12.158 Lecture 11

Petroleum Formation and Occurrence

- Introduction to petroleum occurrence and origins
- Concept of organofacies
- Source rock evaluation and characterisation
  - Rock-Eval &TOC
    - Quality
    - Maturity
    - Mineral Matrix Effects
- Derivation of kinetics of petroleum generation

Outline

- Geochemical tools for the characterisation of petroleum
    - Bulk properties; Biomarker hydrocarbons

  Controls on the hydrocarbon composition of petroleum
    - Source and Maturity
    - Migration
    - In-reservoir alteration.

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Peters K.E., Walters C.C. and Moldowan J.M. (2005) *The Biomarker Guide*. Cambridge University Press (Vols 1 & 2)

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Nature Insight Issue: Fossil Fuels, Hydrocarbons, Alternative Energy Sources Volume 246, November 20, 2003

Papers by Hall et al, Head et al, Berner, White and one by Lewan 1998

Theories on the Origins of Petroleum

Petroleum and natural gas are primordial carbon compounds and were accreted when the planet formed. Hydrocarbons migrate upwards from the mantle whereby they provide carbon and energy for a subsurface biosphere. These hydrocarbons derive their biological signatures from the subsurface organisms that feed on them

Gold T. (2001) *The Deep Hot Biosphere : The Myth of Fossil Fuels*. Freeman Dyson.

"Rock oil originates as tiny bodies of animals buried in the sediments which, under the influence of increased temperature and pressure acting during an unimaginably long period of time transform into rock oil" -- M.V. Lomonosov 1757AD.

Organic matter that is preserved in sedimentary rocks is biological in origin and was buried with those sediments. Petroleum and natural gas are formed and expelled from sediments when this organic matter becomes deeply buried and heated

Triebs A. (1936) Chlorophyll and hemin derivatives in organic mineral substances. *Angewandte Chemie* **49**, 682-686.

Eglinton G. and Calvin M. (1967) Chemical fossils. *Scientific American* **261**, 32-43.

Whitehead E. V. (1973) Molecular evidence for the biogenesis of petroleum and natural gas. In *Proceedings of Symposium on Hydrogeochemistry and Biogeochemistry*, Vol. 2 (ed. E. Ingerson), pp. 158-211. The Clarke Co.

Published estimates of world oil ultimate recovery

Source	Volume (trillions of barrels)
USGS, 2000 (high) (ref. 11)	3.9
USGS, 2000 (mean) (ref. 11)	3.0
USGS, 2000 (low) (ref. 11)	2.25
Campbell, 1995	1.85
Masters, 1994	2.3
Campbell, 1992	1.7
Bookout, 1989	2.0
Masters, 1987	1.8
Martin, 1984	1.7
Nehring, 1982	2.9
Halbouty, 1981	2.25
Meyerhoff, 1979	2.2
Nehring, 1978	2.0
Nelson, 1977	2.0
Folinsbee, 1976	1.85
Adam and Kirby, 1975	2.0
Linden, 1973	2.9
Moody, 1972	1.9
Moody, 1970	1.8
Shell, 1968	1.85
Weeks, 1959	2.0
MacNaughton, 1953	1.0
Weeks, 1948	0.6
Pratt, 1942	0.6

Hydrocarbons and the evolution of human culture

Charles Hall, Pradeep Tharakan1 John Hallock,
Cutler Cleveland and Michael Jefferson

NATURE | VOL 426 | 2003 318

Most of the progress in human culture has required the exploitation of energy resources. About 100 years ago, the major source of energy shifted from recent solar to fossil hydrocarbons, including liquid and gaseous petroleum. Technology has generally led to a greater use of hydrocarbon fuels for most human activities, making civilization vulnerable to decreases in supply. At this time our knowledge is not sufficient for us to choose between the different estimates of, for example, resources of conventional oil.

Most estimates of the quantity of conventional oil resources remaining
The best-known model of oil production was proposed by Marion
King Hubbert, who proposed that the discovery, and production, of
petroleum over time would follow a single-peaked, symmetric bellshaped
curve with a peak in production when 50% of the URR had
been extracted.

This hypothesis seems to have been based principally
on Hubbert’s intuition, and it was not a bad guess as he famously predicted in
1956 that US oil production would peak in 1970, which in fact it did.

Hubbert also predicted that the US production of natural gas would peak in about 1980, which it did, although it has since shown a major recovery with production of ‘shale gas’ and ‘tight gas’.

He also predicted that world oil production would peak in about 2000. There was a slight downturn in world production in 2000, but production in the first half of 2003 is running slightly above the rate in 2000.

The future: other technologies

The world is not about to run out of hydrocarbons, and perhaps it is not going to run out of oil from unconventional sources any time soon. What will be difficult to obtain is cheap petroleum, because what is left is an enormous amount of low-grade hydrocarbons, which are likely to be much more expensive financially, energetically, politically and especially environmentally. As conventional oil becomes less important, society has a great opportunity to make investments in a different source of energy, one freeing us for the first time from our dependence on hydrocarbons.

Subsidies and externalities, social as well as environmental, affect energy markets. With few exceptions, these subsidies and externalities tilt the playing field towards conventional sources of energy.

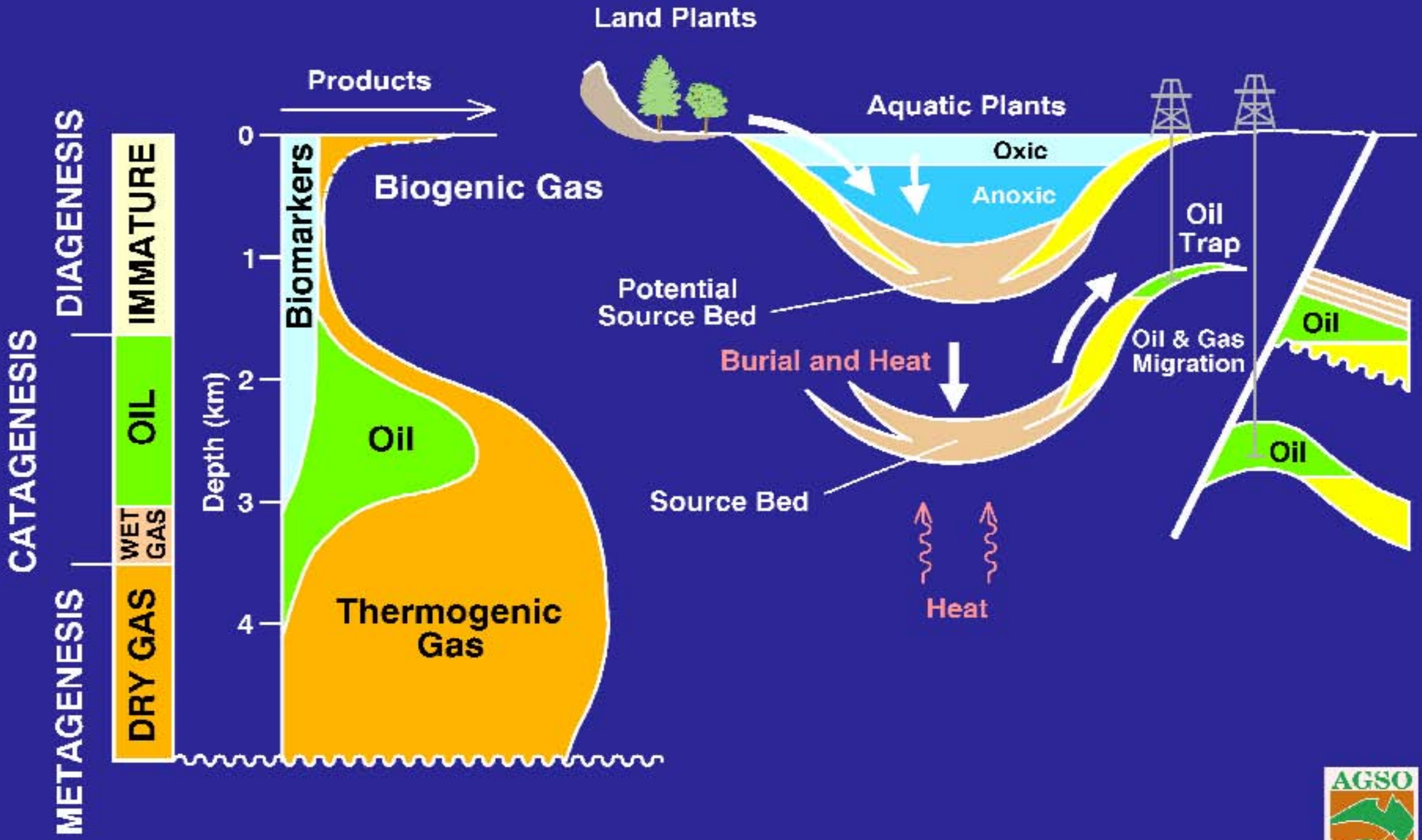
It is time to think about possibilities other than the next cheapest hydrocarbons, if for no other reason than to protect our atmosphere, and for this task we must use all of our science, both natural science and social science, more intelligently than we have done so far.

Klemme, H. D. & Ulmishek, G. F. Effective petroleum source rocks of the world: stratigraphic distribution and controlling depositional factors. *Bull. Am. Ass. Petrol. Geol.* **75**, 1809-1851 (1991).

A review, with 201 refs., and survey of main global petroleum source rocks, in terms of stratigraphic distribution and controlling depositional factors for petroleum generation and trapping.

Six stratigraphic intervals, corresponding to 1/3 of Phanarozoic time, contain >90% of the world's original discoverable oil and gas reserves.

The maturation time of these source rocks demonstrated that ~70% of the discovered oil and gas has been generated since the Coniacian, and ~50% of the world's petroleum has been generated and trapped since the Oligocene.


Land Plants
Products
Aquatic Plants
DIAGENESIS
CATAGENESIS
METAGENESIS
IMMATURE
OIL
WET GAS
DRY GAS
Depth (km)
0
1
2
3
4
Biomarkers
Biogenic Gas
Oil
Thermogenic Gas
Oxic
Anoxic
Potential Source Bed
Oil Trap
Oil & Gas Migration
Burial and Heat
Oil
Oil
Source Bed
Heat

AGSO
97/926

The Fate of OM: Diagenesis, Metagenesis

Organic matter from defunct organisms is almost quantitatively remineralized back to carbon dioxide in most modern aquatic environments. However, a small fraction of total biomass, on average less than 0.1 % (Holser et al., 1988), escapes remineralization, and eventually accumulates in sediments. As compounds with rapid biological turnover rates - including carbohydrates, proteins and nucleic acids - are most prone to recycling, more resistant molecules such as lipids and recalcitrant structural biopolymers become concentrated (Tegelaar et al., 1989). During transport through the water column, and subsequently in the unconsolidated sediment, this organic matter is further altered by a variety of chemical and biological processes commonly referred to as diagenesis (e.g. Hedges and Keil, 1995; Hedges et al., 1997; Rullkötter, 1999). During diagenesis a large fraction of the lipid and other low-molecular-weight components react via condensation and sulfur-vulcanization and combine with degradation-resistant macromolecules to form kerogen (e.g. de Leeuw and Largeau, 1993; Derenne et al., 1991). Formally, kerogen is defined as the fraction of large chemical aggregates in sedimentary organic matter that is insoluble in solvents. In contrast, the fraction of organic matter that can be extracted from sediments with organic solvents such as dichloromethane and methanol, is defined as bitumen (pyrobitumen and radiobitumen are residues of migrated petroleum that was cross linked and immobilized by heat and radioactivity, respectively). Bitumen in Recent sediments is predominantly composed of functionalized lipids.

The Fate of OM: Diagenesis, Metagenesis

During diagenesis, these lipids undergo oxidation, reduction, sulfurization, desulfurization and rearrangement reactions, generating an array of partly or entirely defunctionalized breakdown products that can have different stereo- and structural isomers. Analysis of these alteration products often yields valuable information about prevailing chemical conditions in the sediment during and after deposition because the extent and relative speed of diagenetic reactions is dependent on environmental conditions such as redox state, pH and availability of catalytic sites on mineral surfaces. Where reducing conditions prevail in the sediment biolipids eventually lose all functional groups but remain identifiable as geologically stable hydrocarbon skeletons.

Diagenetic reactions in the presence of reduced sulfur species have a profound effect on the sedimentary fate of lipids and other biological debris (Sinninghe Damsté and de Leeuw, 1990) and the preservation of diagnostic carbon skeltons (e.g. Adam et al., 1993; Kenig et al., 1995; Kohnen et al., 1992; Kohnen et al., 1993; Kohnen et al., 1991a; Kohnen et al., 1991b; Schaeffer et al., 1995; Wakeham et al., 1995) in complex, sulfur-rich macromolecules. The subsequent release of these skeletons upon burial provides one of the most important mechanisms for preserving the structural integrity of organism-specific biomarkers.

The Fate of OM: Diagenesis, Metagenesis

With increasing burial over millions of years, geothermal heat will initiate catagenesis, the thermal degradation of kerogen and bitumen. Kerogen is cracked into smaller fragments, releasing increasing volumes of bitumen that eventually might be expelled from its source rock as crude oil. Weaker chemical bonds, such as S-S and S-C, are cleaved at relatively low temperatures with the result that sulfur-rich kerogens might commence oil generation at lower temperatures (e.g. Koopmans et al., 1997; Lewan, 1985). Hydrocarbon chains attached to kerogen via stronger C-O and C-C bonds are sequentially released at higher temperatures. Also, with increasing heat flux, biomarkers and other components in the bitumen undergo thermal rearrangement and cracking reactions. By measuring the relative abundances of these thermal products, it is possible to assess the maturity of an oil or bitumen. With continuing burial, and at temperatures and pressures that initiate low-grade metamorphism of the host rock, most or all of residual bitumen is expelled or cracked to gas and the kerogen becomes progressively depleted in hydrogen to form a partly crystalline, semi-graphitic carbon phase (metagenesis). The exact temperature and time constraints of metagenesis and the preservation of hydrocarbon biomarkers are much debated (e.g. Mango, 1991; Price 1997).

Organic Facies

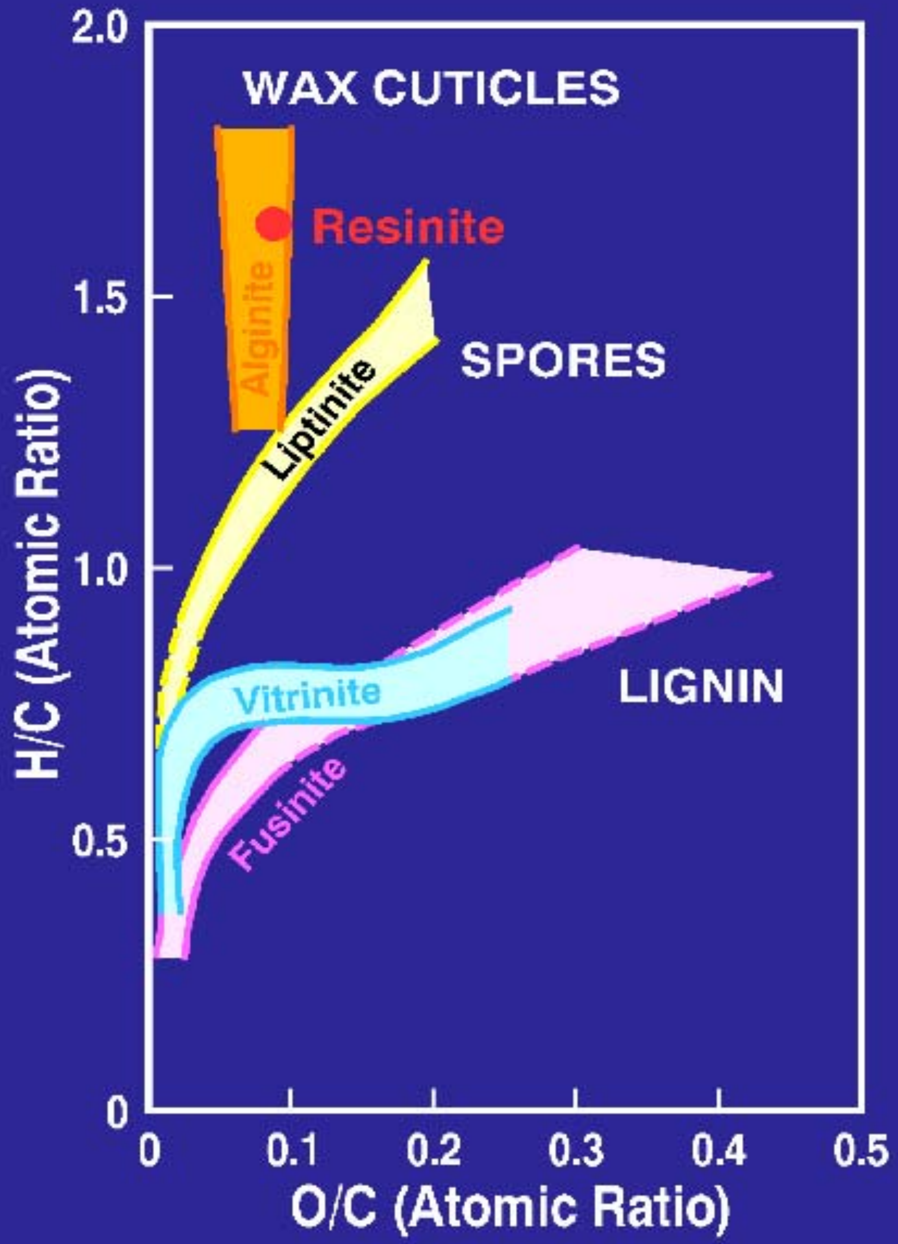
‘An organic facies is a mappable subdivision of a stratigraphic unit, distinguished from the adjacent subdivisions on the character of its organic constituents, without regard to the inorganic aspects of the sediment’

R.W. Jones ‘Advances in Petroleum Geochemistry’
(ed. J. Brooks & D. Welte) 1987

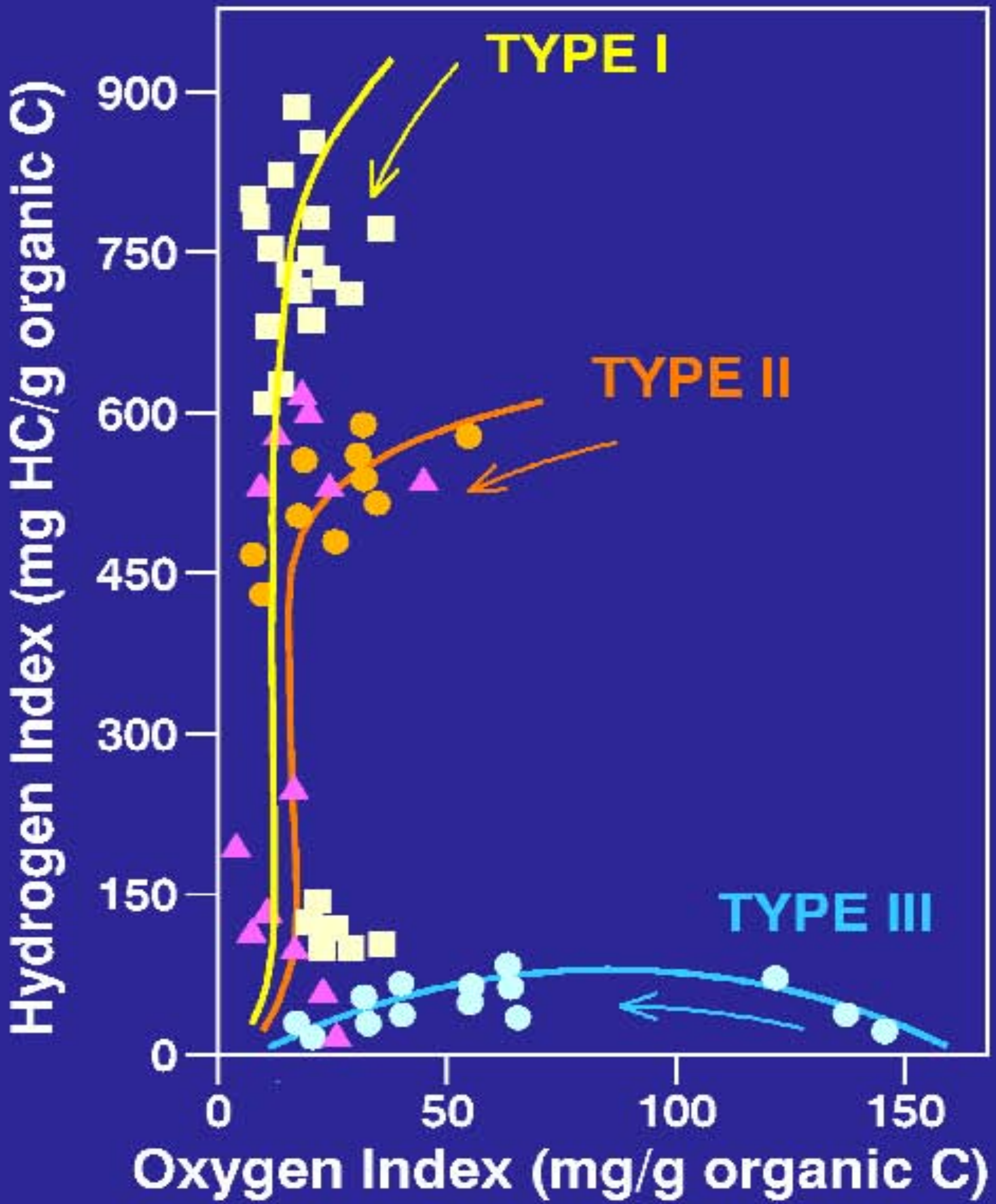
Kerogen and Bitumen

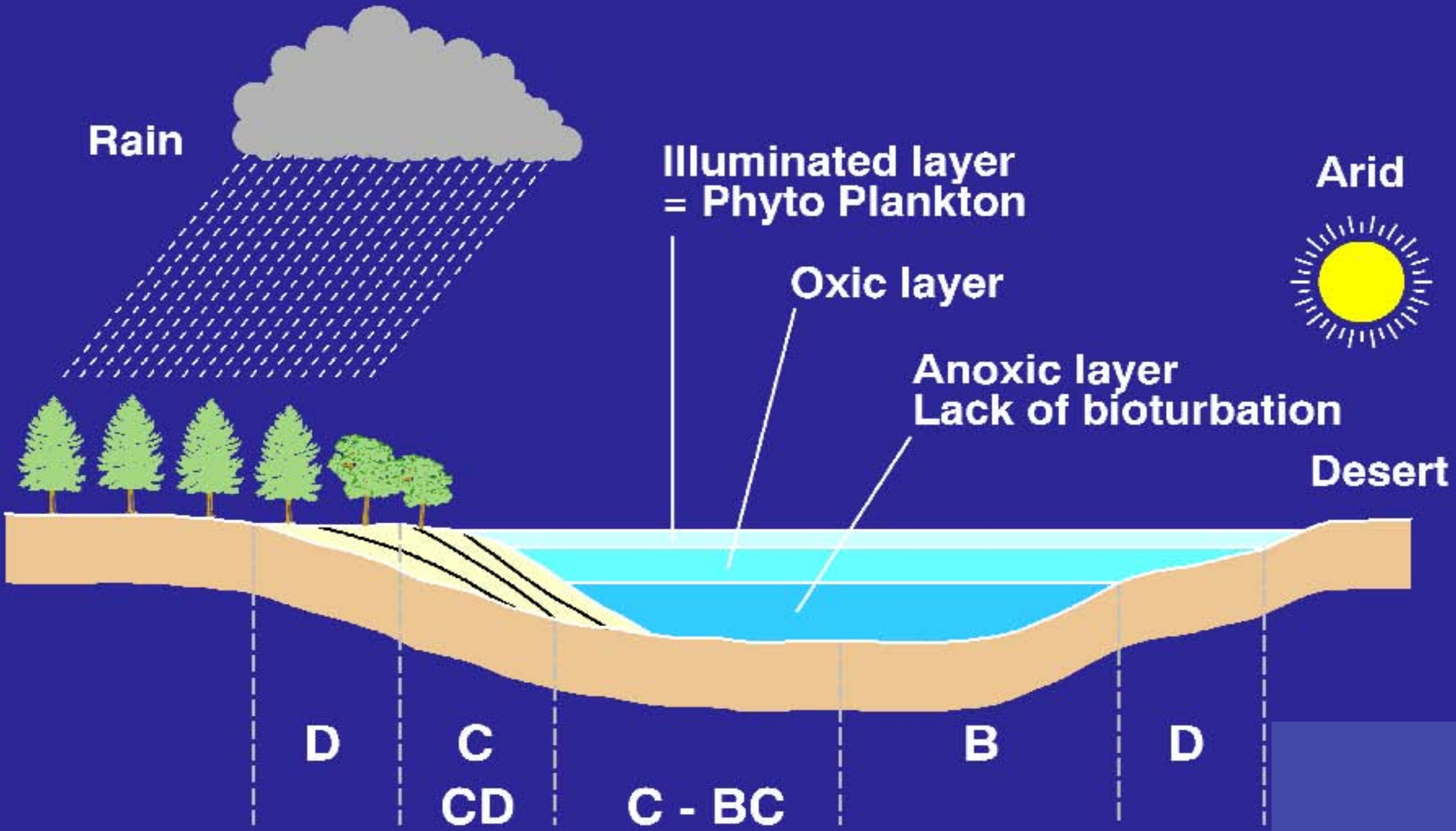
Kerogen is the component of organic matter that is insoluble in inorganic and organic solvents (Durand, 1980)

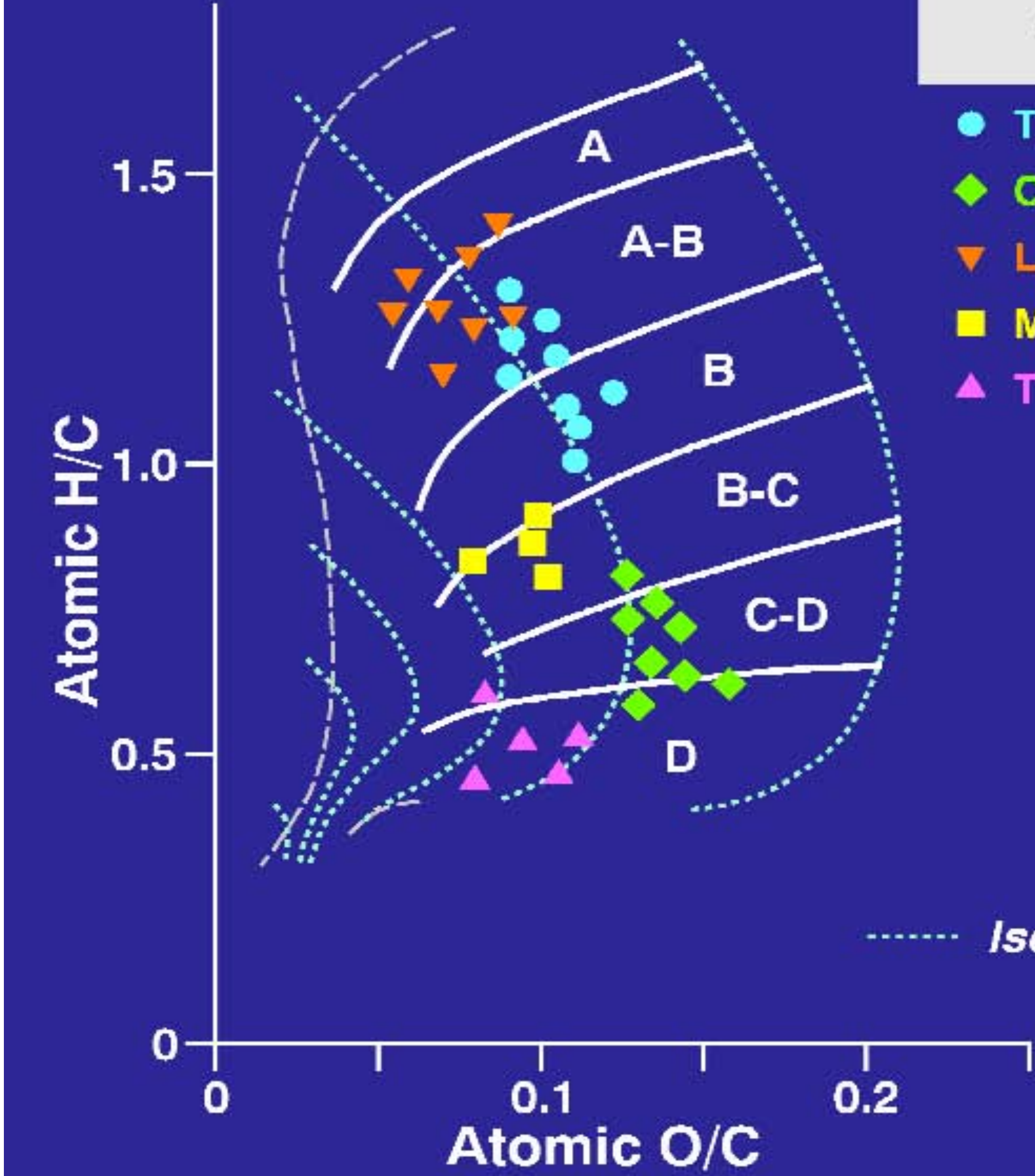
In contrast, bitumen is the component of organic matter that is soluble in organic solvents



2.0
1.5
1.0
0.5
0
WAX CUTICLES
Resinite
Alginite
Liptinite
SPORES
Vitrinite
LIGNIN
Fusinite
0
0.1
0.2
0.3
0.4
0.5
H/C (Atomic Ratio)
O/C (Atomic Ratio)


TYPE I
TYPE II
TYPE III
Hydrogen Index (mg HC/g organic C)
900
750
600
450
300
150
0
0
50
100
150
Oxygen Index (mg/g organic C)


Rain
Illuminated layer
= Phyto Plankton
Arid
Oxic layer
Anoxic layer
Lack of bioturbation
Desert
D
C
CD
C - BC
B
D



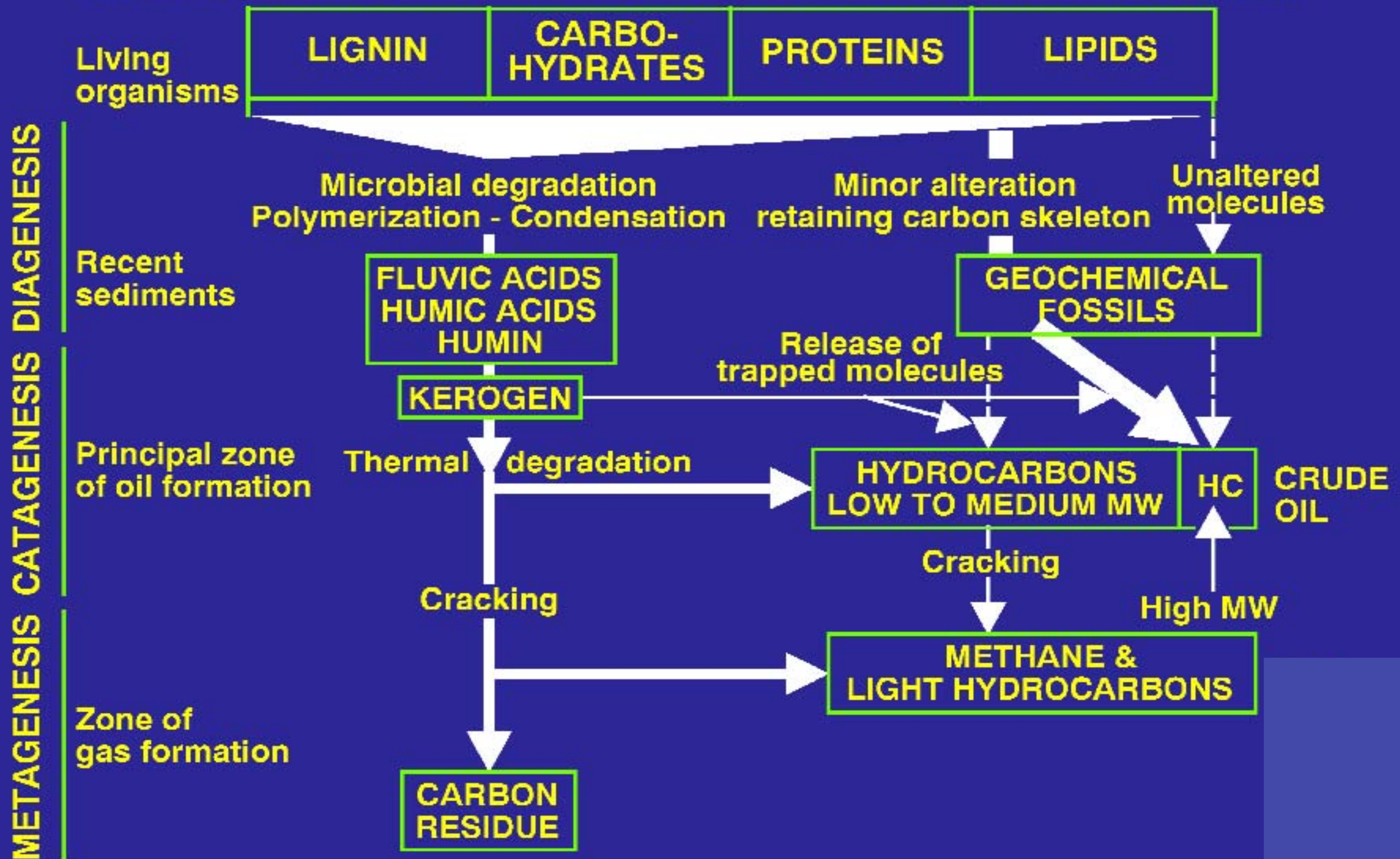
	Age	Organic Facies	Depositional Environment
●	Tertiary	B,BC	*Marine - mixed*
◆	Cretaceous	CD	*Open marine*
▼	L. Jurassic	B	*Restricted marine*
■	M. Jurassic	C	*Terrestrial - coal*
▲	Triassic	D	*Terrestrial - Red bed*

······ *Isorank, % vitrinite reflectance*

Organismic Controls on Organic Matter Types

	Sapropelic	Humic		
Kerogen	Algal + Amorphous	Herbaceous	Woody	Coaly
Macerals	Liptinite	Exinite	Vitrinite	Inertinite
	Alginite + Amorphous	Sporinite Cutinite Resinite	Telinite Collinite	Fusinite Micrinite Sclerotinite
Kerogen	Types I, II	Type II	Type III	Type III
H/C	1.7-0.3	1.4-0.3	1.0-0.3	1.45-0.3
O/C	0.1-0.02	0.2-0.02	0.4-0.02	0.3-0.02
ORGANIC SOURCE	Marine & lacustrine	Terrestrial	Terrestrial	Terrestrial & recycled
FOSSIL FUELS	Oil Oil shales, boghead and cannel coals	Oil and gas	Gas Humic coals	No oil, trace of gas

CONVERSION OF PRIMARY ORGANIC MATTER TO PETROLEUM



DIAGENESIS

CATAGENESIS

METAGENESIS

Living organisms

LIGNIN

CARBO-HYDRATES

PROTEINS

LIPIDS

Microbial degradation
Polymerization - Condensation

Minor alteration
retaining carbon skeleton

Unaltered molecules

Recent sediments

FLUVIC ACIDS
HUMIC ACIDS
HUMIN

GEOCHEMICAL FOSSILS

Release of trapped molecules

KEROGEN

Principal zone of oil formation

Thermal degradation

HYDROCARBONS
LOW TO MEDIUM MW

HC

CRUDE OIL

Cracking

Cracking

High MW

METHANE &
LIGHT HYDROCARBONS

Zone of gas formation

CARBON RESIDUE

Principles of Rock-Eval 4

Classification of kerogen types

Peters and Moldowan, 1993

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Principles of Rock-Eval 5

Maturity Evaluation

Peters and Moldowan, 1993

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Principles of Rock-Eval 6
Mineral Matrix Effects

Peters and Moldowan, 1993

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Principles of Rock-Eval 7
Maturation Trends

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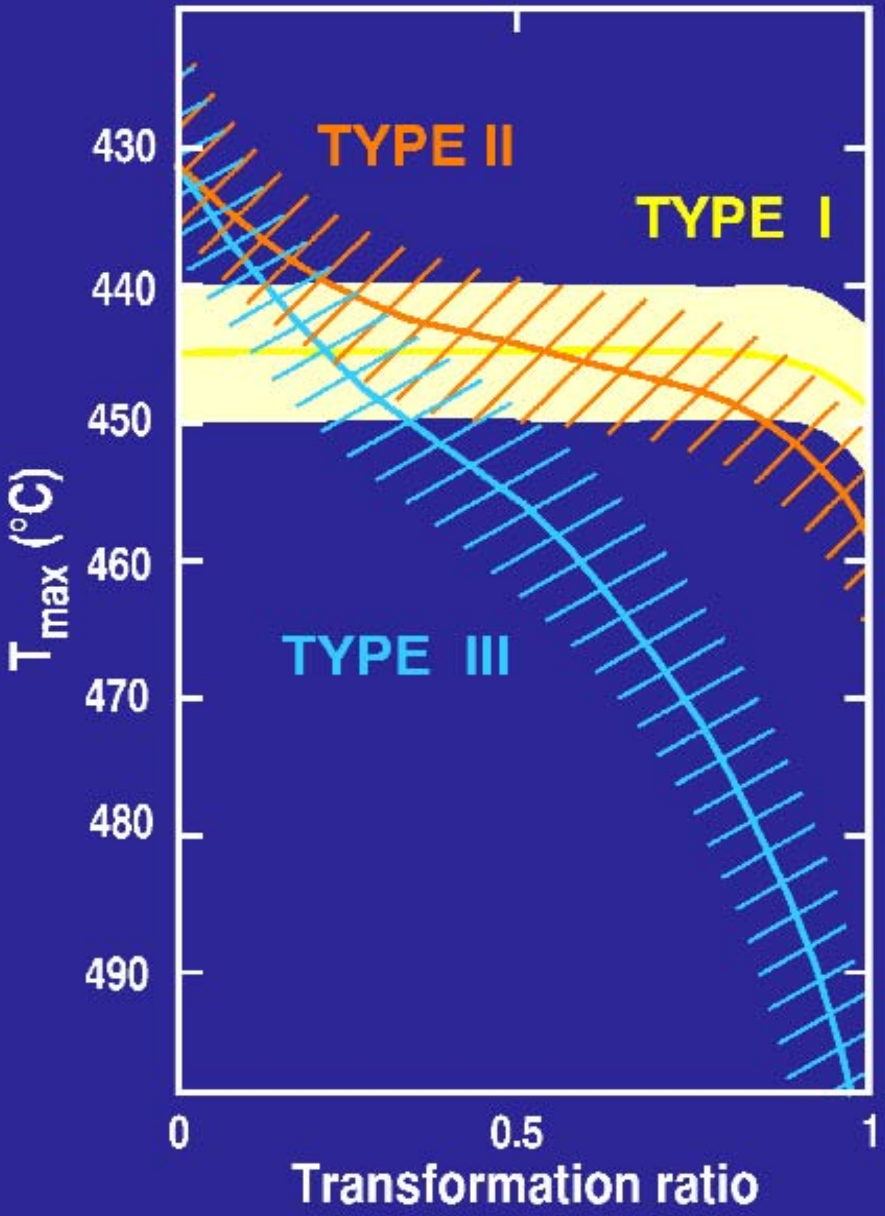
MATURATION INDEX / TRANSFORMATION RATIO FOR MAIN KEROGEN TYPES



Principles of Rock-Eval 8

Comparisons with other indicators

Peters and Moldowan, 1993

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Effect of geological heating rates on generation *vs* maturity indicators

Peters and Moldowan, 1993

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Kinetics of Hydrocarbon Generation

Schenk et al in Engel and Macko, 1993

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Kinetics Parameters of Hydrocarbon Generation

Schenk et al in Engel and Macko, 1993

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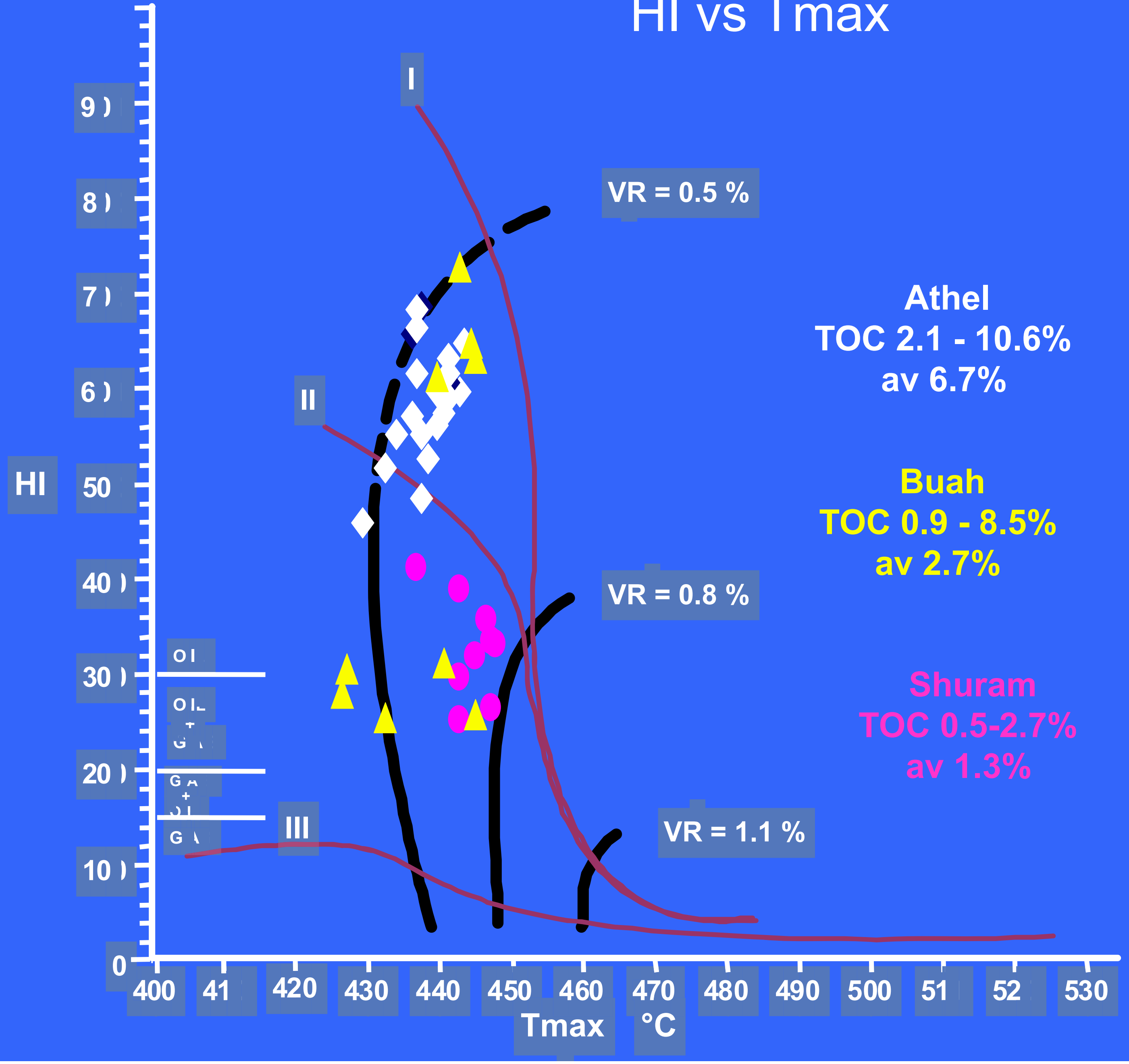
Neoproterozoic Ara Group Source Rocks

HI vs Tmax

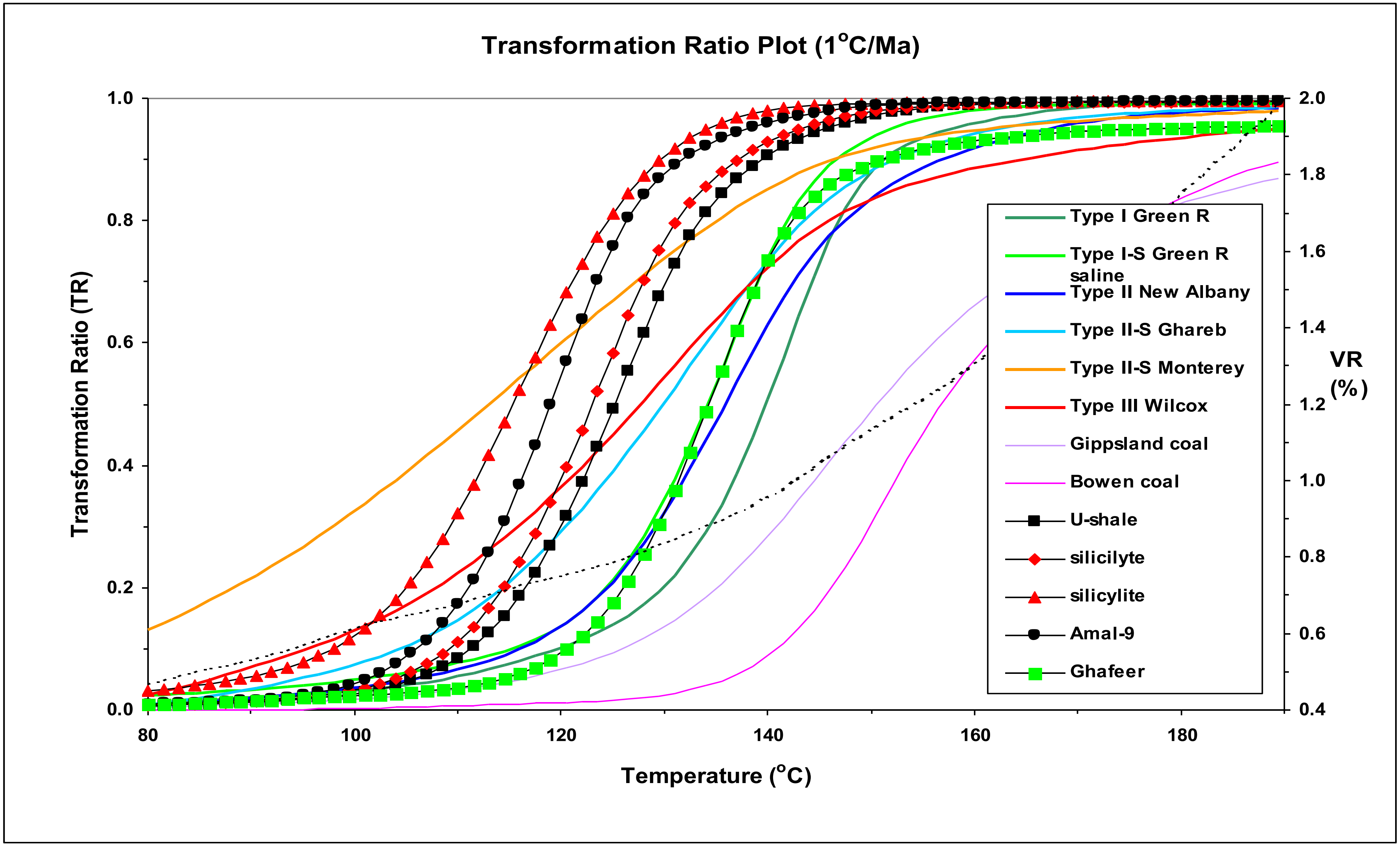


Athel
TOC 2.1 - 10.6%
av 6.7%

Buah
TOC 0.9 - 8.5%
av 2.7%

Shuram
TOC 0.5-2.7%
av 1.3%

Kerogen Kinetics -Ara vs Phanerozoic Rocks



Open system pyrolysis Py-GC (Pyroprobe-GC-MS)

Provides a quantitative and qualitative picture of kerogen make-up and hydrocarbon yields

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Schenk et al in Engel and Macko, 1993

Sulphur-radical control on petroleum formation rates

Michael D. Lewan

Nature 1998, 391 164

Most petroleum is formed through the partial decomposition of kerogen (an insoluble sedimentary organic material) in response to thermal stress during subsurface burial in a sedimentary basin1,2. Knowing the mechanisms and kinetics of this process allows the determination of the extent and timing of petroleum formation, which, in turn, are critical for evaluating the potential for petroleum occurrences within a sedimentary basin. Kinetic models of petroleum generation are derived mainly from pyrolysis experiments1,2, in which it is usually assumed that formation rates are controlled by the strength of the bonds within the precursor compounds: this agrees with the observation that petroleum formation rates increase with increasing sulphur content of thermally immature kerogen2–4, C–S bonds being weaker than C–C bonds. However, this explanation fails to account for the overall composition of petroleum.

Here I argue, on the basis of pyrolysis experiments, that it is the presence of sulphur radicals, rather than the relative weakness of C–S bonds, that controls petroleum formation rates. My findings suggest that the rate of petroleum formation depends critically on the concentration of sulphur radicals generated during the initial stages of thermal maturation. The proposed mechanism appears to provide a realistic explanation for both the overall composition of petroleum and the observed variation in formation rates.

Figure 1 Plot of the activation energy for expelled oil generation from type-II kerogen against the sulphur mole fraction ((S=½S þ Cÿ) of the original thermally immature kerogen; New Albany Shale (P), Woodford Shale (O), Alum Shale (B), Phosphoria Formation (I), and Monterey Formation (X). Sulphur values are for organic sulphur and do not include inorganic sulphur (such as pyrite/ marcasite).

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Another important implication is that laboratory pyrolysis methods used to derive kinetic parameters for petroleumformation in sedimentary basins must simulated this mechanism in order to provide meaningful extrapolations to the lower temperatures and longer times experienced in the subsurface of sedimentary basins. In particular, the mechanism is not likely to be stimulated by open system pyrolysis methods used to determine kinetic parameters, in which volatilized products are collected by sweeping carrier gas over a sample as it is isothermally heated from 300 to 600 °C within tens of minutes. The problem here is that initiating sulphur radicals generated in the early stages of heating in open-system pyrolysis are removed from the maturing organic matter and unavailable to participate fully in initiating thermal cracking reactions. Conversely, closed-system pyrolysis, such as hydrous pyrolysis, at temperatures between 280 and 360 °C would maintain initiating sulphur radicals in contact with thermally maturing kerogen. This difference between open- and closed-system pyrolysis provides an explanation as to why the former does not always show a relationship between rates of petroleum generation and organic sulphur content of type-II kerogen.

Determining the temperature of petroleum formation from the kinetic properties of petroleum asphaltenes

Rolando di Primio*†, Brian Horsfield‡ & Mario A. Guzman-Vega§
NATURE |VOL 406 | 13 JULY 2000 173

Knowledge of the timing and location of petroleum formation is important in assessing the extent of available reserves in hydrocarbon- forming basins. This can be predicted from the thermal history of a basin and the kinetic parameters that characterize the thermal breakdown of kerogen in source rocks. At present, the kinetic parameters of kerogen breakdown are experimentally determined using immature rock samples from basin margins, but questions remain about the accuracy of this approach, especially when significant variability is observed within individual source units. Here we show that the kinetics of hydrocarbon generation from petroleum asphaltenes can be used to determine the temperature conditions of the actual source rock at the time of expulsion of the sampled petroleum. This relationship reflects the structural similarity of asphaltenes to the parent kerogen. We expect that our approach may be used as a comparatively simple alternative method for assessing the petroleum generation characteristics of a given basin, which will allow for better estimates of the available oil resources and the risks associated with their exploration.

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Figure 2 Activation energy distributions and calculated transformation ratios. **a**, **b**, Source rock kerogen correlated to the 2/2-5 oil. **c d**, Petroleum asphaltenes from the 2/2-5 oil. Arrows on the TR diagrams indicate inferred temperature of oil-phase generation and expulsion (120 oC) as determined from the 2/2-5 petroleum asphaltene kinetics (**d**) and extent of transformation of the kerogen based on this temperature (15% TR, **b**). Thick line, TR; thin line, computed % vitrinite reflectance (Ro).

Organic–inorganic interactions in petroleum-producing sedimentary basins

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Petroleum deposits form as a consequence of the increased temperatures that accompany progressive burial of organic matter deep within sedimentary basins. Recent advances in petroleum geochemistry suggest that inorganic sedimentary components participate in organic transformations associated with this process. Water is particularly important because it facilitates reaction mechanisms not available in dry environments, and may contribute hydrogen and oxygen for the formation of hydrocarbons and oxygenated alteration products. These findings suggest that petroleum generation and stability is influenced by subsurface chemical environments, and is a simple function of time, temperature and the composition of sedimentary organic matter.

Figure 1 Chemical evolution of kerogen and petroleum during thermal maturation in sedimentary basins. **a**, Van Krevelen diagram showing the chemical evolution of immature kerogen of varying composition (type I, II, III and IV) at increasing levels of thermal maturity (based on ref. 2). Levels of thermal maturity are indicated by isochors of vitrinite reflectance (%*R*0), a widely used geochemical indicator that integrates the effects of time and temperature during thermal maturation of sediments. In general, kerogen composition moves from the upper right regions of the figure to the lower left with increasing maturity. **b**, Traditional model of the amount and timing of organic alteration products generated during progressive burial in sedimentary basins that assumes oxygen and hydrogen in organic alteration products are derived only from kerogen (modified from ref. 2). The form of this figure is constrained by the maturation trends shown in the Van Krevelen diagram. **c**, Schematic illustration of the amount and timing of organic alteration products generated if water and minerals are allowed to contribute the requisite hydrogen and oxygen for the formation of hydrocarbons and oxygenated compounds such as carbon dioxide and carboxylic acids. Ultimately, production of oxygenated products and methane will cease owing to exhaustion of a reactive carbon source. The depth at which this occurs is unknown.

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Figure 2 Reaction pathways responsible for the stepwise oxidation of aqueous *n*-alkanes at elevated temperatures and pressures. Mineral oxidants in subsurface environments may consume molecular hydrogen generated by these reactions, allowing the overall reaction to proceed continuously. Saturated hydrocarbons produced in step (5) may re-enter the sequence at the top and undergo subsequent oxidation. The net effect is the conversion of long-chain alkanes in oil to short-chain hydrocarbons in natural gas. The overall reaction indicated at the bottom has been written assuming that decarboxylation is responsible for the decomposition of acetic acid in the final step of the sequence.

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Figure 3 Evidence for the production of oxygenated organic alteration products at levels deep within sedimentary basins. **a**, Concentrations of organic acids in oilfield brines plotted as a function of subsurface temperature (modified from ref. 82). The existence of acids at temperatures in excess of peak petroleum generation (see Fig. 1) is consistent with generation through late-stage reactions involving *n*-alkanes and water. **b**, Carbon and oxygen isotope composition of carbonate cements in US Gulf Coast sedimentary rocks (modified from ref. 58). The trend of decreasing ^{13}C with decreasing δ18O indicates an increased contribution of carbon dioxide containing organically derived (isotopically depleted) carbon at temperatures approaching 200 °C. The temperature scale in **b** was calculated assuming equilibrium ^{18}O fractionation (ref. 83) during formation of carbonate cements from a typical of Gulf Coast formation water characterized by an ^{18}O content of 6‰ (ref. 83).

Biological activity in the deep subsurface and the origin of heavy oil

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NRG petroleum group, School of Civil Engineering and Geosciences, Unbiversity of Newcastle upon Tyne, Newcastle, NEI 7RU, UK

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At temperatures up to about 80 °C, petroleum in subsurface reservoirs is often biologically degraded, over geological timescales, by microorganisms that destroy hydrocarbons and other components to produce altered, denser ‘heavy oils’. This temperature threshold for hydrocarbon biodegradation might represent the maximum temperature boundary for life in the deep nutrient-depleted Earth. Most of the world’s oil was biodegraded under anaerobic conditions, with methane, a valuable commodity, often being a major by-product, which suggests alternative approaches to recovering the world’s vast heavy oil resource that otherwise will remain largely unproduced.

- The world's oil reserves are dominated by biodegraded heavy and super-heavy oils in the super-giant tar sands common in shallow reservoirs on the flanks of foreland basins in North and South America and elsewhere.

- Oils are classified for economic value according to API gravity, based on a surface measurement of the specific gravity of degassed oil16. Heavy oils have API gravities of 20 or less, super-heavy oils have API gravities of 10 or less, and a typical light marine non-biodegraded oil has an API gravity around 36–38 API. Tar sands are sandstones saturated with heavy or super-heavy oil: the oils in the Canadian and Venezuelan tar sands have API gravities of 6–12. The vast majority of heavy oils result from microbial alteration of oils in the reservoir1, 15, 16, 37, 84, 85, with over 50% of the Earth's oil inventory occurring as biodegraded oils in heavy oil and tar sand accumulations1. The largest single accumulations are the supergiant deposits of tar sands trapped on the flanks of the Alberta (Canada) and Eastern Venezuelan (Venezuela) foreland basins1, 84.

Figure 3 The palaeopasteurization model35 of Wilhelms *et al*. compares continuously subsiding (for example, Viking Graben, North Sea) and uplifted sedimentary basins (for example, Barents Sea or Wessex Basin) and shows schematic burial history (top), reservoir temperature history (middle) and petroleum system (lower) events. This illustrates key differences with respect to biodegradation in petroleum reservoirs. Biodegradation of petroleum occurs only in sedimentary units that have not been exposed to temperatures exceeding 80 °C (palaeopasteurization) before oil charging. We speculate that this 'pasteurization temperature' may represent the effective maximum temperature boundary for most life in Earth struggling to survive over geological timescales in hot oligotrophic sediments.

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Figure 2 Saturated hydrocarbon contents and gas chromatograms of petroleum extracted from reservoir cores show a progressive increase in biodegradation in three wells from a Chinese oilfield19. Hydrocarbons diffuse towards the oil–water contact, where they are degraded by microorganisms living near the oil–water contact using nutrients derived from the water-saturated zone below the oil column.

Nutrients such as phosphorus are probably buffered by mineral dissolution reactions72. Fresh oil is charged to the reservoir at the same time that degradation occurs. Compositional gradients reflect this complex charge and degradation scenario.

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Please see the caption on next page.

Figure 4 The putative chemistry of hydrocarbon degradation in most petroleum reservoirs with an absence of abundant sulphate. The overall conversion of hydrocarbons to biomass, methane and carbon dioxide may well involve water–hydrocarbon reactions47, 49, with the carbon dioxide produced being further reduced to methane using hydrogen produced either externally to or within the reservoir. Nutrient supply from mineral diagenesis may ultimately control the extent of hydrocarbon destruction and methane production69-72. The detailed mechanisms of anaerobic hydrocarbon degradation are now being elucidated and many mechanisms involve addition of fumarate48 or carboxylation of hydrocarbons to produce functionalized intermediates, which can either be metabolized to carbon dioxide or accumulate as dead-end metabolites. For example, a reductive pathway for the anaerobic degradation of naphthalene and 2-methylnaphthalene has been proposed by Annweiler and co-workers50. Initial carboxylation of naphthalene is followed by degradation of 2-naphthoic acid and, then, via a series of hydrogenation steps, to 5, 6, 7, 8-tetrahydro-2-naphthoic acid. Further hydrogenation to octahydro-2-naphthoic acid may then be followed by further degradation steps to produce energy and carbon dioxide or by further hydrogenation to give decahydro-2-naphthoic acid (a possible dead-end metabolite). We have found these reduced naphthoic acid derivatives indicative of anaerobic hydrocarbon degradation in oils from all the biodegraded oil provinces that we have examined51.

Microorganisms in petroleum reservoirs

One of the first microbiological studies of a deep subsurface environment resulted in the isolation of sulphate-reducing bacteria from produced waters from an oil well3. Since that time a wide range of bacteria have been isolated from petroleum systems. These have exclusively come from samples of produced waters. Produced waters from reservoirs undergoing water injection to enhance oil recovery are prone to contamination from the injected waters, thus samples from non-water flooded reservoirs are more likely to yield organisms native to the petroleum reservoir, but even then non-indigenous organisms may be introduced during drilling and grow in pipework in the oil well. Consequently many aerobic heterotrophic bacteria, many of which are capable of hydrocarbon degradation only in the presence of oxygen, have been isolated from well head water samples. These organisms, however, are unlikely to be native populations from the petroleum reservoir.

A wide range of anaerobic bacteria and archaea with physiological properties consistent with a deep subsurface existence have also been isolated (for an excellent review, see ref. 40). These include fermentative thermophilic heterotrophic bacteria including *Thermotoga*, *Thermoanaerobacter* and *Fervidobacterium*. Hyperthermophilic archaea such as *Thermococcus* and *Archaeoglobus* have also been isolated from non-flooded reservoirs. In addition, sulphate-reducing bacteria, iron-reducing bacteria and methanogenic archaea have been identified in wellhead waters42. No bacteria capable of degrading hydrocarbons under *in situ* conditions have yet been isolated from petroleum reservoirs. Sediment samples have now been recovered from many deep subsurface environments. These have yielded isolates with characteristics that suggest that they are true representatives of the subsurface biosphere, and it has been possible to measure important biogeochemical processes in these sediments. Interestingly, there are no reports in the literature of successful isolation or characterization of the microbial communities in sediments recovered from a petroleum reservoir. The isolation and characterization of the deep slow biosphere in petroleum reservoirs thus remains a major challenge.

The deep biosphere

Although bacteria putatively associated with deep subsurface environments were characterized in the first part of the twentieth century, it is only recently that the existence of a deep subsurface biosphere has been widely accepted in the scientific community. Scepticism about the deep subsurface biosphere stemmed largely from concerns about the provenance of organisms detected in samples taken from the subsurface, but with improved sampling techniques and methods to corroborate the authenticity of organisms recovered from deep within the Earth's crust many of these concerns have been dispelled. Soils and surface sediments can harbour billions of prokaryotic cells per cubic centimetre, but their abundance drops off exponentially with increasing depth82. Nevertheless, some deep subsurface sediments still hold around 105 to 106 cells cm–3, and where carbon and energy sources are abundant, numbers may increase at depth. Evidence suggests that a deep crustal biosphere beneath both land and sea has reached approximately 3 km below the Earth's surface, with oil biodegradation suggesting that this can be extended to at least 4 km. Although the number of cells per unit volume of deep subsurface sediments is relatively small, the vast extent of the sediments (estimated at 51025 cm3) means that total prokaryote cell numbers in all subsurface environments are of the order of 1030 (ref. 83). Although there are uncertainties in the estimates, and they are based on extrapolation from a small number of samples, deep subsurface microbial biomass may account for greater than 90% of global prokaryotic biomass, exceeding the values for all of the world's oceans and terrestrial environments by some margin. Subsurface prokaryotic biomass may contain 3–51017 g of carbon, representing 60–100% of the carbon present in global plant biomass. Prokaryotic cells typically contain a higher proportion of nitrogen and phosphorus than plant biomass (about 10 times more), and thus the contribution of deep crustal microorganisms to global nitrogen and phosphorus pools is extremely significant83. The deep biosphere is clearly of global significance simply in terms of key elemental budgets. However, the fact that many of the organisms present may be consuming and producing inorganic and organic compounds to generate energy and biomass extends their significance to the realms of biogeochemical processes. One such crucial process in the deep subsurface is the transformation of petroleum hydrocarbons to produce heavy oils by biodegradation.

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Deep bacterial biosphere in Pacific Ocean sediments

R. J. Parkes, B. A. Cragg, S. J. Bale, J. M. Getlifff,
K. Goodman, P. A. Rochelle, J. C. Fry,
A. J. Weightman & S. M. Harvey

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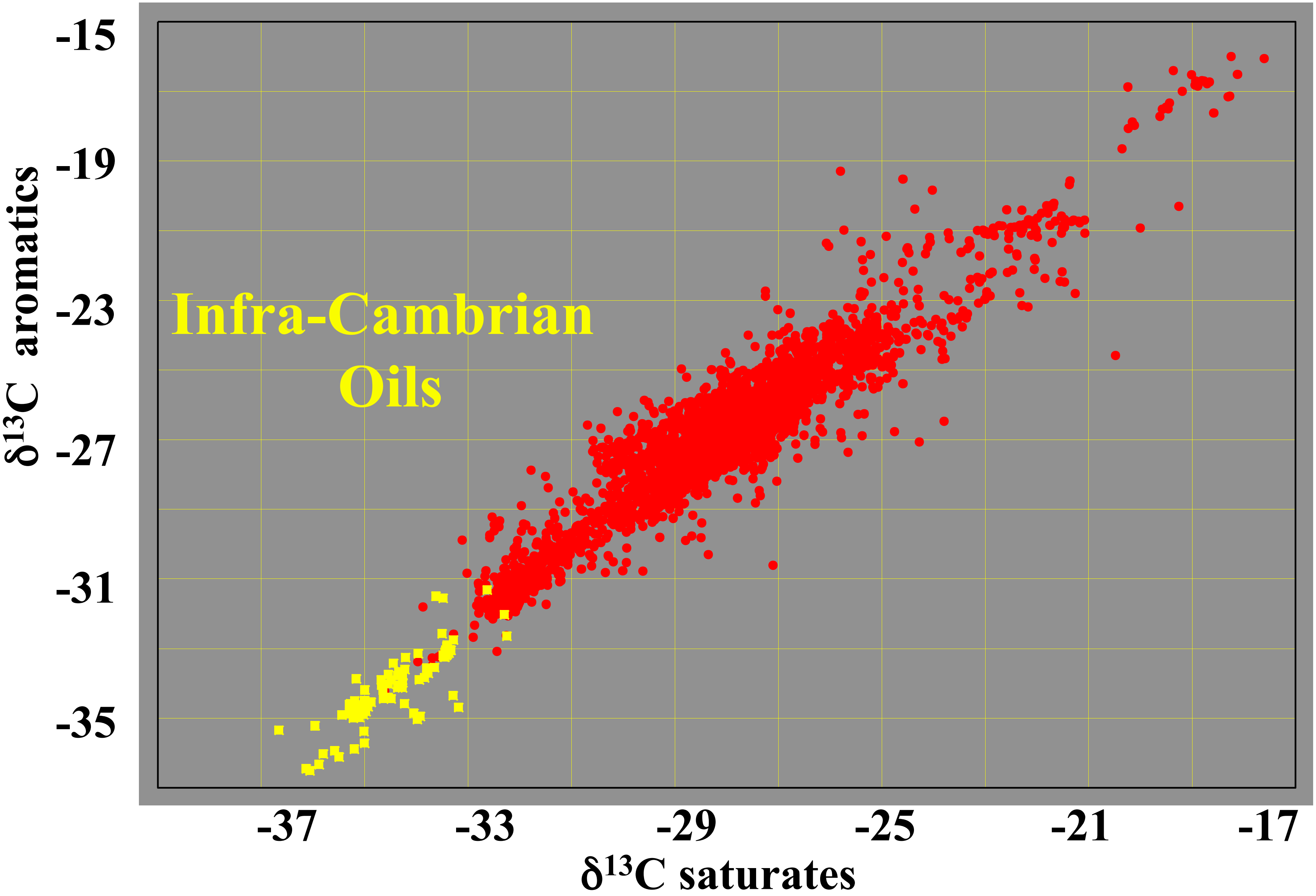
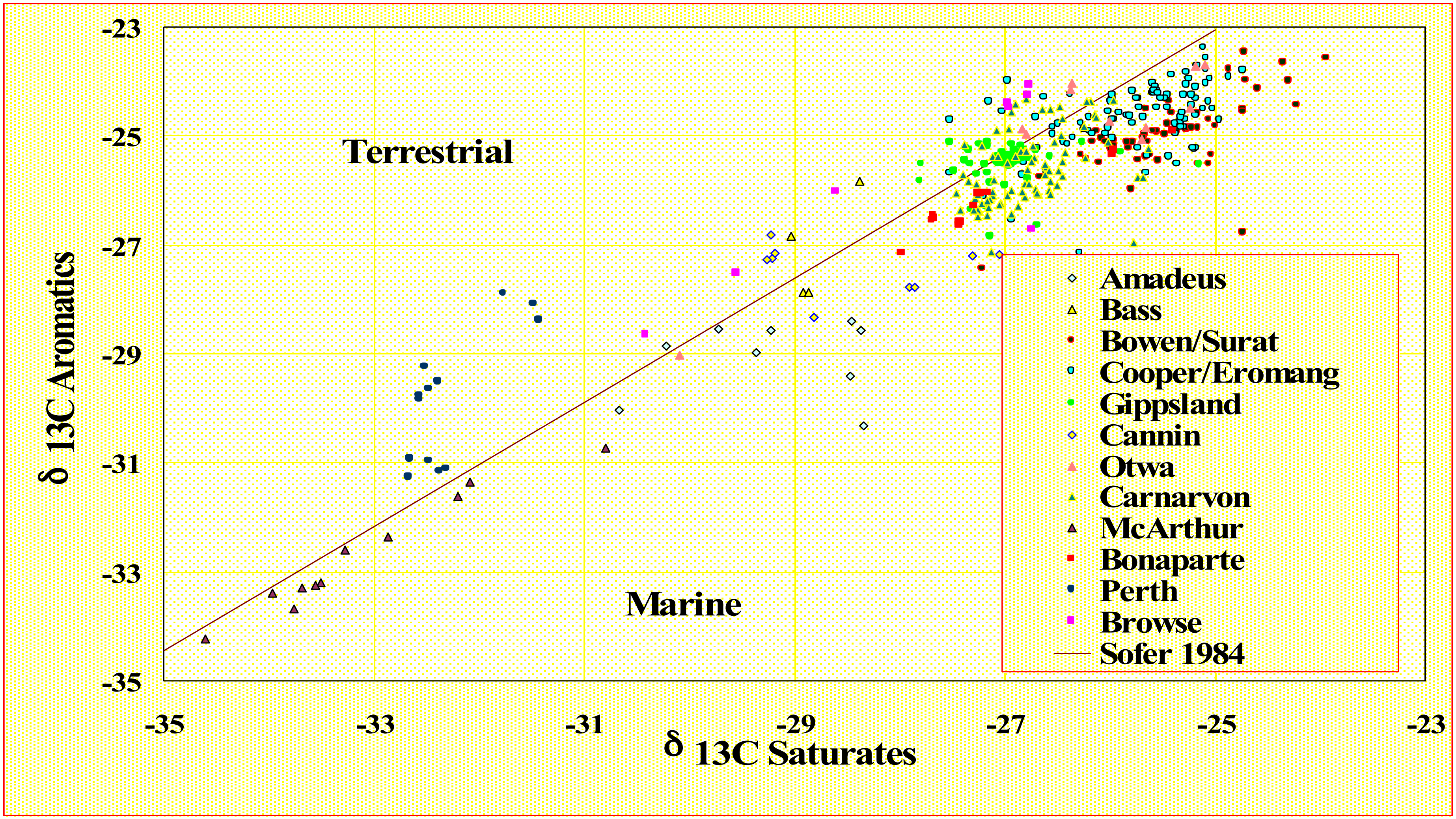
Bulk Properties

- Bulk carbon isotopes of saturates and aromatics fractions
- API gravity. USA measure related to specific gravity
- API = [(141.5 / SG@16°C) – 131.5]. Water has gravity 10° API. Heavy oils < 25°. Medium 25° to 35°. Light 35° to 45°. Condensates > 45°

Bulk ^{13}C Composition for 3,000 oils of global extent



Bulk ^{13}C Composition for 420 Australian Oils



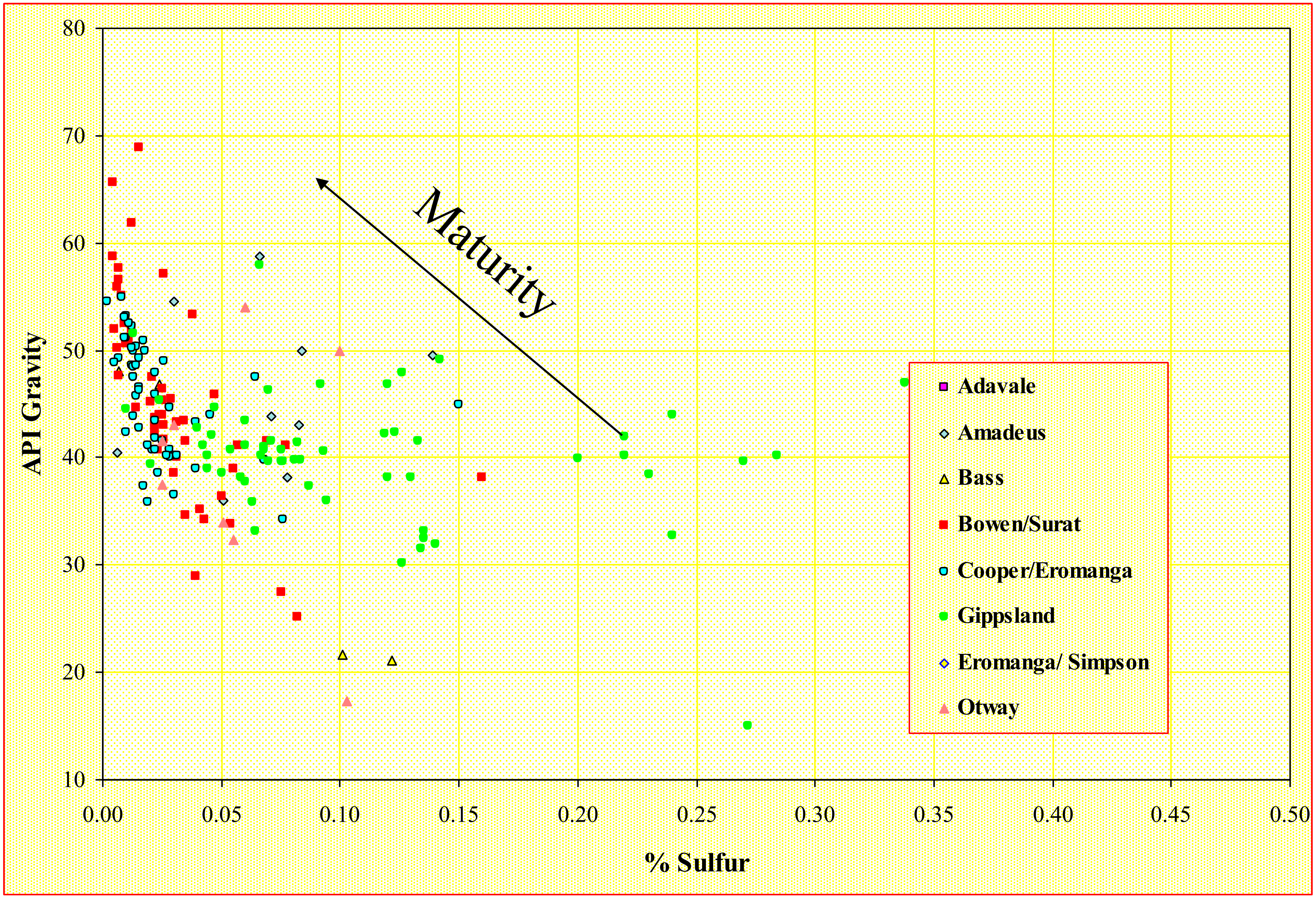
Sulfur, Nickel and Vanadium

- Sulfur: High in marine and some saline lacustrine oils; generally decreases as a function of maturity
- Can be a useful correlation tool where there are S-rich petroleum systems but Australian oils generally low in sulfur.
- Nickel and Vanadium contents; largely exist in porphyrin content. Generally decrease with maturation.

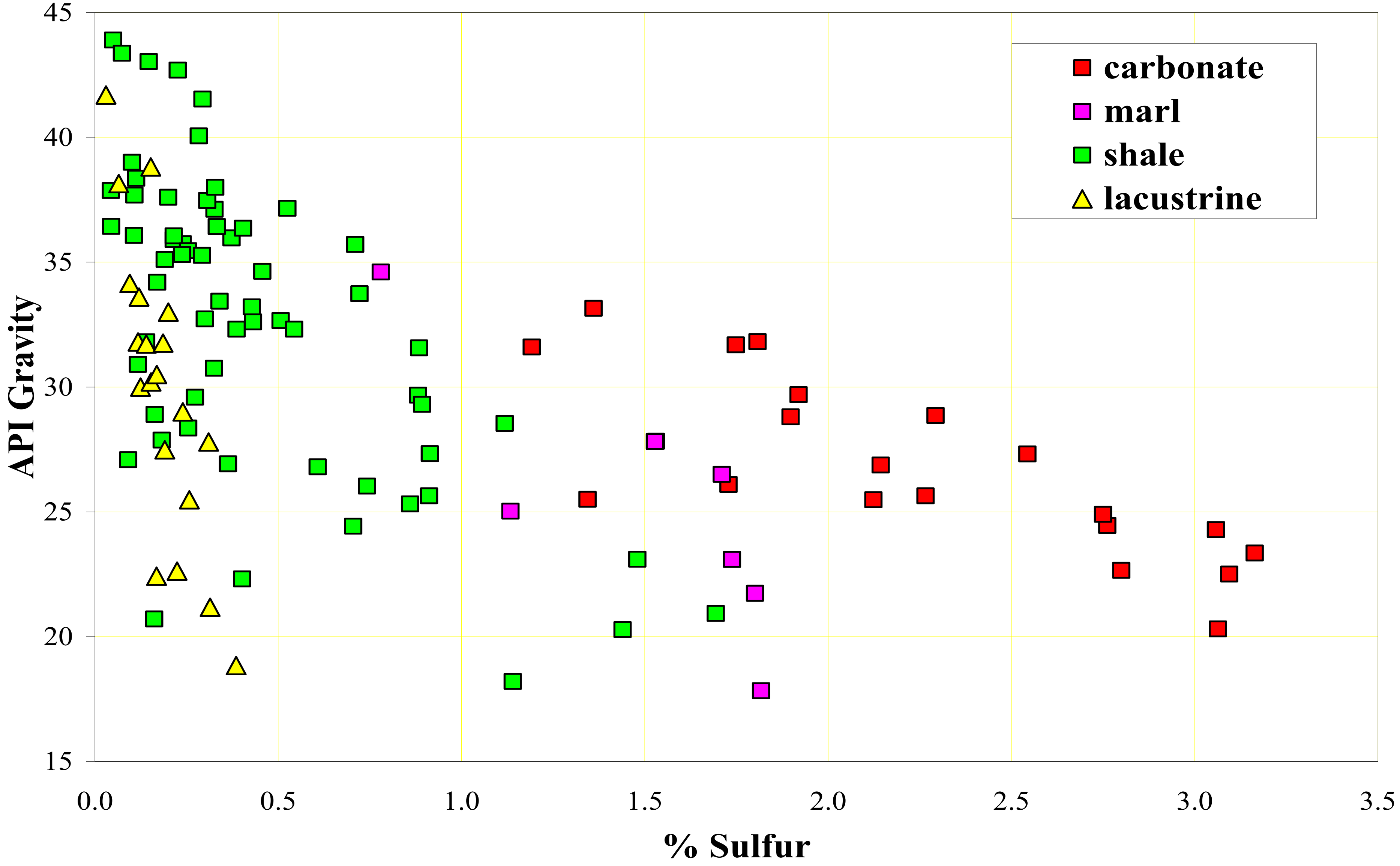
Sulfur, Nickel and Vanadium

- Non-marine oils with high terrigenous organic matter contents show high wax, low sulfur and very low metals contents
- Marine carbonates & siliciclastics show low wax, moderate to high-S, high overall nickel and vanadium but a low (<1) Ni/V ratio.
- Lacustrine oils show high wax, low-S, moderate Ni and V and high (>2) Ni/V ratio

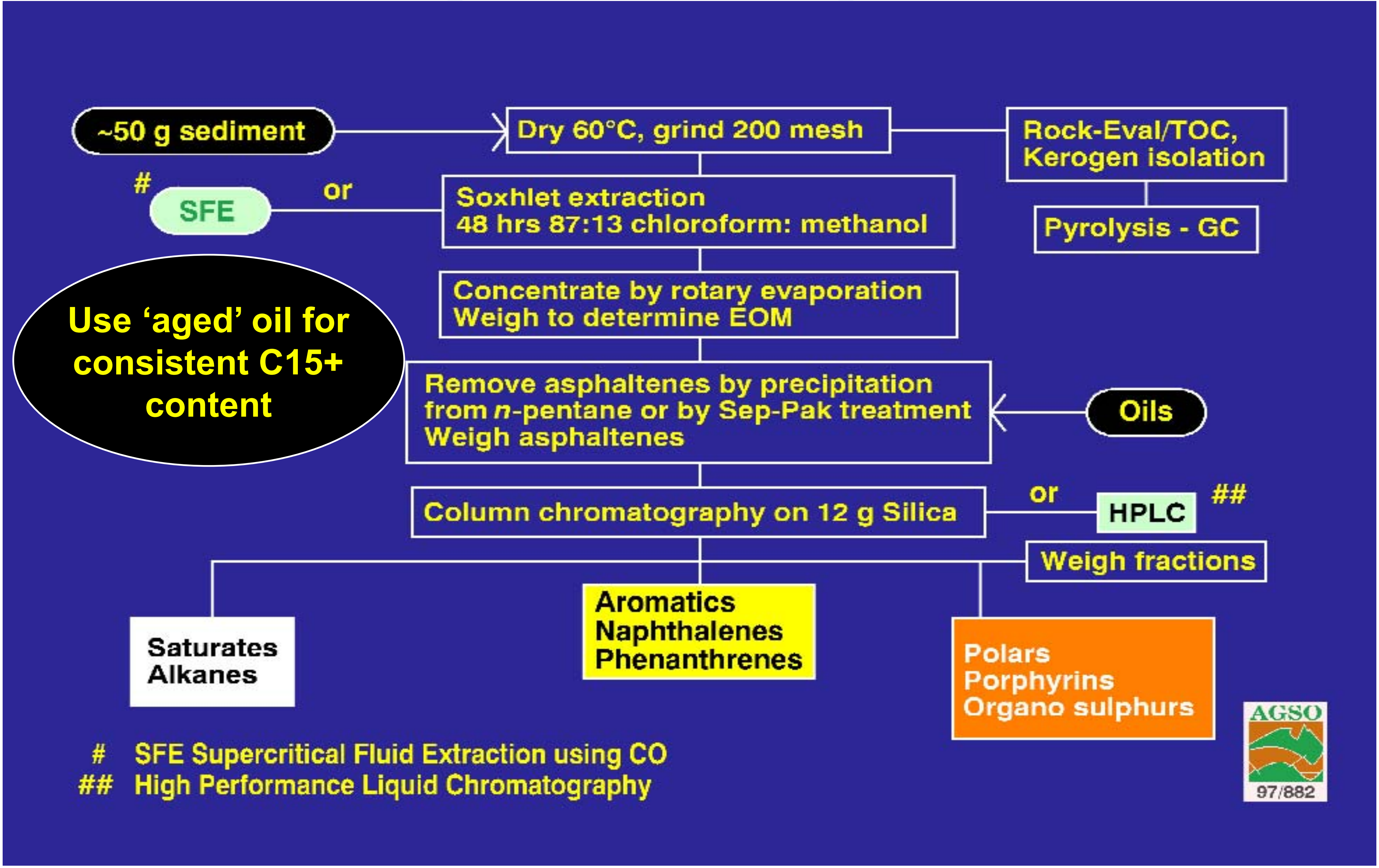
Sulfur vs API Plot



API vs Sulfur vs Lithology



Compound Class Separation



~50 g sediment

Dry 60°C, grind 200 mesh

Rock-Eval/TOC,
Kerogen isolation

Pyrolysis - GC

SFE or

Soxhlet extraction
48 hrs 87:13 chloroform: methanol

Concentrate by rotary evaporation
Weigh to determine EOM

Use ‘aged’ oil for consistent C15+ content

Remove asphaltenes by precipitation
from *n*-pentane or by Sep-Pak treatment
Weigh asphaltenes

Oils

Column chromatography on 12 g Silica

or HPLC ##

Weigh fractions

Saturates
Alkanes

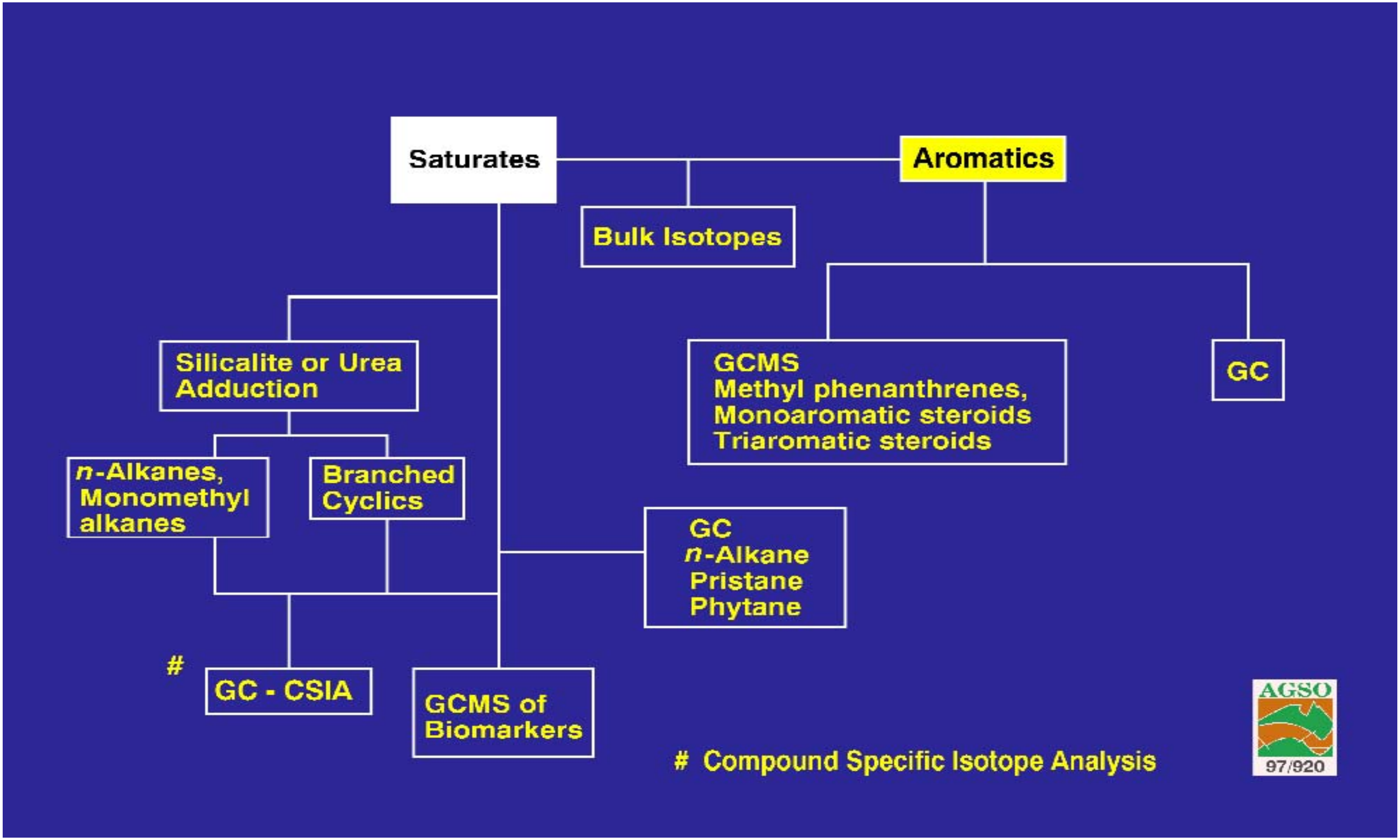
Aromatics
Naphthalenes
Phenanthrenes

Polars
Porphyrins
Organo sulphurs

\# SFE Supercritical Fluid Extraction using CO
\## High Performance Liquid Chromatography

AGSO
97/882

Further Analytical Schemes



Saturates

Aromatics

Bulk Isotopes

Silicalite or Urea Adduction

n-Alkanes, Monomethyl alkanes

Branched Cyclics

GCMS
Methyl phenanthrenes,
Monoaromatic steroids
Triaromatic steroids

GC

GC
n-Alkane
Pristane
Phytane

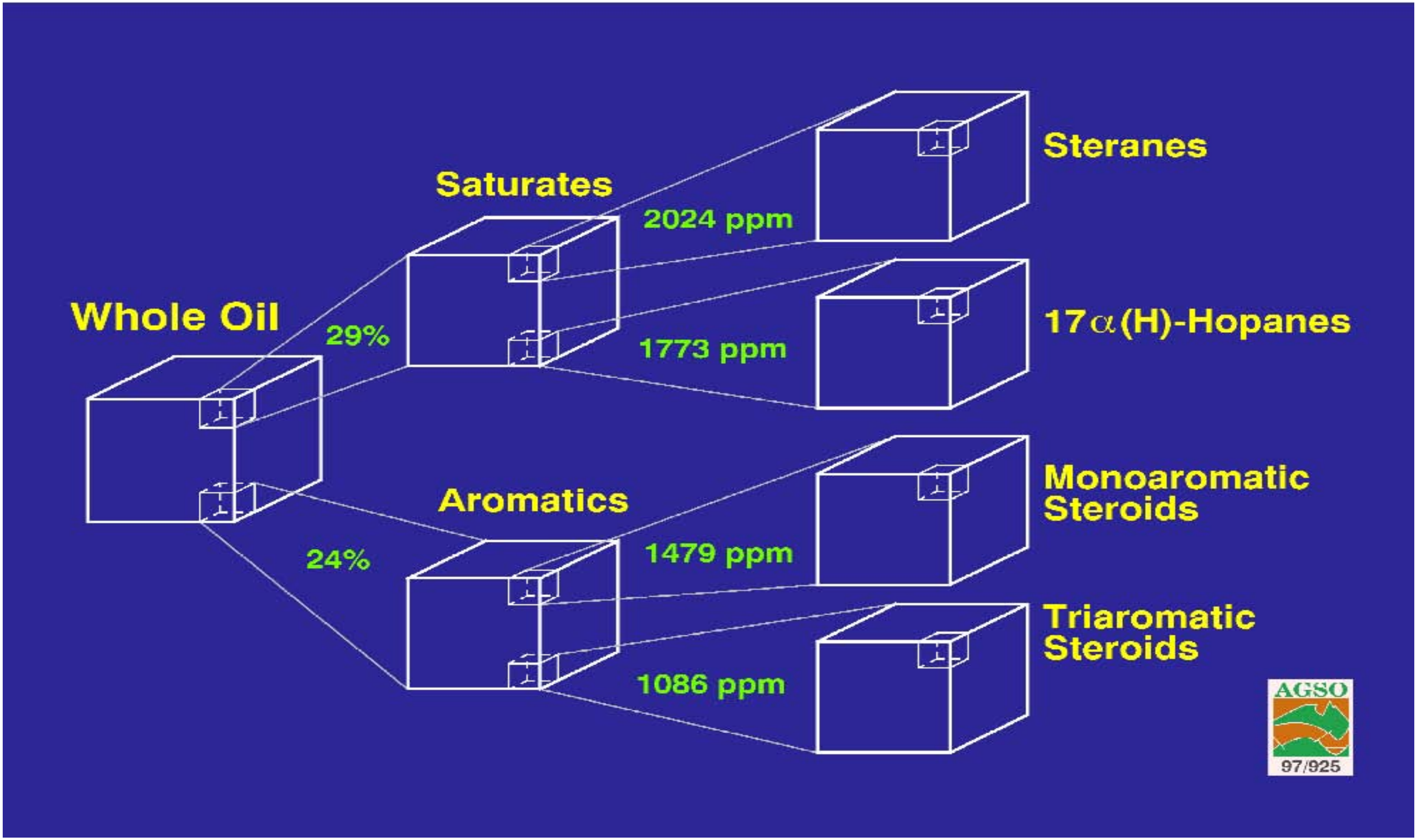
GC - CSIA

GCMS of Biomarkers

Compound Specific Isotope Analysis

AGSO 97/920

Petroleum Composition



Gas Chromatography

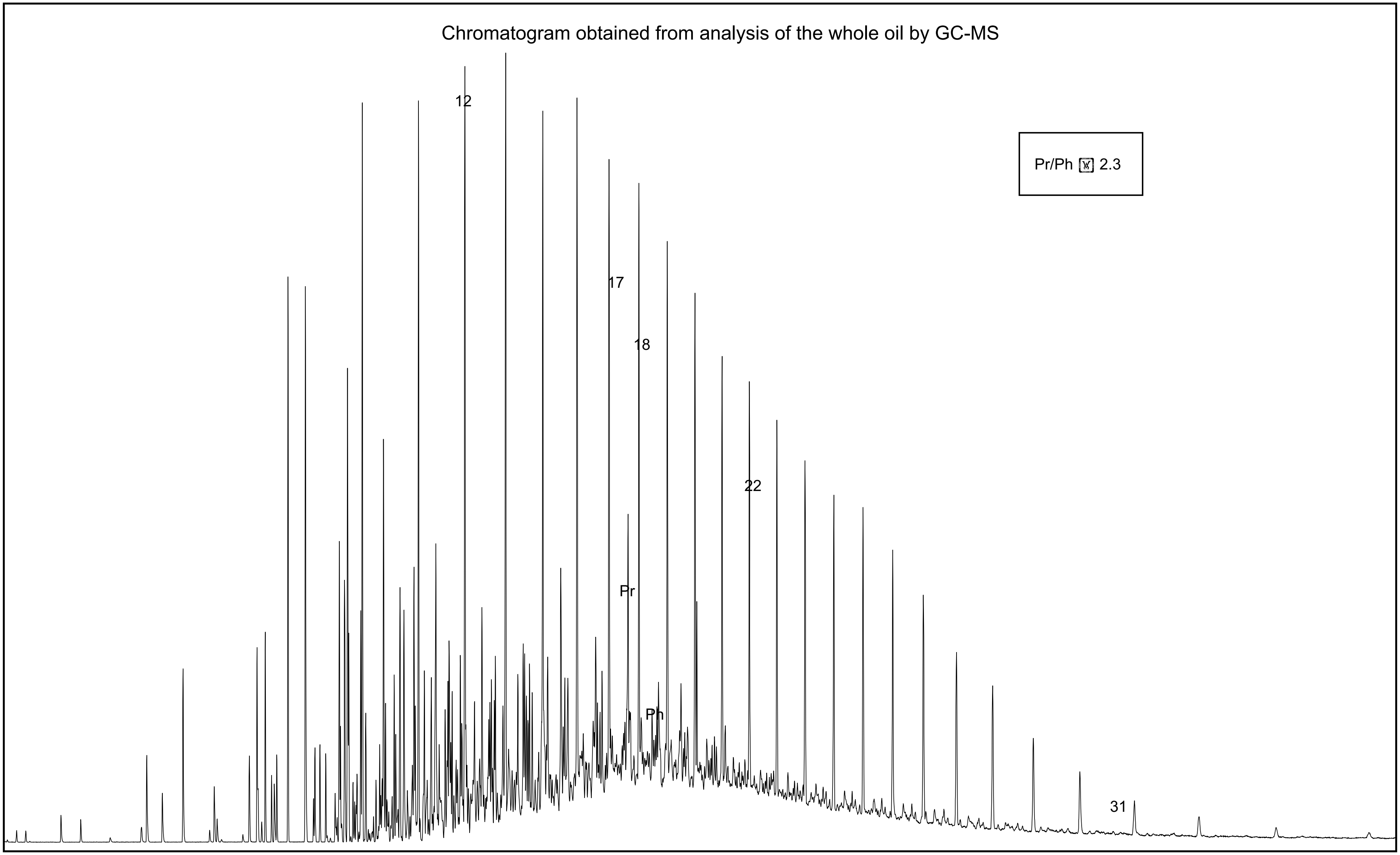
- Whole oil gas chromatography is essential for light hydrocarbon analysis. Also preferred for getting Pr/Ph and Pr/C17 ratios

- Requires dedicated GC and good data system for peak detection and integrations

- Data should be screened manually for accuracy

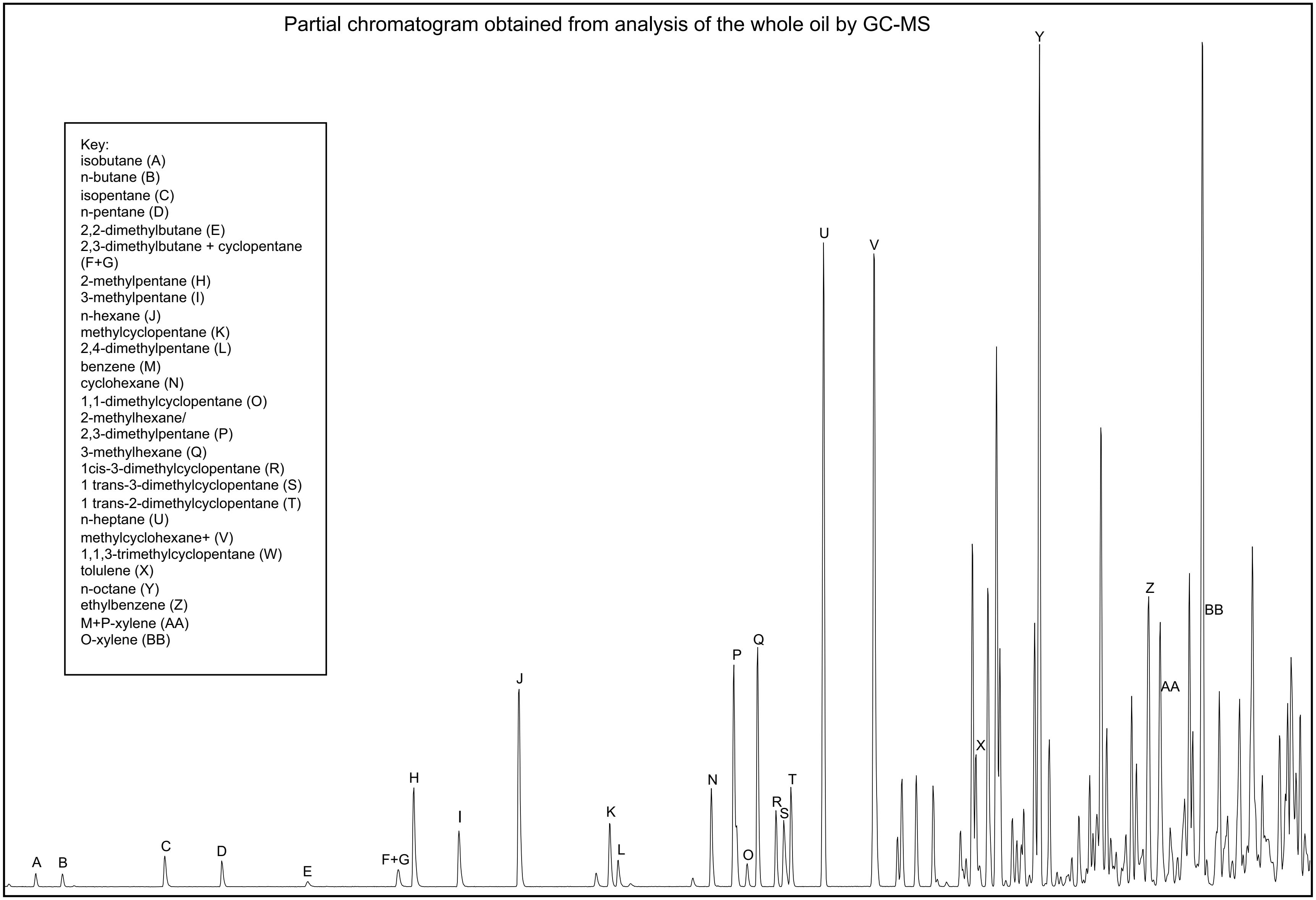
- Pr/Ph and Pr/C_{17} and C17/C27 ratios very useful correlation parameters

Sample : **Carnarvon Condensate**



Chromatogram obtained from analysis of the whole oil by GC-MS

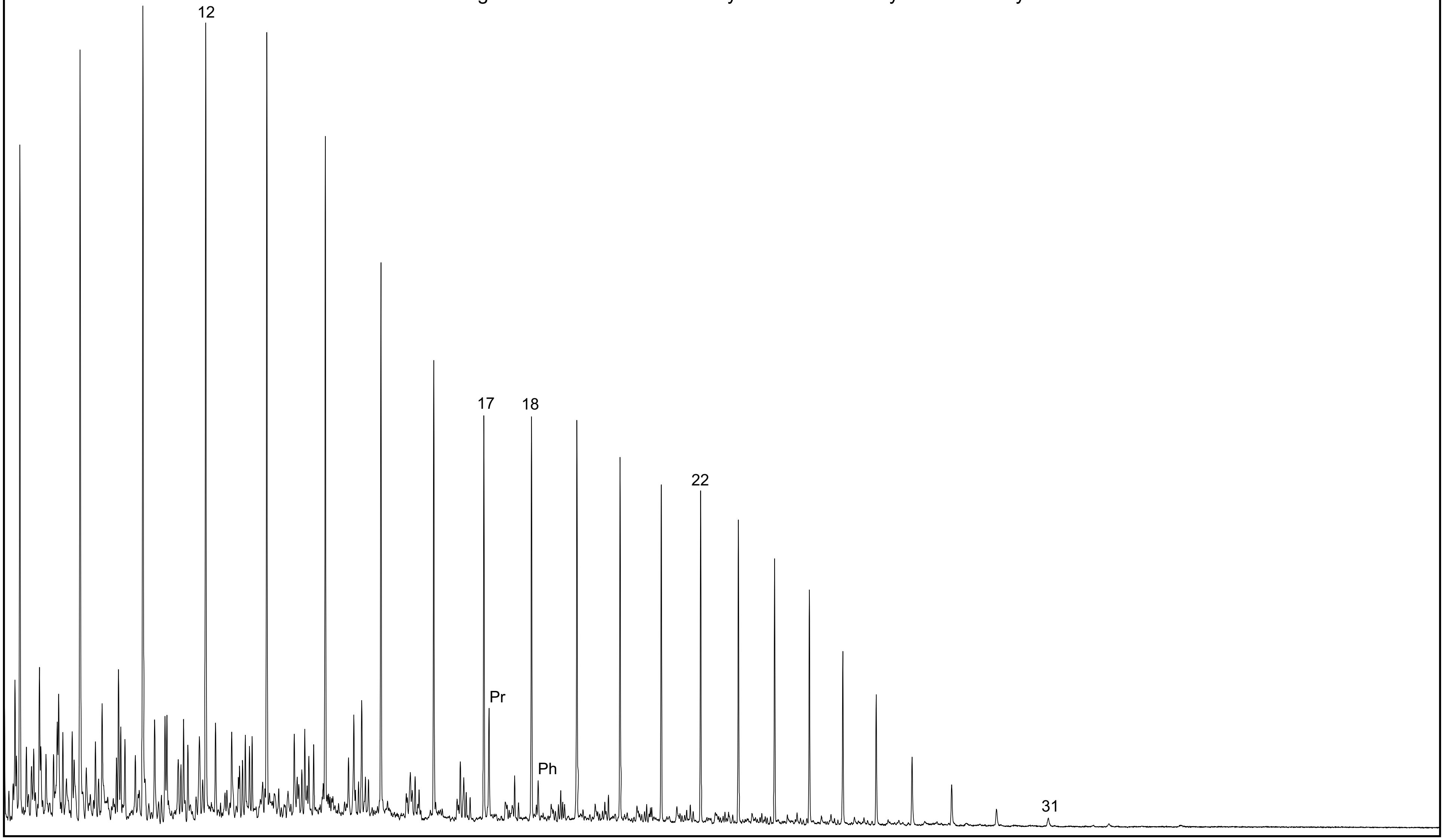
Sample : **Carnarvon Condensate**



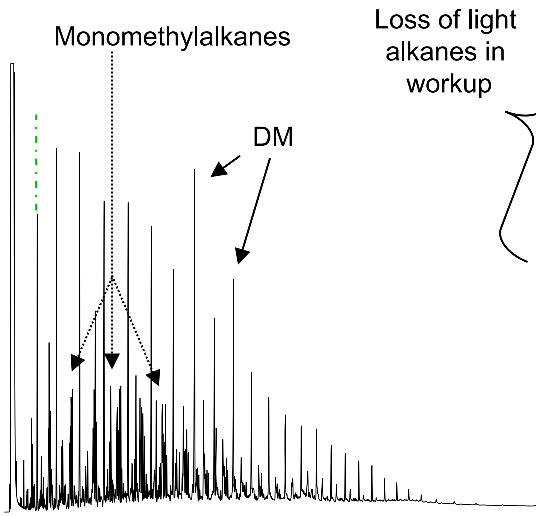
Partial chromatogram obtained from analysis of the whole oil by GC-MS

Sample : **Carnarvon Condensate**

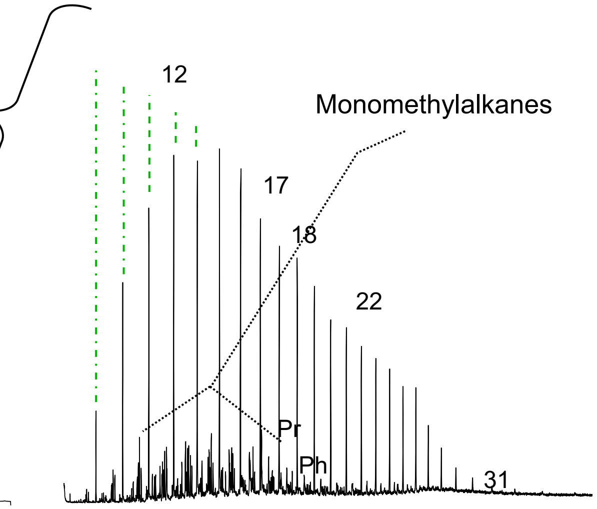
Chromatogram obtained from the analysis of saturated hydrocarbons by GC-MS



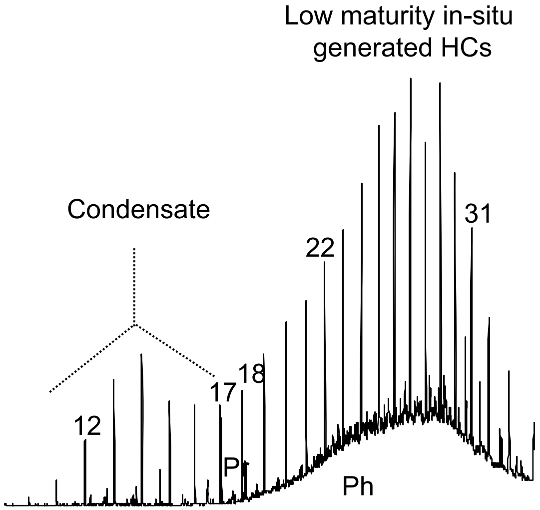
Gas Chromatograms of Bonaparte Basin Oils and Shows



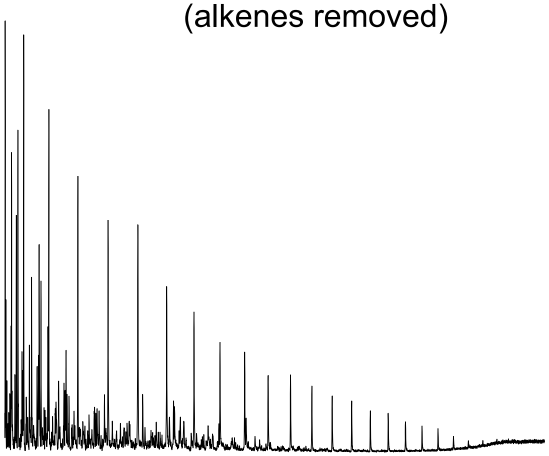
Ludmilla-1 Crude Oil, 3289m (alkenes removed)



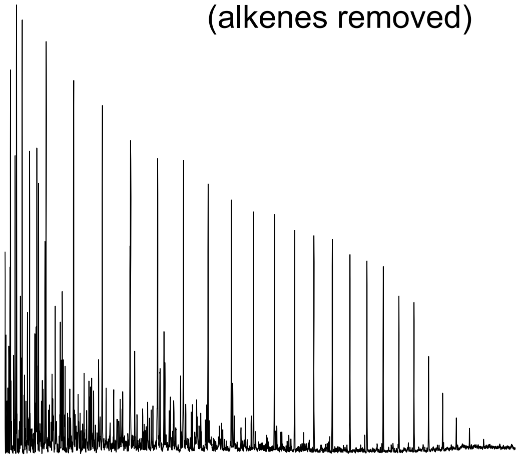
Fannie Bay-1 4143.9 core extract, (alkenes removed)



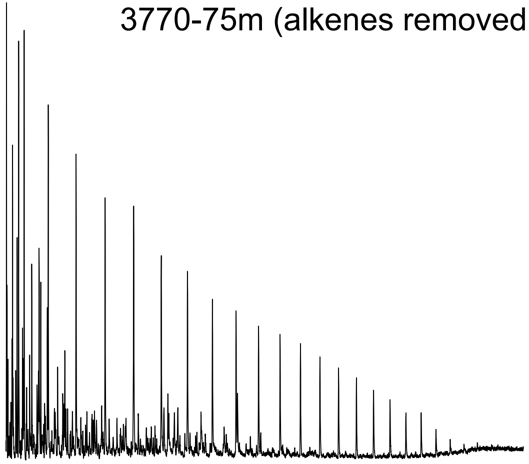
Mandorah-1, extract of cuttings, 3770-75m (alkenes removed)



Corallina-1 Crude Oil



Jahal-1 Crude Oil



Elang-1 Condensate

Biomarkers for Organisms and their Habitats/ Environments 1

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Peters and Moldowan, 1993

Biomarkers for Organisms and their Habitats/Environments

2

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Peters and Moldowan, 1993

Biomarkers for Organisms and their Habitats/Environments 3

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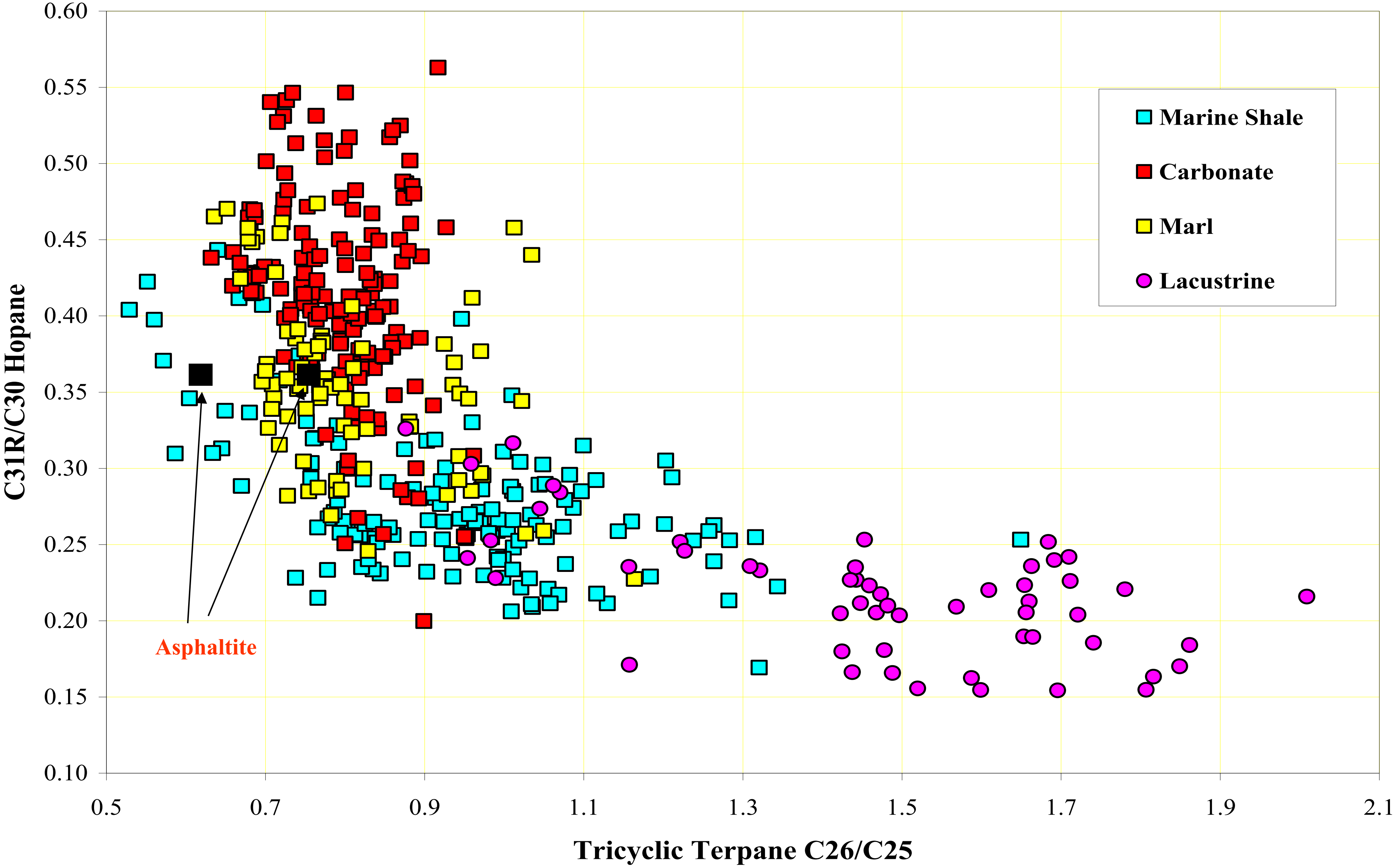
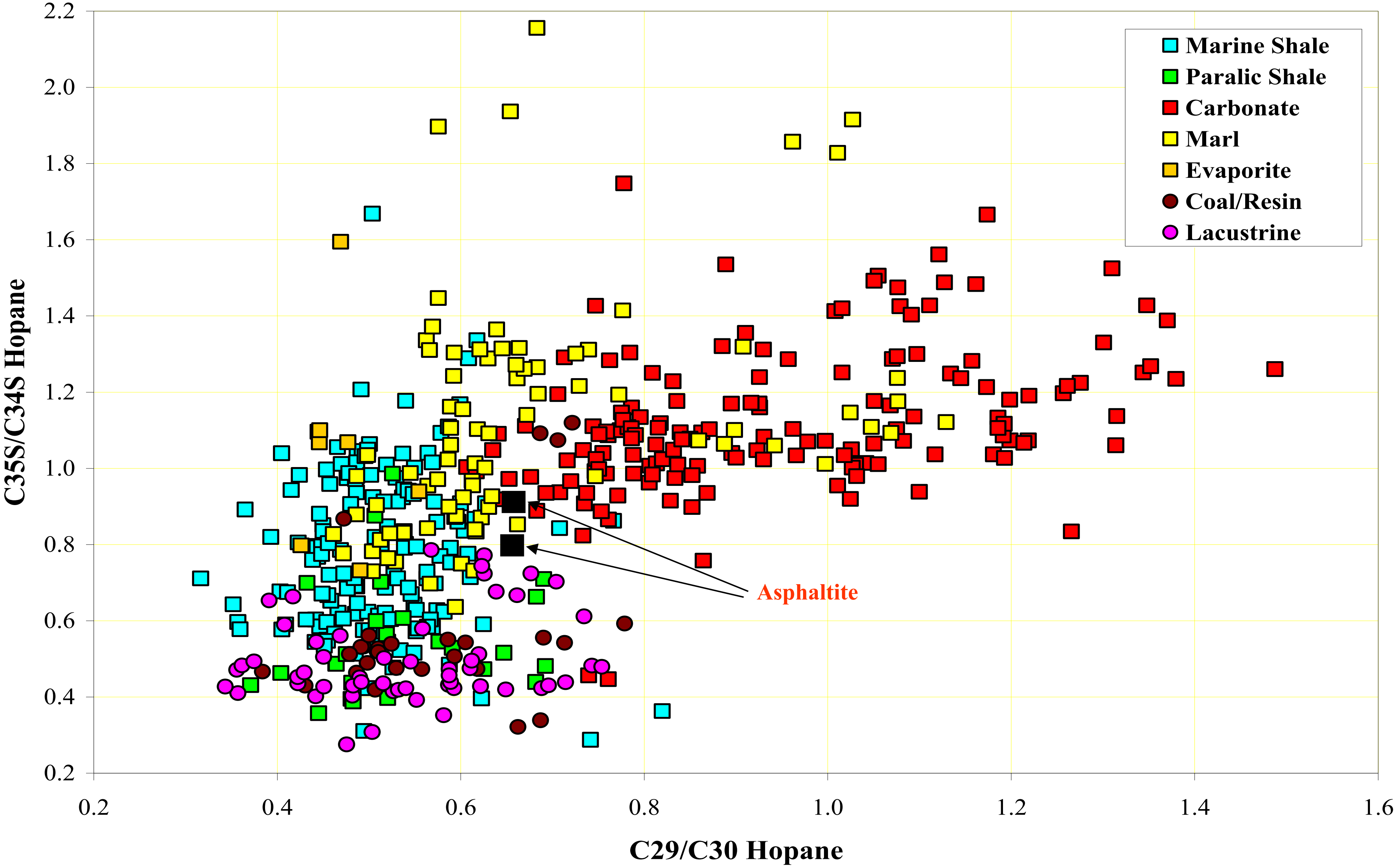
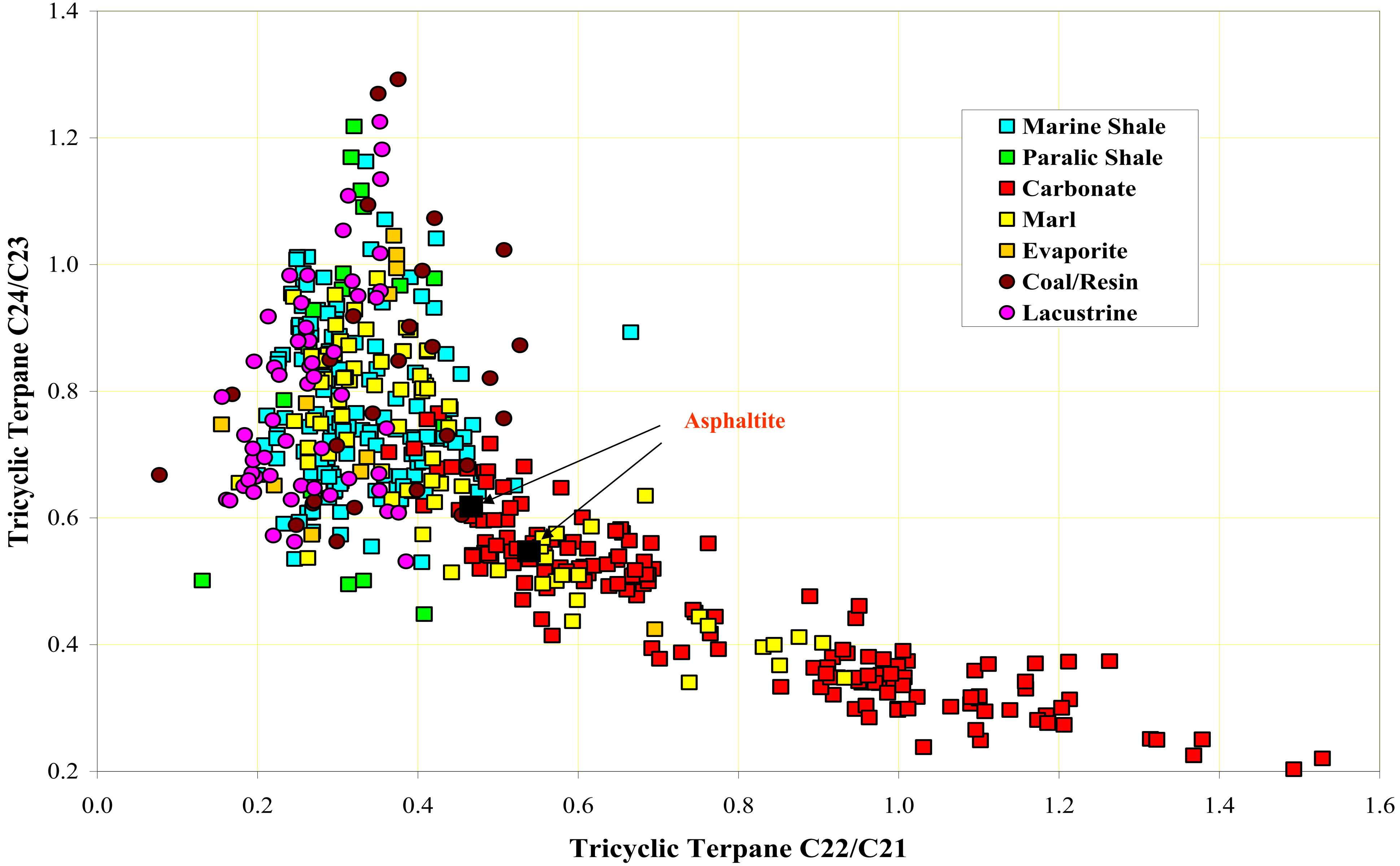
Peters and Moldowan, 1993



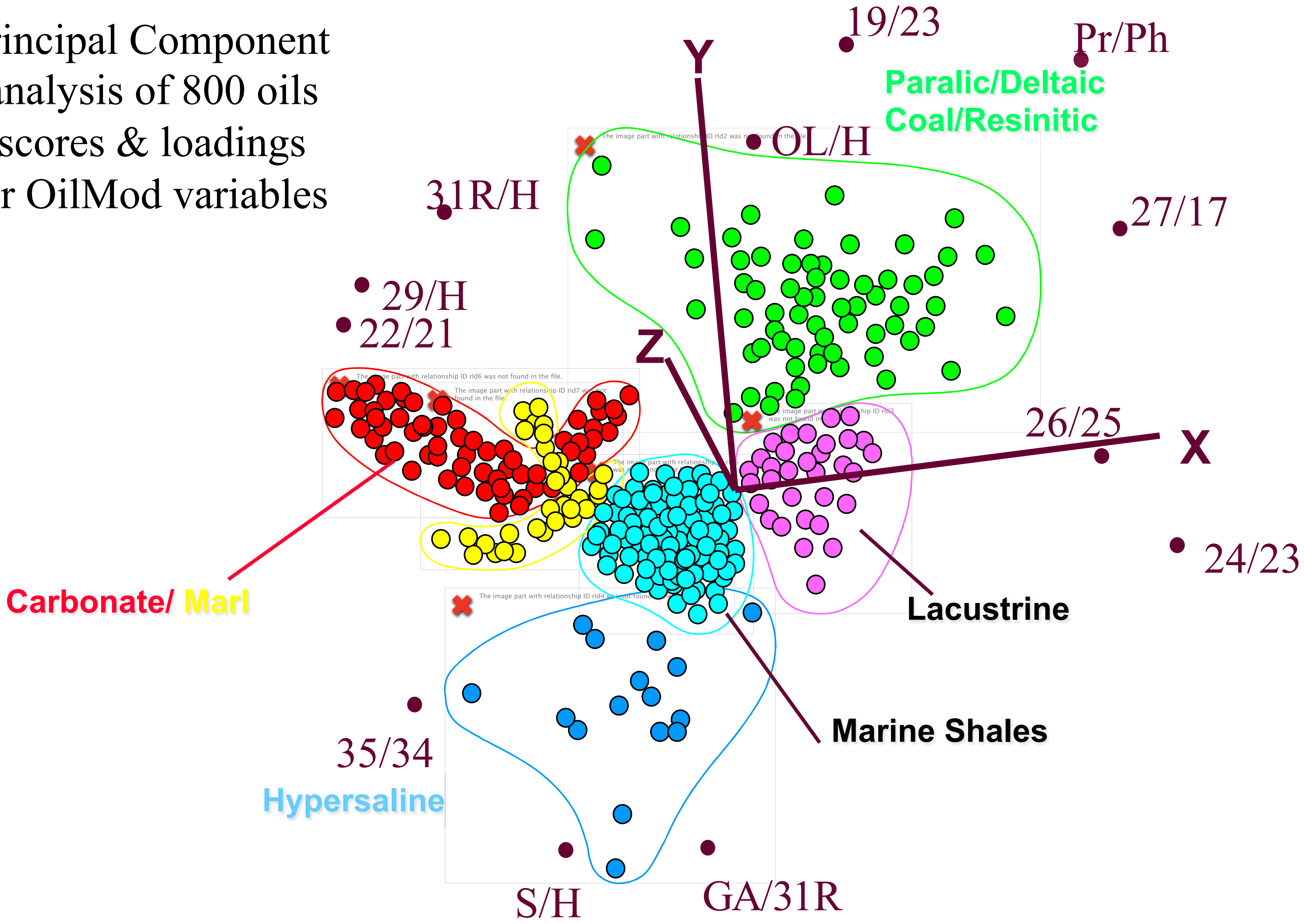
C31R/C30 Hopane
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
Tricyclic Terpane C26/C25
0.5
0.7
0.9
1.1
1.3
1.5
1.7
1.9
2.1
Marine Shale
Carbonate
Marl
Lacustrine
Asphaltite



2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
C35S/C34S Hopane
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
C29/C30 Hopane
Marine Shale
Paralic Shale
Carbonate
Marl
Evaporite
Coal/Resin
Lacustrine
Asphaltite

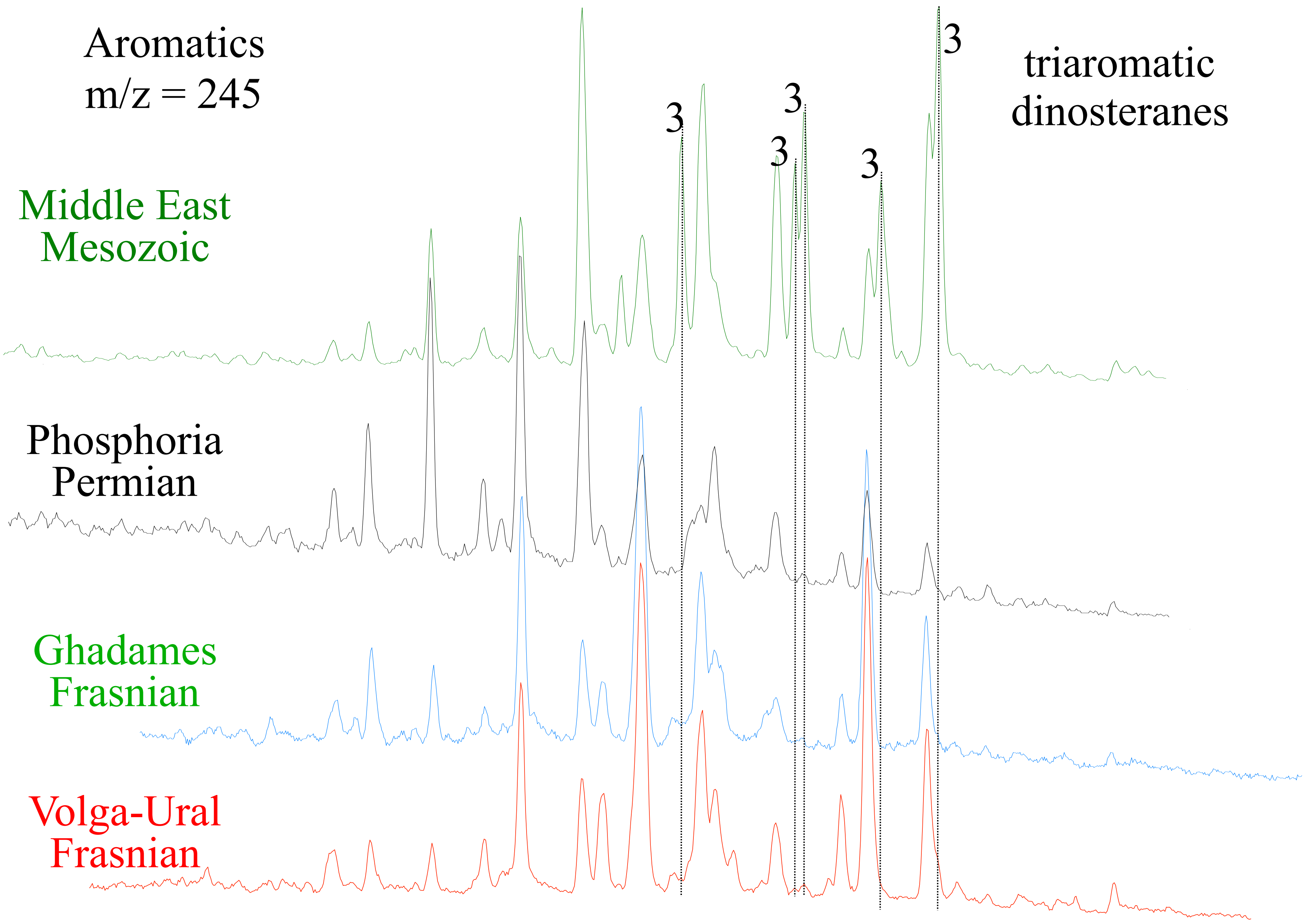

1.4
1.2
1.0
0.8
0.6
0.4
0.2
Tricyclic Terpane C24/C23
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Tricyclic Terpane C22/C21
Marine Shale
Paralic Shale
Carbonate
Marl
Evaporite
Coal/Resin
Lacustrine
Asphaltite

Principal Component analysis of 800 oils scores & loadings for OilMod variables



Age Diagnostic Biomarkers

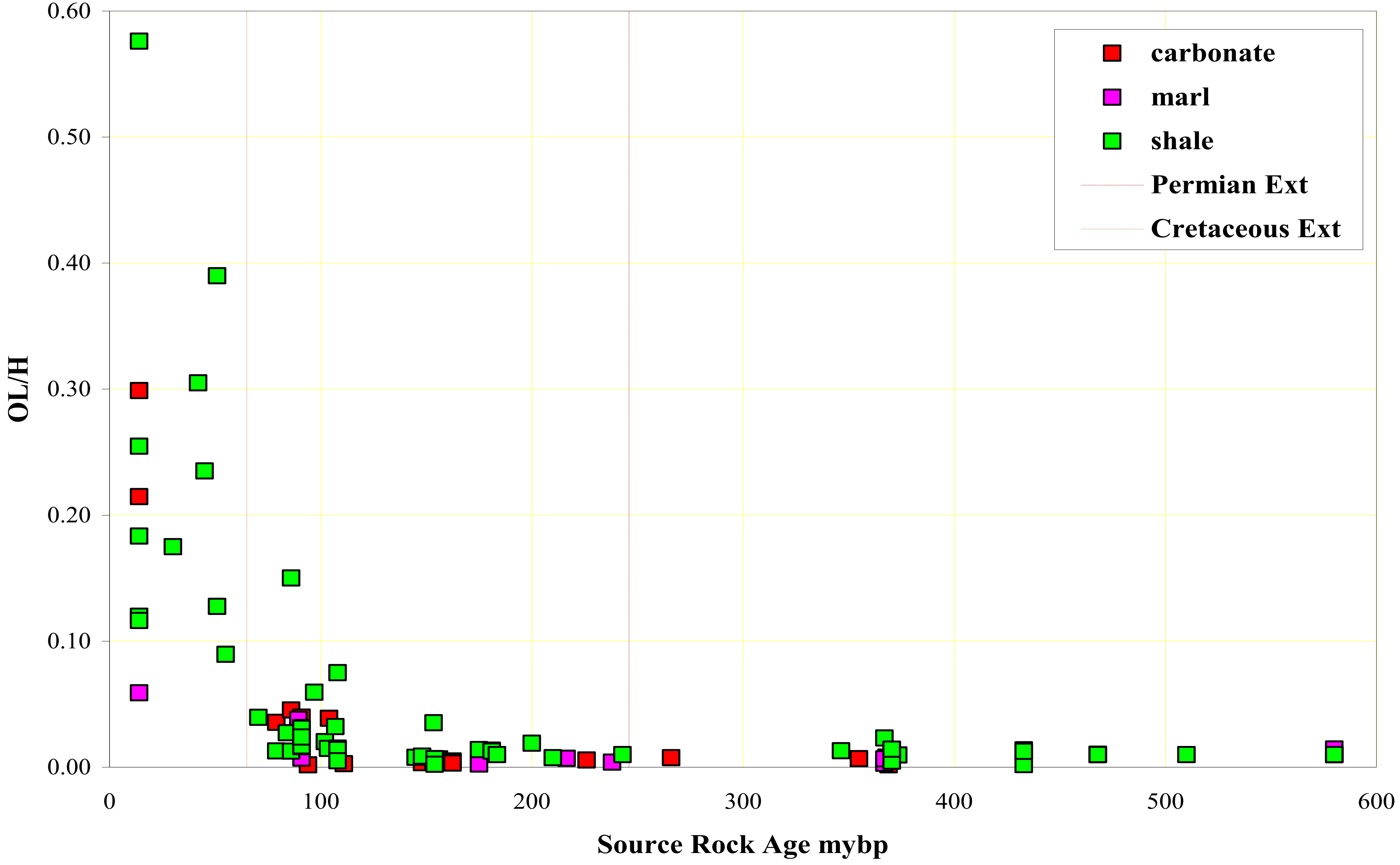
- Biochemistry is very conservative
- No succession as for body fossils
- Strong environmental controls on isotopes
- Strong facies and other controls on biomarkers
  - marine/non-marine
  - palaeogeography
- Consider a variety of clues


Aromatics
m/z = 245
triaromatic
dinosteranes
3
3
3
3
3
3
Middle East
Mesozoic
Phosphoria
Permian
Ghadames
Frasnian
Volga-Ural
Frasnian

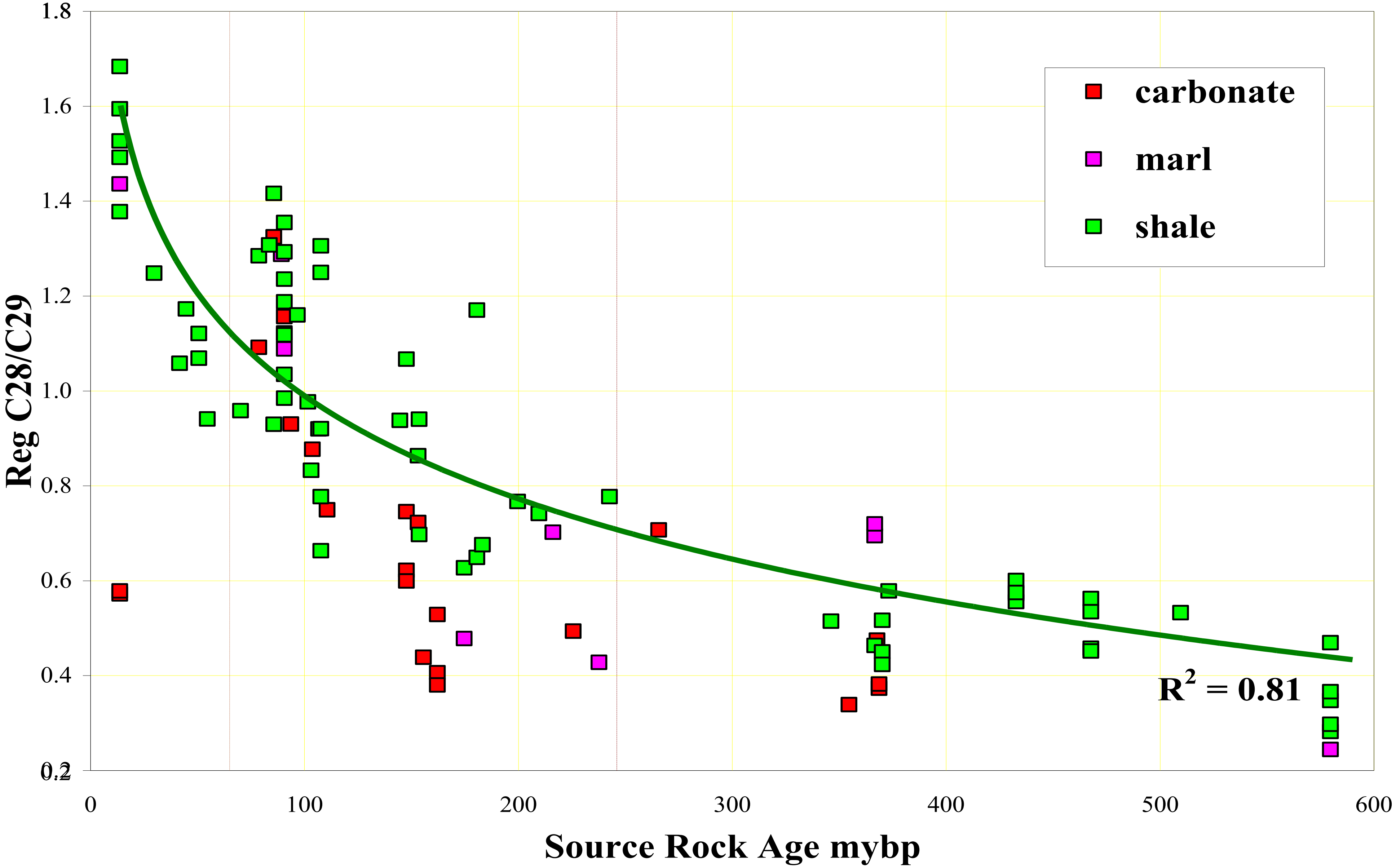
Age Diagnostic Biomarkers

Feature	Biological Origin	Oldest Observation
4-methyl steranes (dinosteranes)	*Dinoflagellates*	Proterozoic but abundant after mid-Triassic
4-methyl steranes 24-ethyl-4 (Me)-cholestanes	*Dinoflagellates and Prymnesiophytes*	Proterozoic but abundant after Permian
n-propylcholestanes (C_{30})	*Chrysophytes*	Proterozoic but abundant after Ordovician
Retene	*Gymnosperms* (pines)	Abundant M. and L. Jurassic
Diterpenoids eg beyerane, phyllocladanes, pimarane, kaurane	*Gymnosperms*	L. Carboniferous (Maastrichtian onwards)
Triterpenoids eg oleananes	*Angiosperms*	L. Cretaceous
Bicadinanes	*Dipterocarpaceae*	L. Cretaceous
Botryococcane	*Botryococcus* (red race)	Tertiary

Oleanane vs Source Rock Age



Sterane C_{28}/C_{29} vs Source Rock Age



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Fall 2011