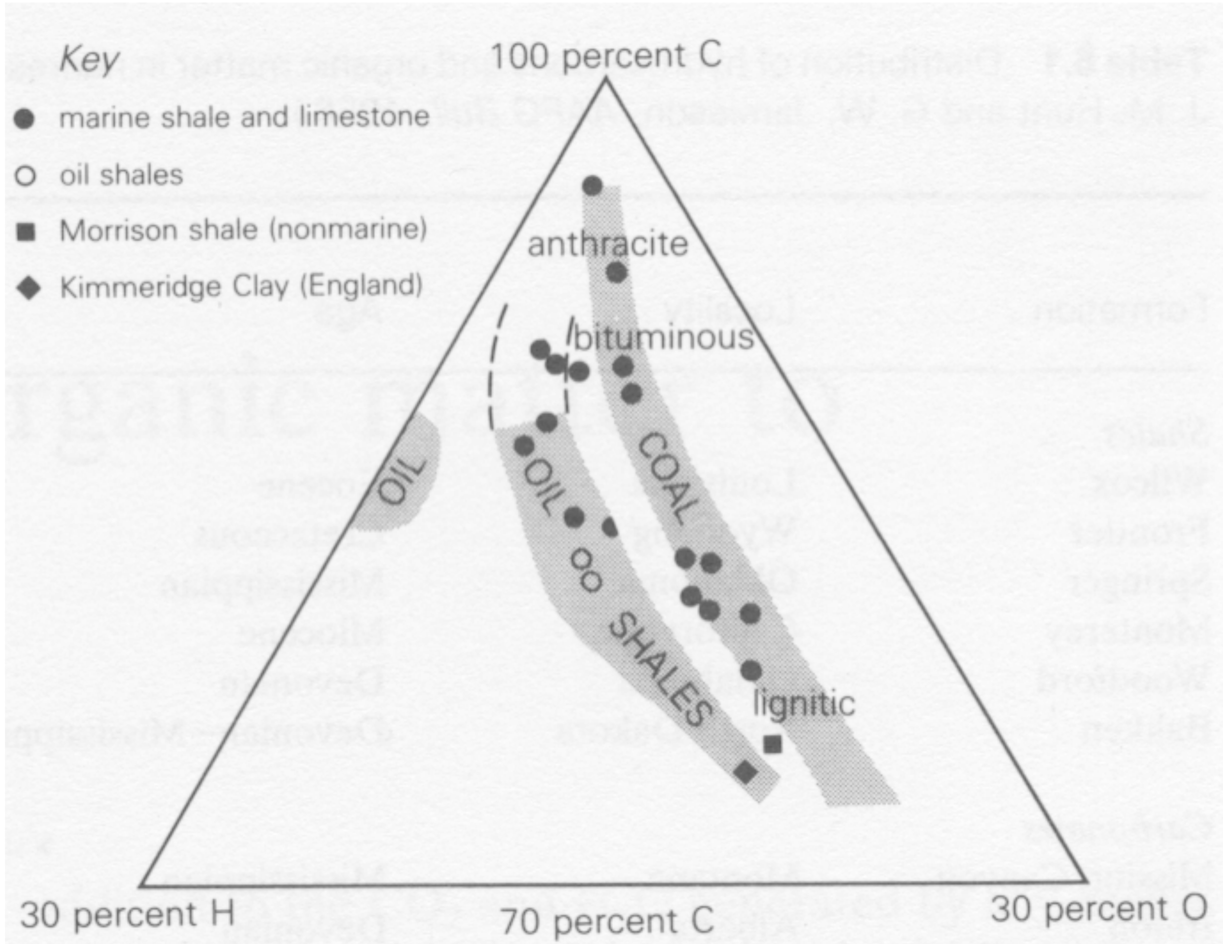
TOC in sedimentary rocks can be divided into two types:

- Bitumen, the fraction that is soluble in organic solvents such as chloroform
- Kerogen, (κεροοσ = wax) the insoluble, non-extractable residue that forms in the transformation from OM

Kerogen is an intermediate product formed during diagenesis and is the principal source of hydrocarbon generation. It is a complex mixture of high-weight organic molecules with the general composition of $(C_{12}H_{12}ON_{0.16})_x$

Composition of Kerogen

Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin



C, H and O of selected kerogens; notice scales

Conversion of OM to HC

The principal condition is that this conversion take place in an essentially oxygen-free environment from the very beginning of the process. Anaerobic bacteria may help extract sulfur to form H_2S and N, in addition to the earlier formation of CO_2 and H_2O. This explains the low sulfate content of many formation waters.

On burial, kerogen is first formed. This is then gradually cracked to form smaller HC, with formation of CO_2 and H_2O. At higher temperatures, methane is formed and HCs from C_{13} to C_{30}.

Consequently, the carbon content of kerogen increases with increasing temperatures. Simultaneously, fluid products high in hydrogen are formed and oxygen is eliminated.

Dehydrogenization and Carbonization

The dehydrogenation and carbonization of organic source material can be illustrated with the H:C ratio during the formation of coals:

Source material	H:C ratio
Wood	1.5
Peat	1.3
Lignite	1.0
Bit. coal	0.8
Anthracite	0.3-0.0

Average, in weight %

Deoxygenization and Carbonization

The deoxygenation and carbonization of the source material is illustrated with the formation of petroleum:

Source material	O:C ratio
Organisms	0.35-0.6
Pyrobitumen (kerogen)	0.1-0.2
Petroleum (average)	0.004

Average, in weight %

Source Rock Quality

The primary factor determining source rock quality is the level of TOC.

Additionally, the quality of the source rock is better for higher H:C ratios before thermal maturation.

As thermal maturation proceeds and HCs are formed, the kerogen will continuously deteriorate as a source for HC formation.

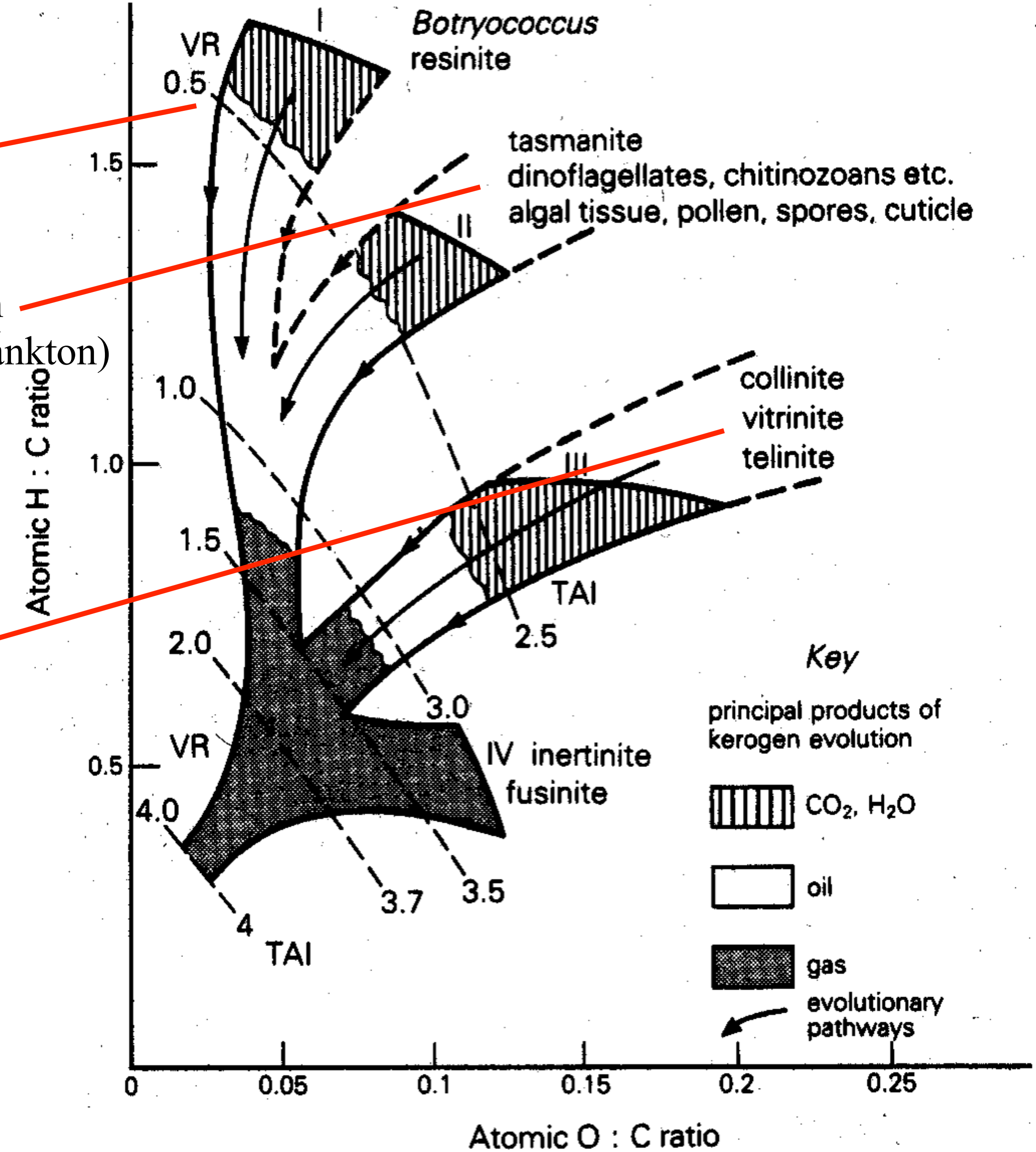
Kerogen Types & Maturation

Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

Sapropelic kerogen (algae)

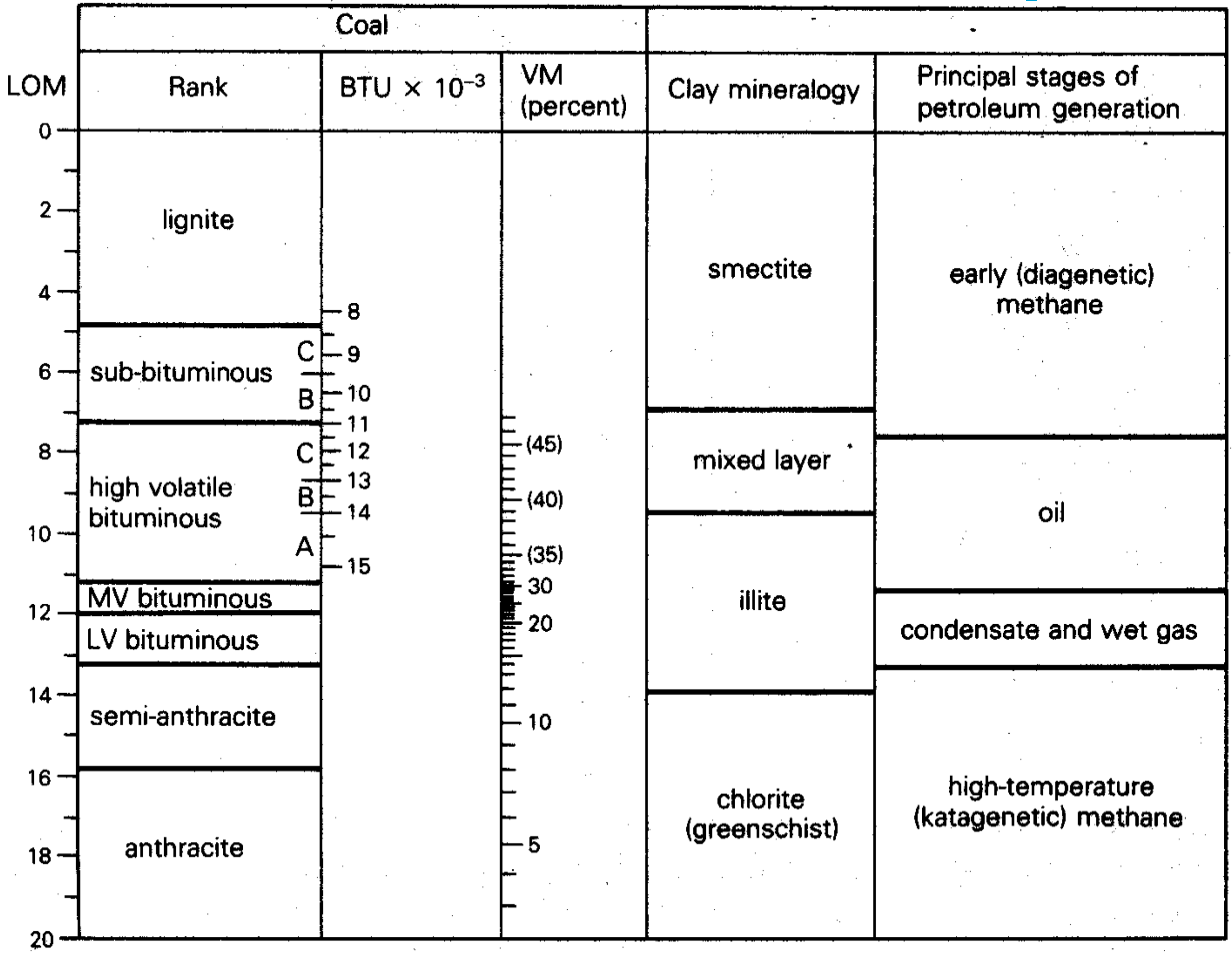
Lipid-rich kerogen (phyto- and zooplankton)

Humic kerogen (land plants)



"Van Krevelen diagram"
TAI, VR: Maturation indicators

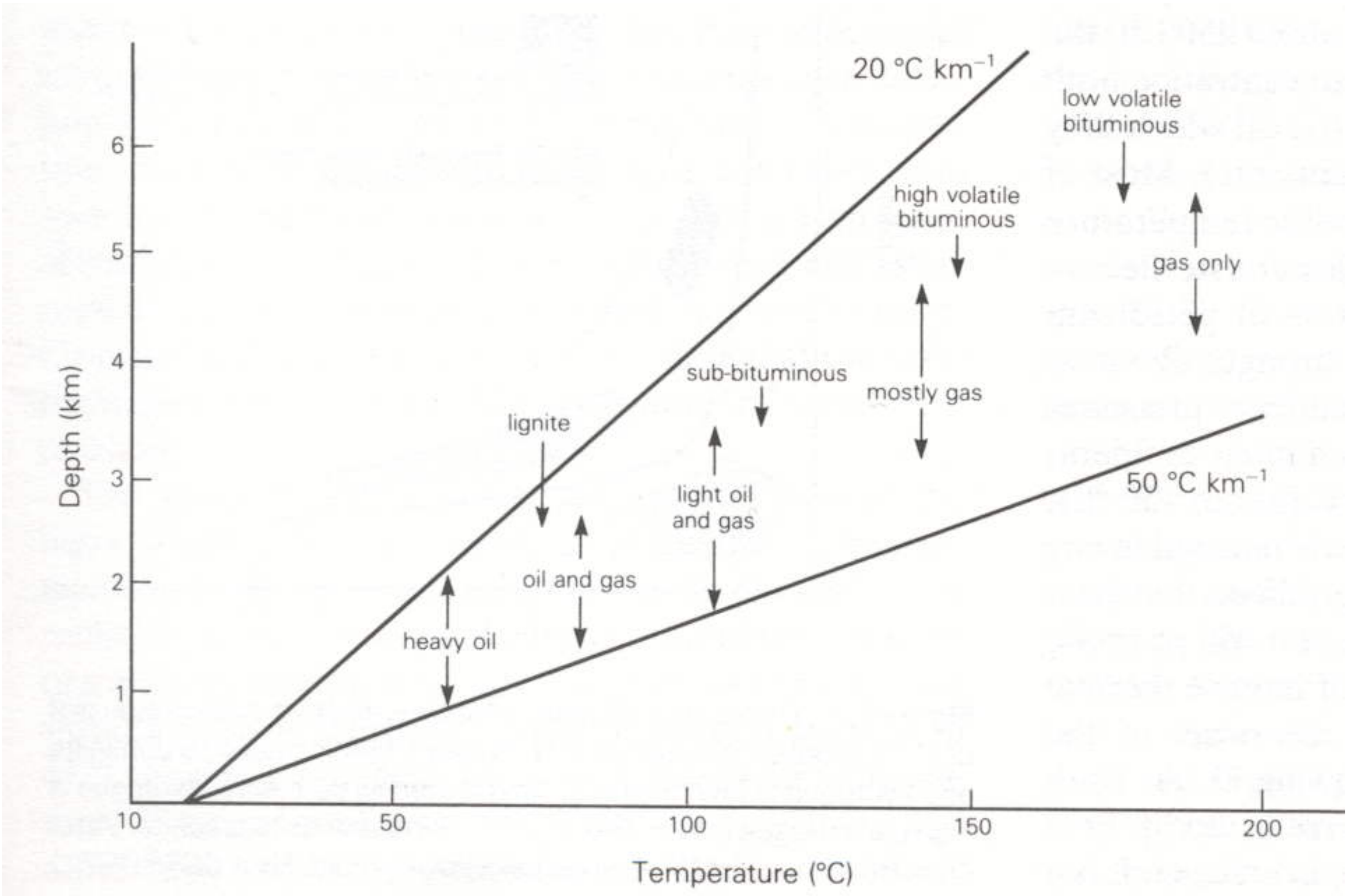
Transformations with Depth



Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

LOM = level of organic metamorphism; BTU = British Thermal Unit; VM = volatile matter

Rate of Maturation



Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

Temperature is the single most important factor in thermal maturation.

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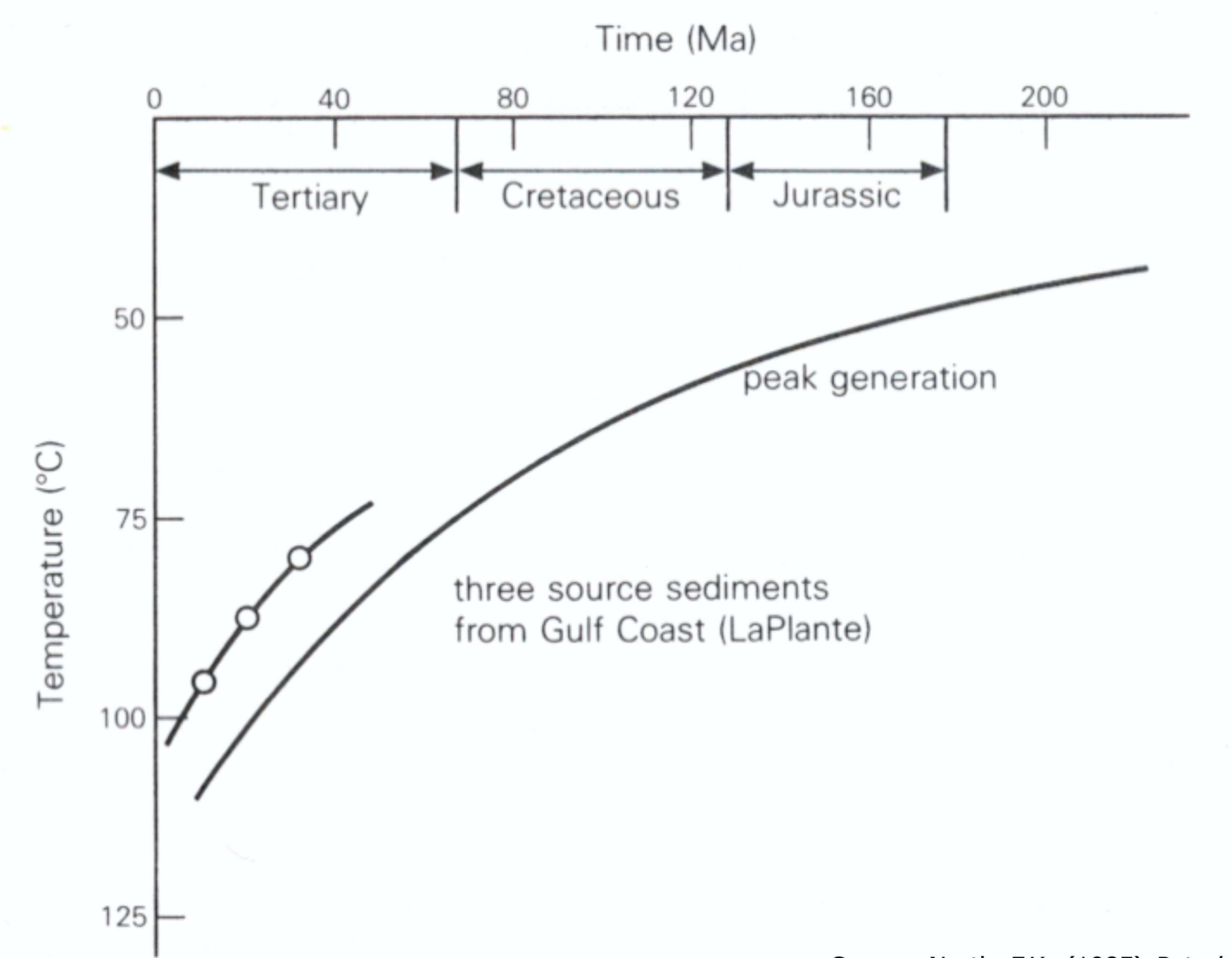
Rate of Maturation ctd.



Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

Time is the second most important factor in thermal maturation

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Purposes of Maturation Indicators

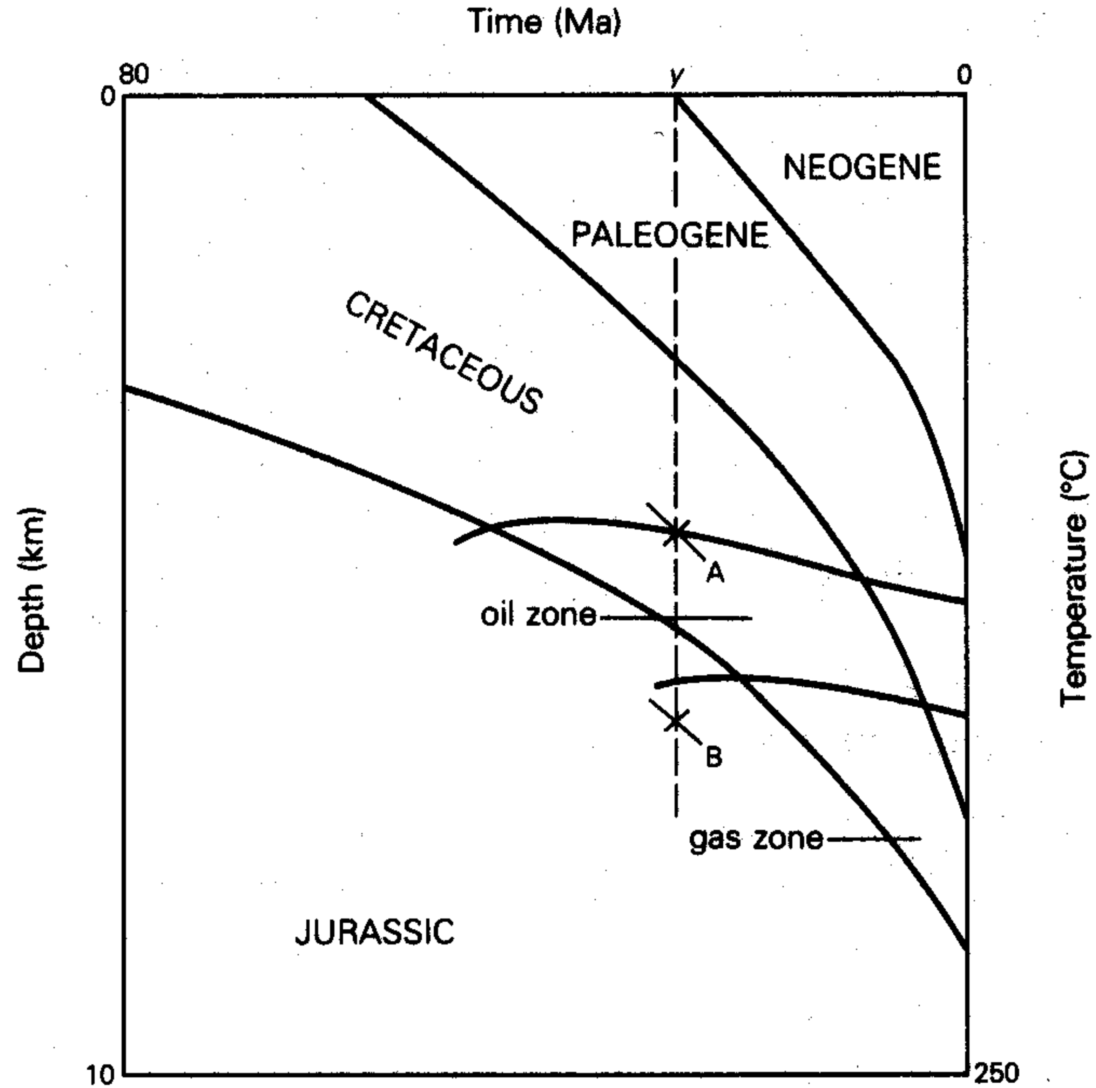
- To recognize and evaluate potential source rocks for oil and gas by measuring their contents in organic carbon and their thermal maturities
- To correlate oil types with probable source beds through their geochemical characteristics and the optical properties of kerogen in the source beds
- To determine the time of hydrocarbon generation, migration and accumulation
- To estimate the volumes of hydrocarbons generated and thus to assess possible reserves and losses of hydrocarbons in the system.

Lopatin's TTI Index

Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

V. Lopatin (1971) recognized the dependence of thermal maturation from temperature AND time. He developed a method wherein the temperatures are weighted with the residence time the rock spent at this temperature. Periods of erosion and uplift are also taken into account. This so-called time-temperature index TTI is still in use, although in variations.

The plot on the right shows a simple depiction of it. Rock of age A enters the oil-generating window at time y, while the older rock B has been at that time already in the gas-generating window and will stay there until the present.



At what time will rock of age A reach the gas window?

Other Maturation Indicators

Several approaches to quantify the degree of maturation have been proposed aside from the TTI. Most of them are sensitive to temperature and time.

- Vitrinite Reflectance (R_o) measures the reflectance of vitrinite (see Kerogen maturation diagram) in oil, expressed as a percentage. It correlates with fixed carbon and ranges between 0.5 and 1.3 for the oil window. Laborious but widely used.
- Thermal Alteration Index (TAI) measures the color of finely dispersed organic matter on a scale from 1 (pale yellow) to 5 (black). This index has a poor sensitivity within the oil window (TAI around 2.5 to 3.0) and is not generally used.
- Level of Organic Maturation (LOM) is based on coal ranks and is adjusted to give a linear scale.

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Correlation of TTI, R_o, and TAI

Stage	TTI	R_o	TAI
onset of oil generation	15	0.65	2.65
peak oil generation	75	1.00	2.9
end of oil generation	160	1.30	3.2
upper TTI limit for occurrence of oil with API gravity <40°	~500	1.75	3.6
upper TTI limit for occurrence of oil with API gravity <50°	~1 000	2.0	3.7
upper TTI limit for occurrence of wet gas	~1 500	2.2	3.75
last known occurrence of dry gas	65 000	4.8	>4.0
liquid sulfur in Lone Star Baden 1 (below dry gas limit)	972 000	>5.0	>4.0

Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

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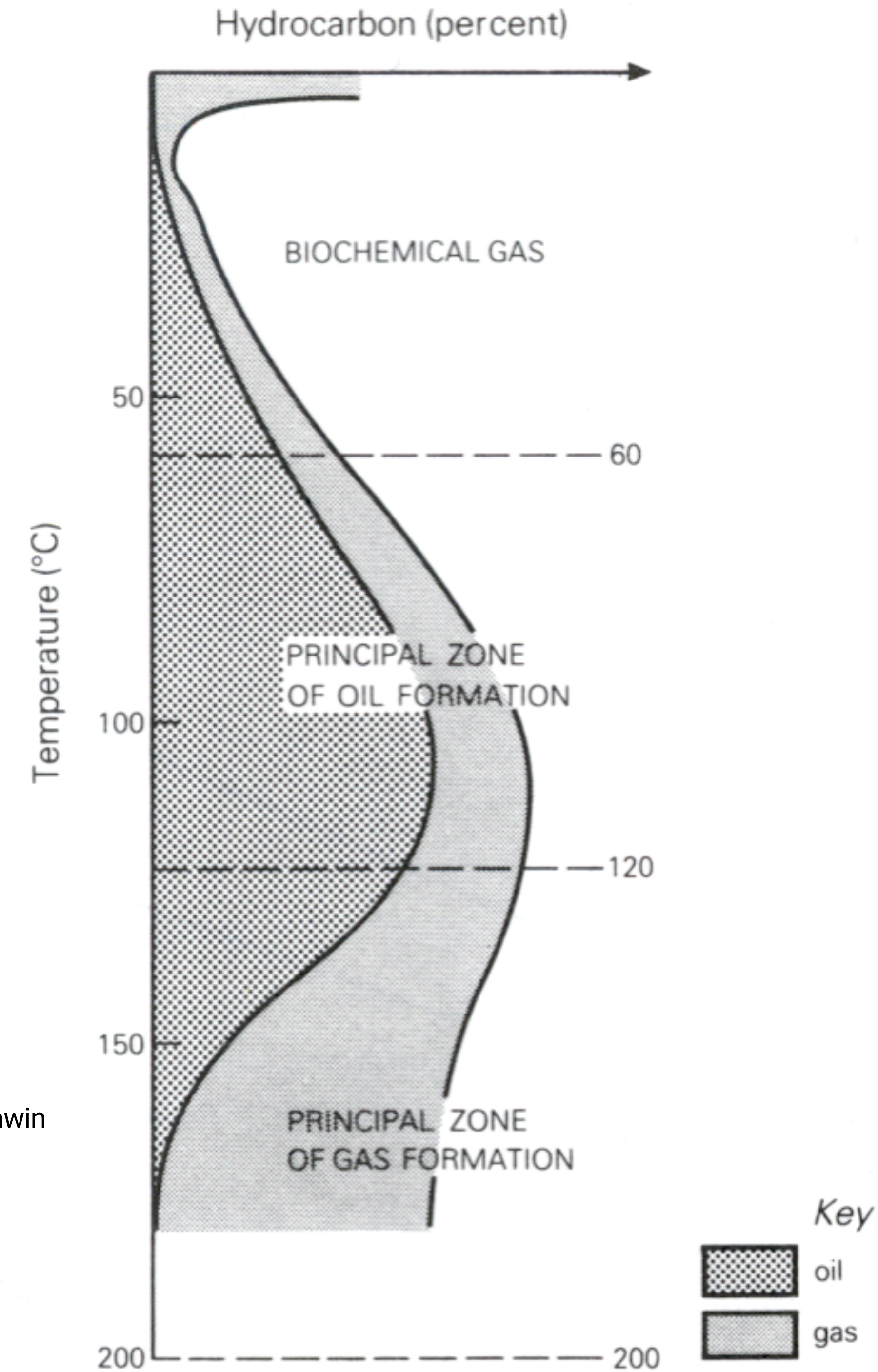
The Oil and Gas Windows

A similar slide as before. It shows clearly at what temperatures oil generation peaks.

Gas generation diminishes above ~180°C



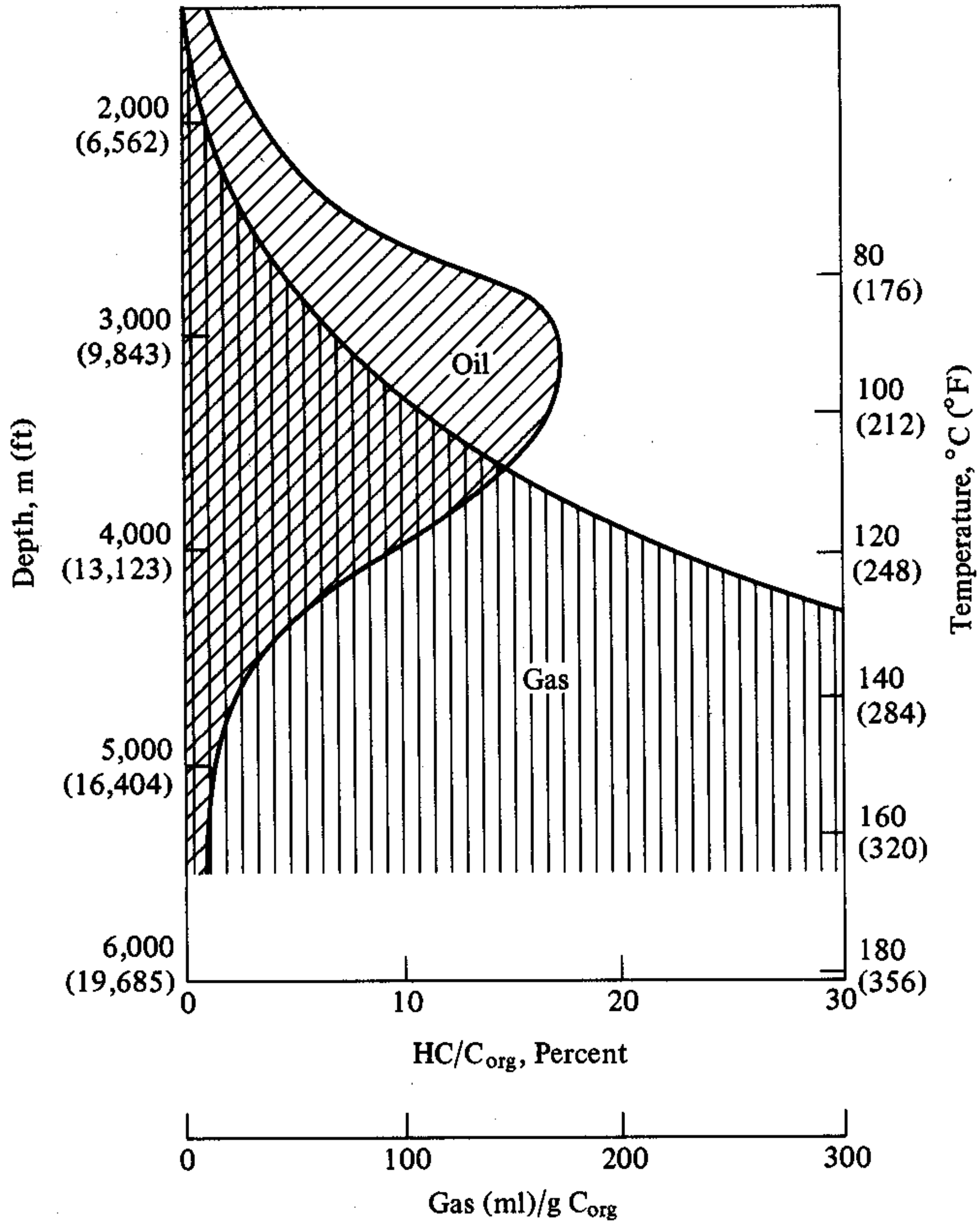
Source: North, F.K. (1985) *Petroleum Geology*, Allen & Unwin

Field Example 1

This example from the Aquitaine Basin in France shows the development of oil and gas with depth, expressed as their volumes divided by organic carbon.

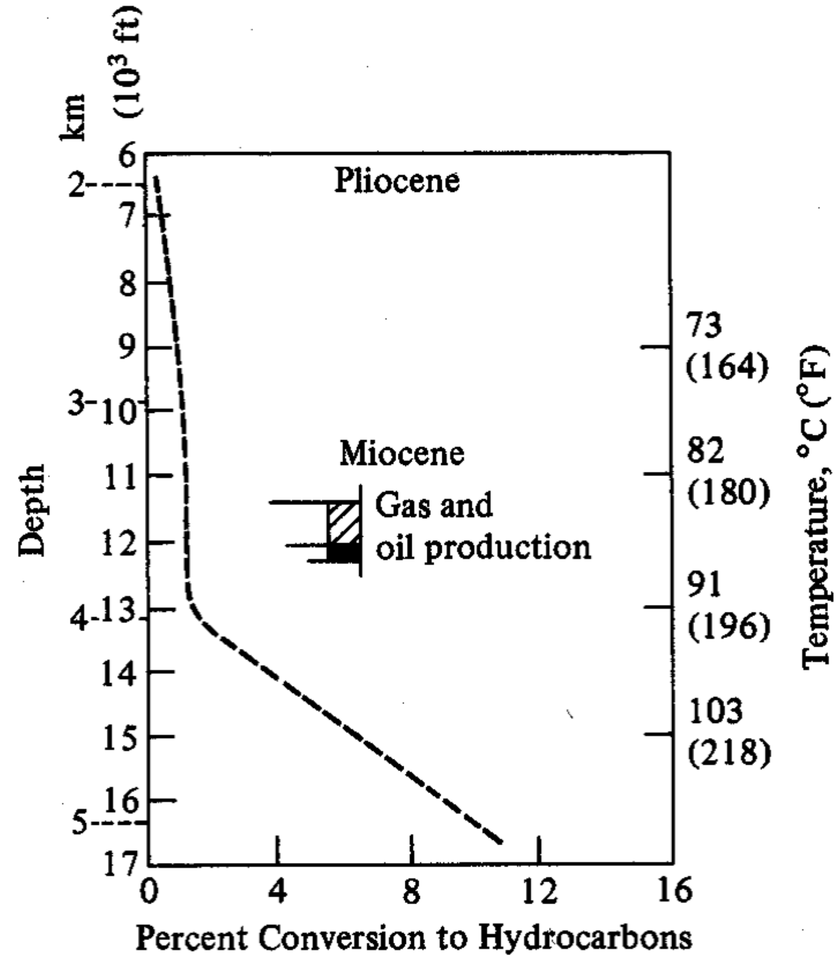
Oil peaks at 90°C, gas at >140°C.

Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology,* 2nd edition. W.H. Freeman & Co



Field Example 2

Generation of hydrocarbons from kerogen with depth in the West Delta area, Gulf Coast (USA). Notice the low geothermal gradient and the relatively lower onset of the HC generation peak.



Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

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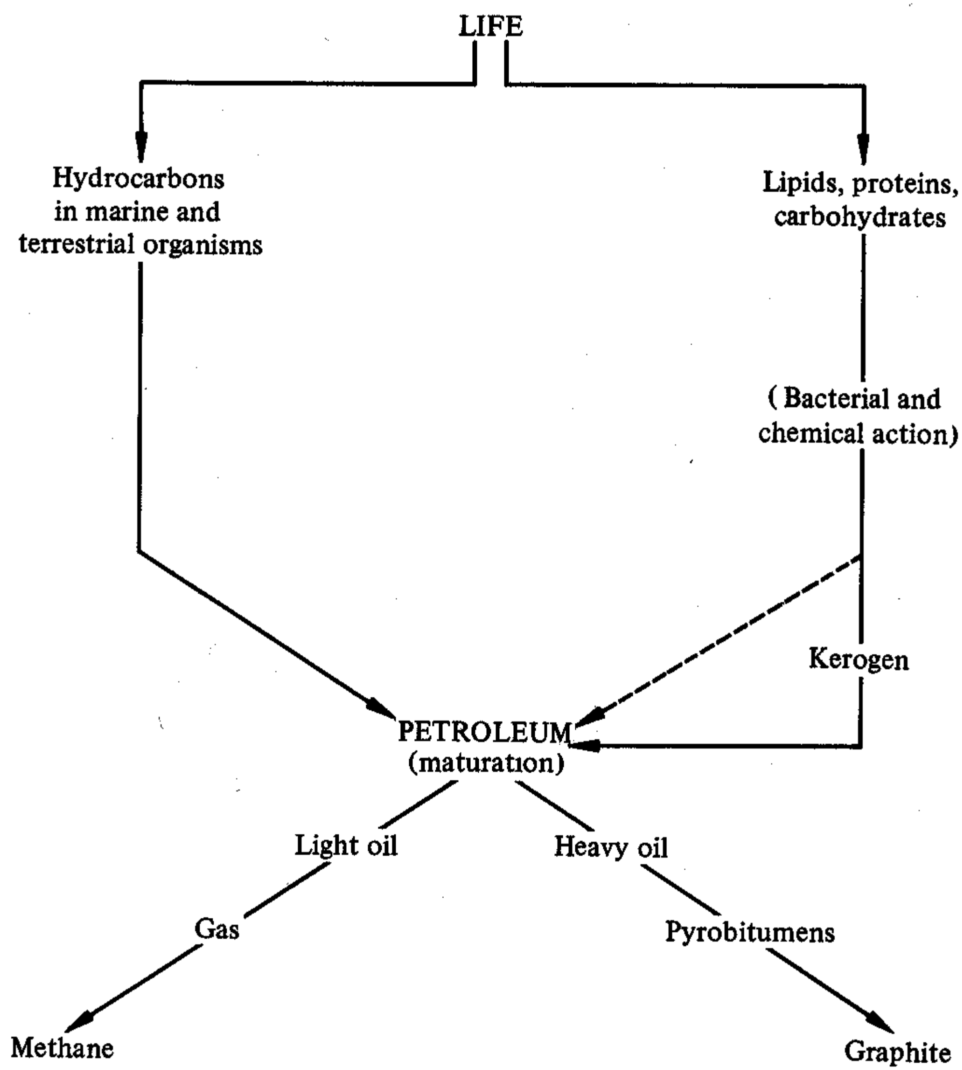
Oil Source Rock Criteria

The criteria for a sedimentary rock to be an effective oil source can be quantitatively described. They are as follows:

- The TOC should be 0.4% or more
- Elemental C should be between 75% and 90% (in weight)
- The ratio of bitumen to TOC should exceed 0.05
- The kerogen type should be I or II (from lipids)
- Vitrinite reflectance should be between 0.6 and 1.3%

Summary: Origin and Maturation

This diagram shows the development of biomolecules into petroleum and, with further maturation, into gas (left branch at bottom) which causes the residues to become increasingly more carbon-rich (right branch at bottom)



Source: Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, 2nd edition. W.H. Freeman & Co

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