

The Dual Role of Heavy Compounds in Conventional and Unconventional Petroleum Systems*

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Abstract

Non-hydrocarbon heavy compounds, particularly asphaltenes, can be problematic in conventional reservoirs. They can obstruct the porosity and the permeability in the near-wellbore, as well as clog production tubing or above-ground flow-lines and facilities. Prevention or remediation of asphaltene deposition adds huge costs to oilfield development. Asphaltenes are also found in source rock. They are a part of the naturally occurring continuum of compounds that result as organic matter is transformed into oil and gas. Interestingly, these compounds of high molecular weights are kerogen moieties and can extend the amount of time that a source rock actively generates hydrocarbons. Also, there is a compelling correlation between source rock age and the amount of asphaltene created. The occurrence of asphaltene is related to the kerogen type and shows an orderly variation through geological time. This fact can be used in our screening process as we select which source rocks to target for unconventional drilling and production. While referring to some well known U.S. unconventional oil /shale gas systems, discussion is presented of the role of heavy compounds at the oil window and their importance in the later stage of hydrocarbon generation for an unconventional play.

Selected References

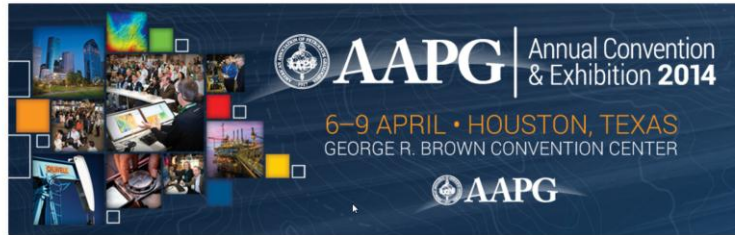
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The Dual Role of Heavy Compounds in Conventional and Unconventional Petroleum Systems



A. Chaouche (Anadarko Petroleum corporation)

Objectives

This presentation is about the fundamental role of the heavy fractions (asphaltenes) in unconventional petroleum systems:

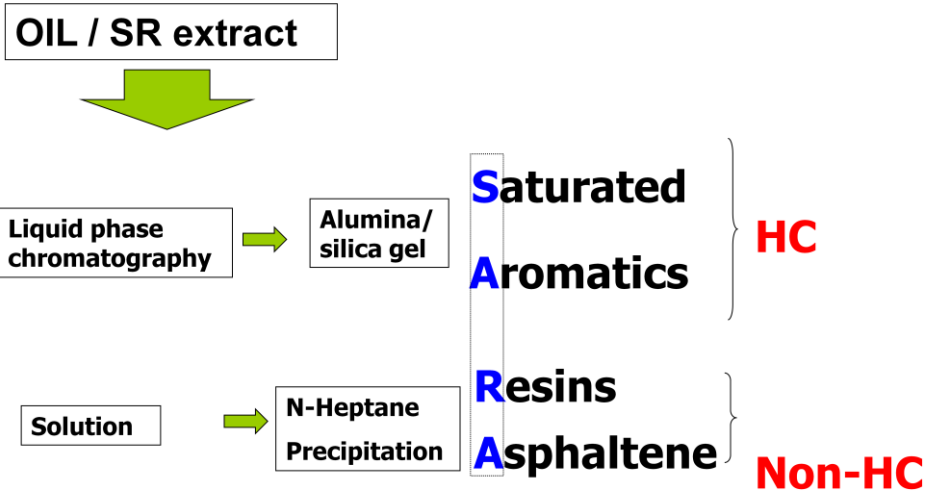
Asphaltenes are indeed problematic for oilfield development but hold huge potential for unconventional resources!

The amount of oil and gas released through their thermal breakdown should be factored into decisions when it comes to unconventional play selection: shale oil versus shale gas?

Their content has steadily increased within the heavy fraction of oils over geological time and shows an orderly variation with organic input.

HC and non-HC fractions in oil and source rock extracts

Conventional separation protocol



Presenter's notes: Stock tank oil and source-rock extracts are commonly analyzed for their hydrocarbon fractions: Saturated /Aromatics and non-hydrocarbons fractions (resins/ asphaltenes) following this analytical protocol.

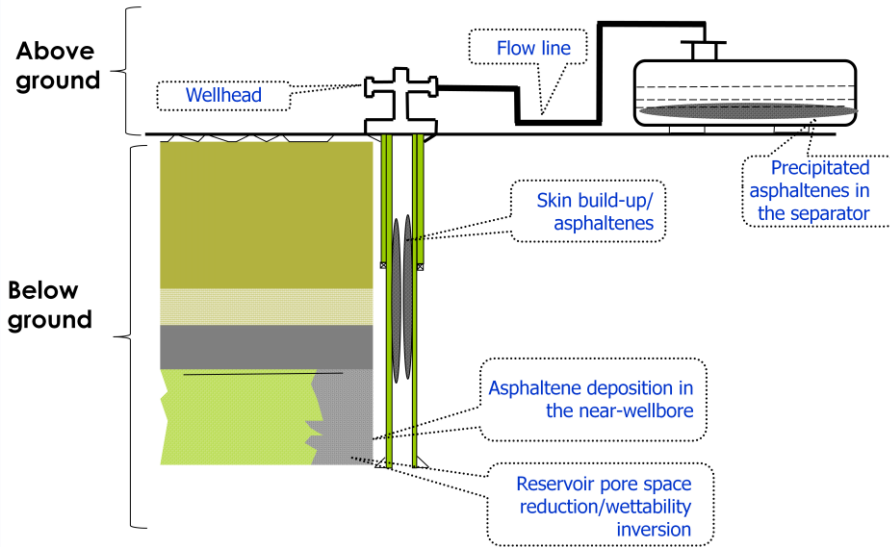
Bitumen



- >The word bitumen encompasses NSO's , Resins, Asphaltenes, Tar
- > The Asphaltene/Resin fractions present in oil have direct connection to bitumen and to the kerogen in the source rock
- >Bitumen is considered as an intermediate “kerogen product” between kerogen and oil
 - > Bitumen contains essentially C and H atoms + NSO products, and organo-metallic compounds (Ni, V, Mo, As, Mg, Fe...)
 - >Oil is derived largely from bitumen (but not exclusively)

Presenter's notes: The word „bitumen” encompasses wide spectra of heavy products derived from the kerogen cracking. Present in suspension in oil as micelles or aggregates and solids products in source rocks, reservoir rock, or carrier beds.

Known for their negative impact in field development ...



Presenter's notes: This illustrates the asphaltene-drop out in the workflow chart; engineers have to plan ahead in order to avoid their production impedance.

Even for their inconvenience!



... but what do they hide?

Organic matter conversion protocol

Organic matter (solubilization/polymerization /polycondensation)

Organic Matter → **Kerogen** *(large chemical aggregates in sedimentary organic matter that is insoluble in solvents)*

Primary
Cracking

Kerogen → **Bitumen** + **Oil** + **Gas** + Refractory kerogen + CO₂
(Solvent extractable organic matter from sediments)

... **Bitumen** → **Oil** + **GAS** + CO₂

Secondary
Cracking

... **Oil** → pyrobitumen + **gas** + CO₂
(non-soluble in organic solvent)

... R. kerogen → **gas** + CO₂ + coke

... Pyrobitumen → **gas** + CO₂?
 ... graphite

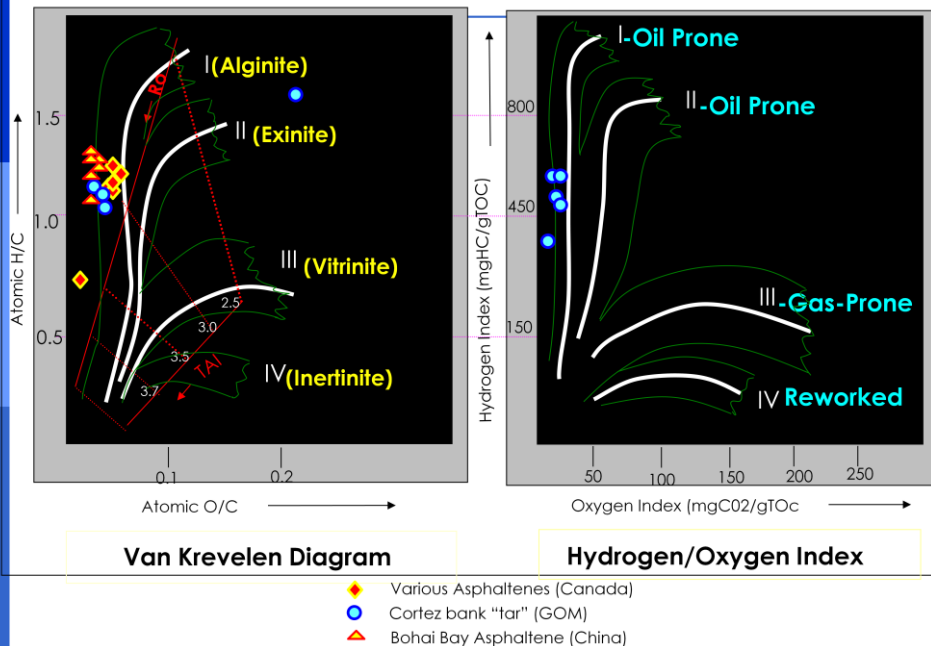
Diagenesis

Catagenesis

Metagenesis

Presenter's notes: Note the CO₂ generation from the time organic-matter sediments to the time it reaches the metamorphism. Its role in the reservoir cementation is discussed below.

Asphaltene / Tar as Kerogen-type behavior

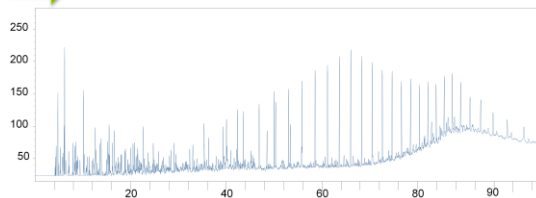


Presenter's notes: Cross-plots of the H/C and O/C ratios in the Van Krevelen diagram and the H/O index diagram of various asphaltenes, tar, and bitumen from three widely separated areas, showing these products as kerogen behaviors.

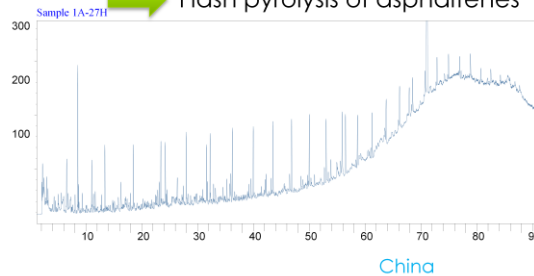
Asphaltene pyrolysis-GC



GC trace of produced oil

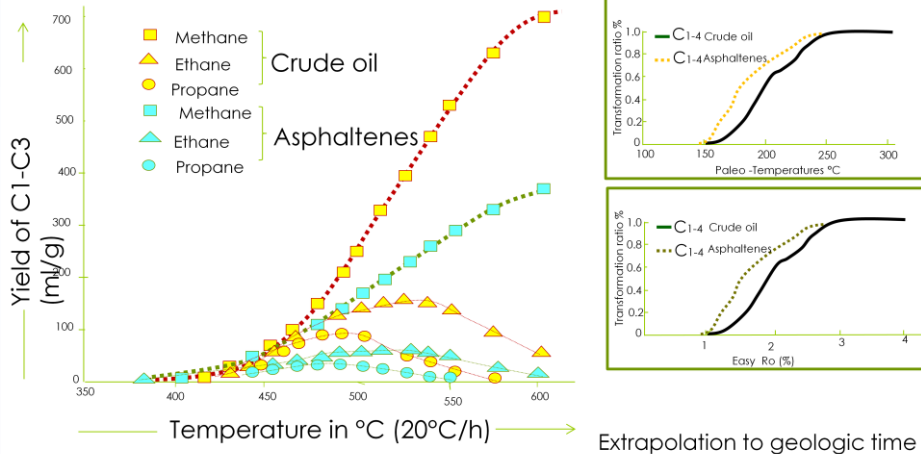


Flash pyrolysis of asphaltenes



Presenter's notes: This is a pyrogram GC trace of asphaltenes, showing n-alkanes distribution that mimic the GC trace of produced oil.

Oil to gas versus asphaltenes to gas cracking

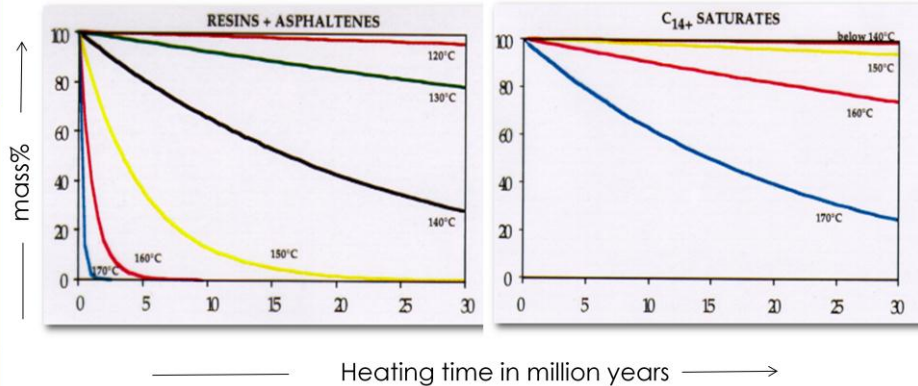


Oil cracking to gas generates 50% more gas than asphaltene cracking to gas

Modified from Tongshan Wang et al., 2009

Presenter's notes: This lab experiment is critical in regard to shale oil and shale gas plays and HC expectations. Indeed, it shows that the cracking to gas of an oil generates more gas than the cracking of bitumen to gas. It also shows that cracking of bitumen requires less heating than oil. This is critical for play selection as we will see later in the presentation. Meso-Cenozoic SR's contain more asphaltene (non HC) than Paleozoic SR's and therefore may ultimately generate earlier and at shallower depths than Paleozoic SR's. Paleozoic SR's, however, have more oil (HC) and therefore will generate gas at higher temperatures and greater depth.

Cracking of hydrocarbon fractions



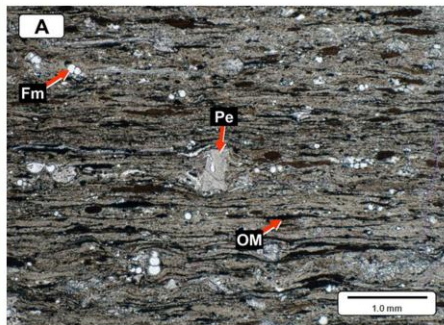
Non hydrocarbons (resins & asphaltenes) transform faster and earlier than hydrocarbons (saturated and aromatics) at higher heating rate

Behar et al., 1996

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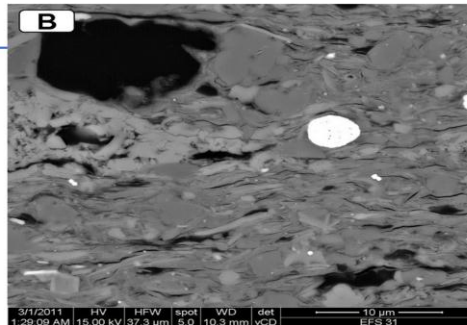
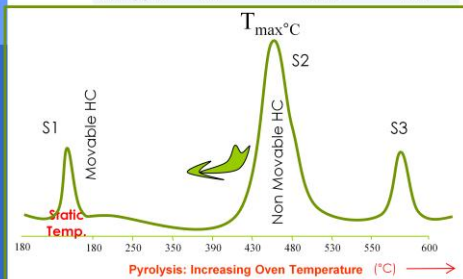
Presenter's notes: Note the difference in heating rate between non-hydrocarbon fractions (resins + asphaltenes) versus hydrocarbon (saturates).

Bitumen in the source rock – typical pyrograms



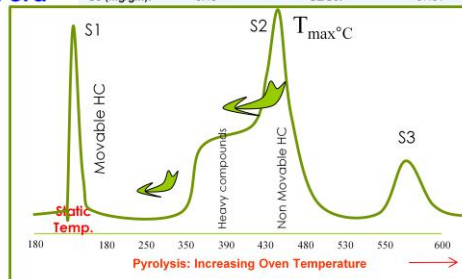
Utica

TOC (wt %):	2.59	R _o :	0.6
S1 (mg/gm):	0.87	S2 (mg/gm):	3.63
S3 (mg/gm):	0.38	S2/S3:	9.55



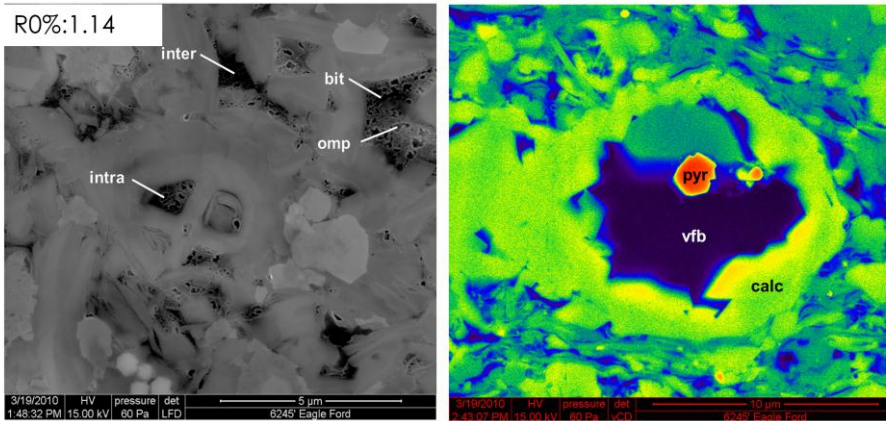
Eagle Ford

TOC (wt %):	4.79	R _o :	-
S1 (mg/gm):	3.53	S2 (mg/gm):	17.30
S3 (mg/gm):	0.46	S2/S3:	37.61



Presenter's notes: These are typical pyrograms of Rock-Eval pyrolysis from Utica (Paleozoic) and Eagle Ford (Mesozoic), the first one with a single peak S2; the second with hump preceding the Peak S2, expressing the significance of the heavy compounds remaining in the source rock.

Eagle Ford - Bitumen phase diagenesis



Camp et al., 2013(AAPG Mem 102)

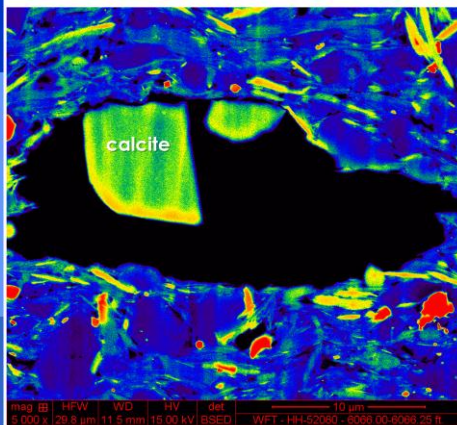
---> Conversion of bitumen to pyrobitumen with liberation of condensate /gas/ CO_2

---> CO_2 combines with Ca^{++} liberated by the albitization of plagioclase forming authigenic calcite.

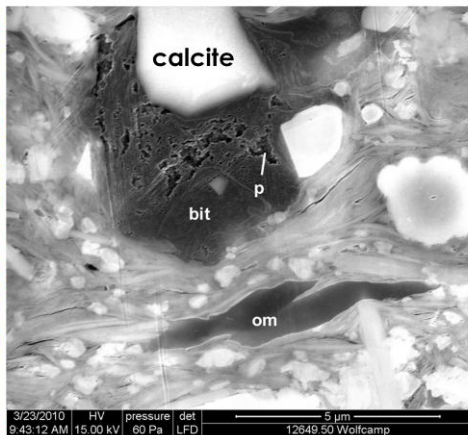
13

Presenter's notes: An electronic microscopy of what is becoming "kerogen porosity" reveals void full of bitumen surrounded by calcite (cement) with an initiation of pyrobitumen in the middle of the cavity. Indeed the conversion of bitumen to pyrobitumen generates condensate, gas, and CO_2 . The CO_2 in absence of water combines with calcium to form authigenic calcite.

Typical calcite growth within void filled by bitumen



Pt Pleasant



Wolfcamp 1.4 %Ro

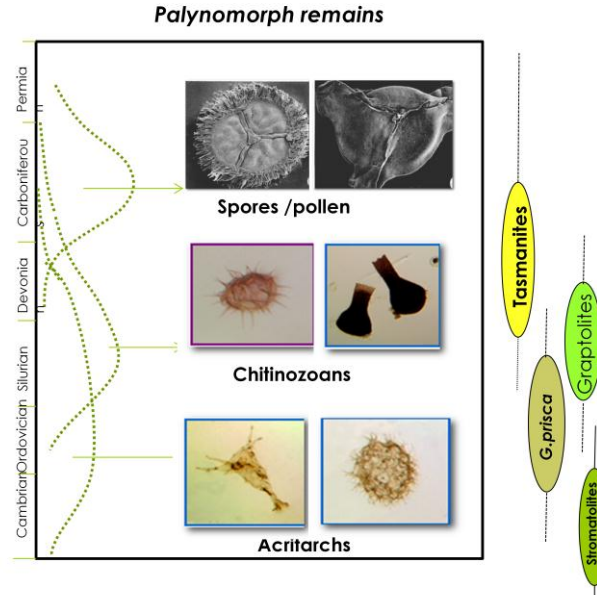
W. Camp 2014., personal communication

Presenter's notes: The calcite growth will ultimately fill the pore space and occlude the reservoir properties.

Eagle Ford versus Utica shale or Cretaceous versus Ordovician SR

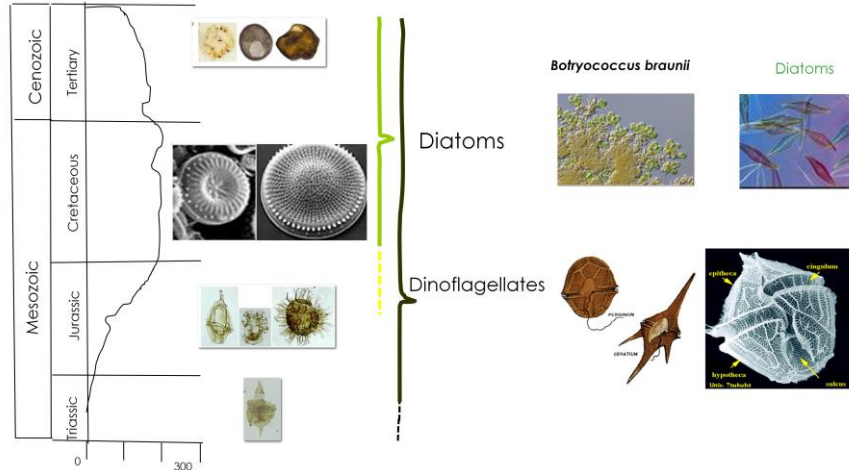
- ❑ The bitumen content of the Cretaceous Eagle Ford "B" is higher than in the Ordovician Utica shale "A". As consequence
- ❑ Condensate generation occurs in the Eagle Ford through bitumen cracking at an early stage followed by gas generation
- ❑ Condensate generation is undissociated from oil in Ordovician Utica shale and significant volume of gas is produced compared to Eagle Ford shale by oil cracking to gas at late maturation stage
- ❑ Eagle Ford and Utica are both marine-deposited shales but at different geological times. Does the primitive organic input of Ordovician versus the more evolved Cretaceous control their variance in bitumen content?

Paleozoic Structured Kerogen



Presenter's notes: Biological markers derived from oil and rock extracts support certain palynological assemblages and their preponderance at given times during the Paleozoic. Acritarchs, chitinozoans, spores, and pollens dominated the Paleozoic palynomorph assemblages. Other representative types include stromatolites, algae (*G. prisca*), graptolites, and Tasmanite cysts that have clear and distinctive markers within oil fractions (e.g., odd/even alkanes) and biomarkers.

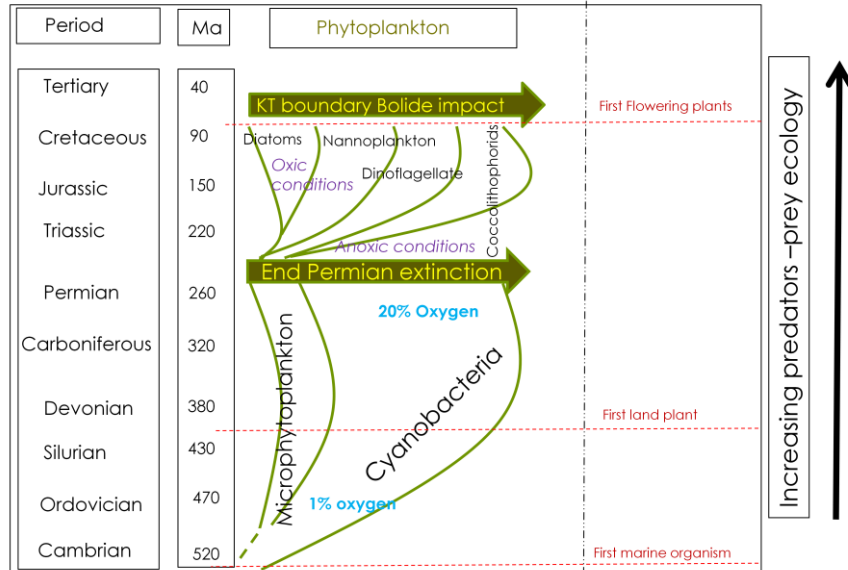
Mesozoic & Cenozoic Structured Kerogen



Modified (after MacRae et al., 1996)

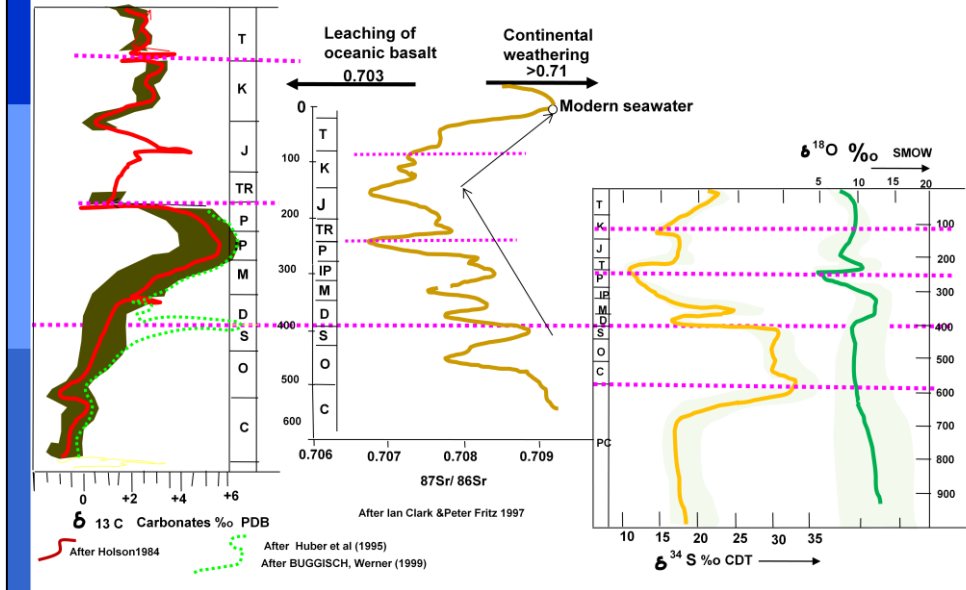
Presenter's notes: Diatoms and dinoflagellates are typical of Meso-Cenozoic floras and faunas and have well represented biomarkers (molecular fossils) in oil and rock extracts (Dinosteranes, Botryococcane, etc.). The flowering plants in the Tertiary also have distinctive biomarkers, such as Oleanane and Lupane, etc.

The fundamental role of the cyanobacteria and the phytoplankton in the organic matter input



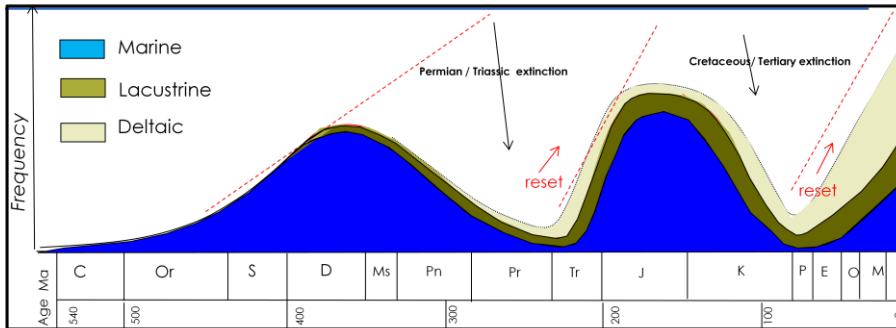
Presenter's notes: The emergence of cyanobacteria and the evolution of the photosystem (which fixes CO_2 and produces O_2) was the most significant biochemical event after the origin of life. The gradual accumulation of oxygen in the ocean and atmosphere ultimately made Earth hospitable for aerobic organisms, including those now reading this! Photosynthesis involving the chlorophyll of land plants significantly increased oxygen in the atmosphere and increased the inputs of organic matter in sedimentary basins. The biodiversity increased, of course, the predators-prey ecology.

In the rock record, isotopes are shifted for many chemical elements over geological time.

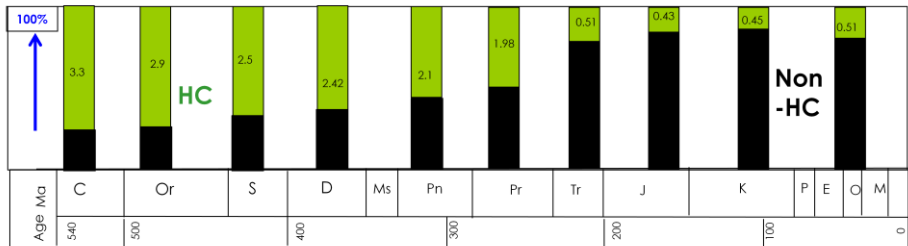


Presenter's notes: If we look back at the rock record, it is clear that multiple isotope shifts expressed in Oxygen, Sulfur, Strontium and Carbon occurred over geological time, reflecting catastrophic events that changed the environment and the organic content. The Permian /Triassic and the Cretaceous/ Tertiary are the most dramatic events with subsequent near-total extinction of certain groups of living organisms.

Estimated frequency of organic matter type over geological time



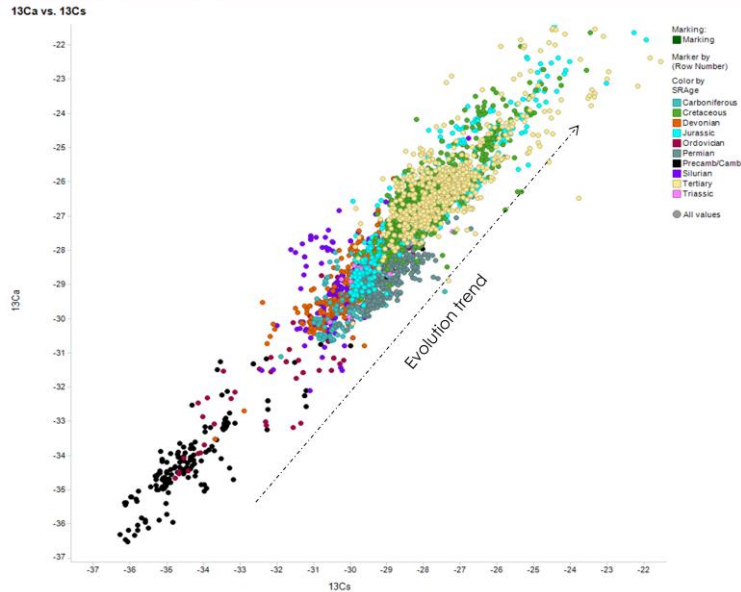
Rock extract over geological time at the oil window $(\text{Sat} + \text{Aro}) / (\text{NSO} + \text{Asph})$



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Presenter's notes: Soluble organic matter of source rock around the world (460 samples) shows a steady increase in the heavy compounds during Paleozoic with a significant change during the Meso /Cenozoic, mainly induced by evolving organic input over geological time.

Stable carbon isotope of Sat/Aro fractions of oil over geologic time



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Presenter's notes: The isotope data from HC fractions of oils suggest a continuum of organic evolution even for the dramatic P/T or K/T extinctions where Sulfur, Strontium, and Carbon isotopes derived from rock records reflect catastrophic events; it seems through the organic record, reset of the clock with any apparent break has been diluted in the overall evolution trend.

Paleo life on earth

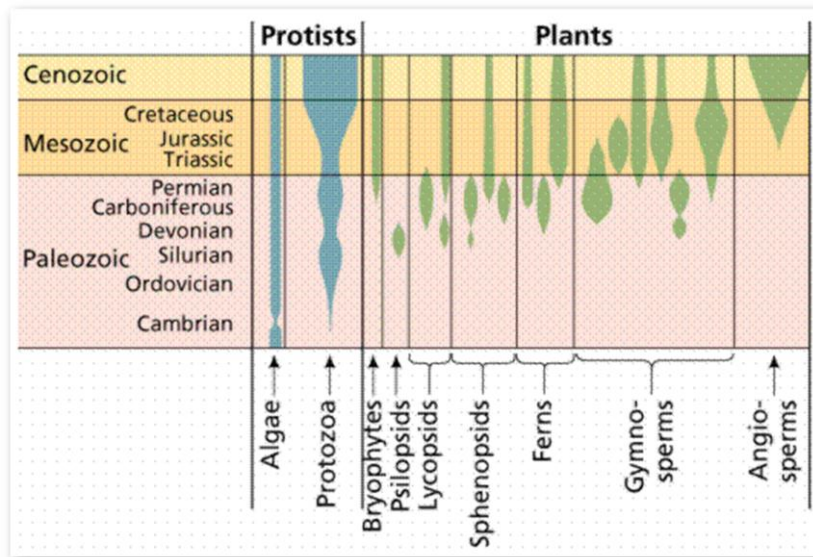
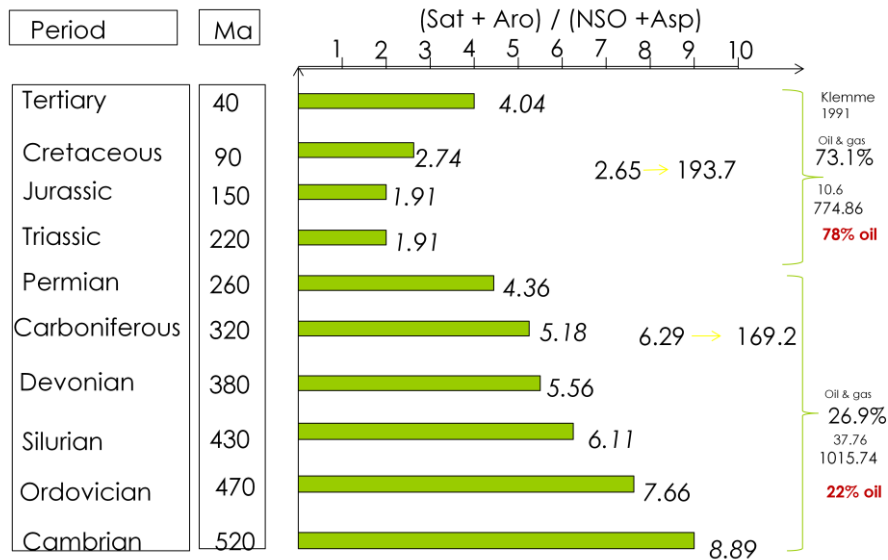


Image from Purves et al., Life: The Science of Biology, 4th Edition, by Sinauer Associates and WH Freeman

Presenter's notes: This figure representing the Protists and Plants corroborates the dramatic change of the "post-mortem" organic input occurring over geologic time. It shows the overwhelming dominance of land plants in the organic budget of the Meso-Cenozoic compared to the Paleozoic. Such dramatic change is reflected in hydrocarbon and non-hydrocarbon fractions of oil and source rock over geologic time.

Generative capacity of HC versus non-HC of known petroleum systems over geological times



Based on more than 5000 worldwide low-maturity oil samples

Presenter's notes: This figure illustrates the main point of the presentation. It is based on SARA of worldwide oil database that contains more than 5000 oil samples from which we extracted age-dated oil. It shows the ratios of hydrocarbons (SAT+ARO) versus non-hydrocarbons (NSO+ASPH). This ratio decreases steadily from Cambrian to Permian--then shows a small increase from Triassic to Tertiary. This variation corroborates the evolution of organic-matter inputs through geologic time. It suggests that Paleozoic source rocks are asphaltene-lean deposits with higher hydrocarbon (SAT+ARO) generation than the Meso-Cenozoic source-rock counterpart. It shows that, for the same volume of SR and richness, Paleozoic SRs are able to generate 3 times more HC than the Meso-Cenozoic SRs.

Implications

Conventional :

The steady increase of the heavy compounds over geologic time in oil fractions and SR extracts corroborates the evolution of organic species. Their low content in the Paleozoic oil and source rock contrasts with their preponderance in the Mesozoic–Cenozoic--subsequently a paraffinic light oil in the Paleozoic as opposed to the naphthenic heavy oil of the Mesozoic. Based on HC reserve assessment by Klemme (1991), we infer that 22% of the Paleozoic oil provided almost the same energy needs to the world as 78% of the oil of the Mesozoic .

Unconventional:

- Heavy compounds(bitumen) are less resistant to cracking and their conversion occurs earlier than any residual oil retained in the source
- Mesozoic /Cenozoic SR holding more heavy compounds generates gas condensate earlier than Paleozoic Source Rock

Acknowledgement



Anadarko Petroleum Corporation

