12.007 Geobiology
Spring 2009

What about all that buried organic matter?

- Methods for characterization of fossil carbon
- Petroleum Generation
  - Migration, leakage and remineralization
- Conversion to Deep Gas
  - Leakage to surface; hydrate formation
- Uplift and Weathering Processes
  - Microbial utilization
- Alternative Hypotheses
  - ‘Myth of Fossil Fuels’

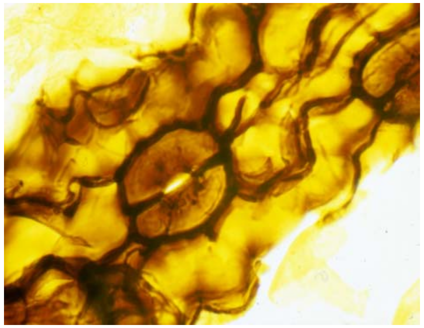
Thomas Gold

- Hydrocarbons are primordial
- As they upwell into the crust, microbial life invades for a free meal
- Hydrocarbons are not biology 'reworked' but , rather, geology reworked by biology thus explaining the presence of all those biological signatures in oils

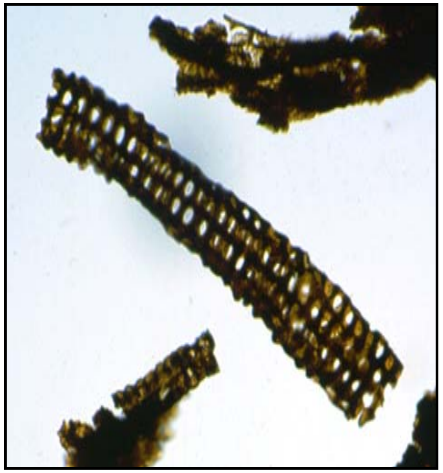
KERGEN

Kerogen is the component of organic matter that is insoluble in inorganic and organic solvents (Durand, 1980). Bitumen is the soluble component. Both widely distributed in sediments; sometimes massive accumulations as in coal and oil deposits

Ordovician spinose
acritarch:
saline indicator



Jurassic cuticle with
Stomate:
Terrestrial indiactor



Permian tracheidal
woody tissue

Dinoflagellate
Modern marine alga

Microscopic examination cansometimes give information on geological age, paleoenvironment, thermal history (colour)- palynology, petrography
But most organic matter is amorphous and unicentifiable – need chemical means to quantify and evaluate origins……….
Bulk Properties, carbon isotopes, biomarkers

Bulk Properties of a carbon-rich rock

Total organic carbon %TOC

% Total C, H, N, O, S

$\delta^{13}C$ (now easily $\delta^{18}O$, δD, $\delta^{15}N$, $\delta^{34}S$)

elemental H/C ratio (originally 1.3→ 0 for C)

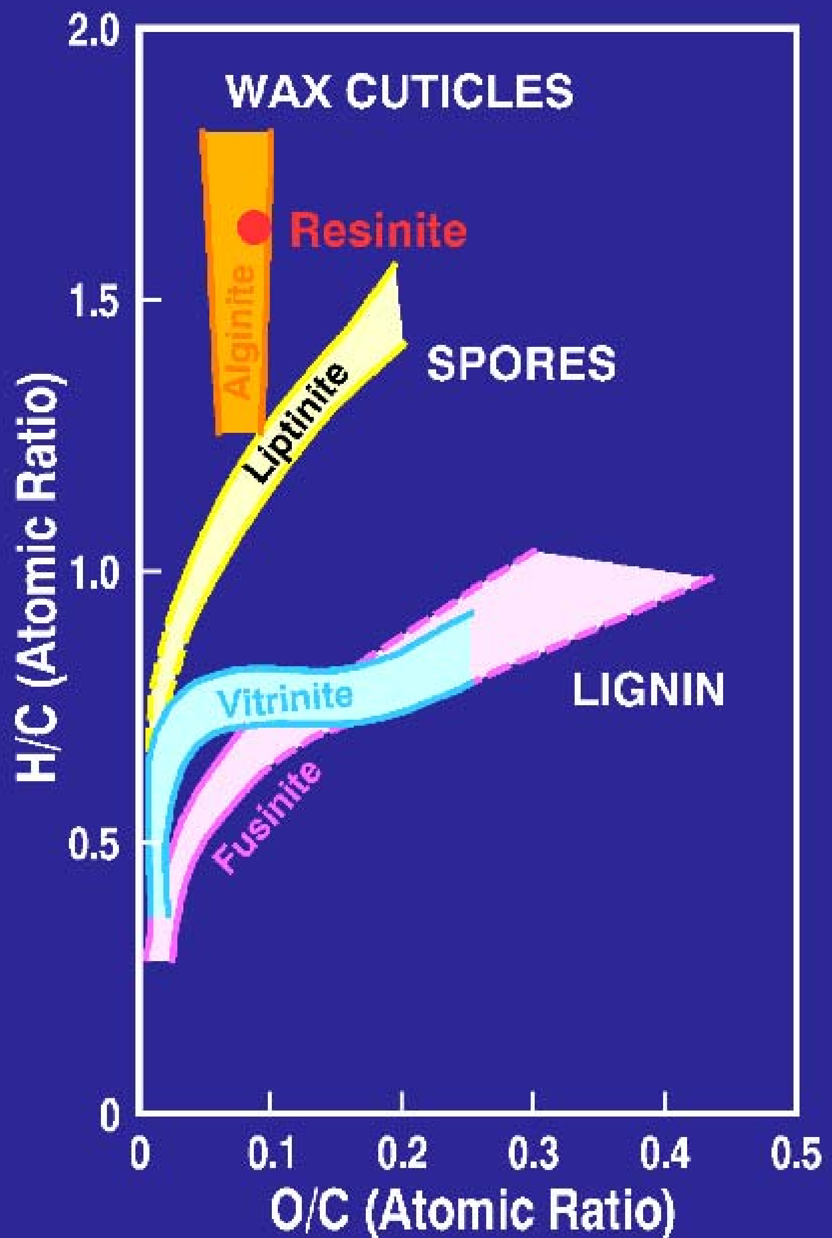
solid phase nmr → environment of C

ie aromatic C,H vs saturate C………………..

The above give limited information on provenance

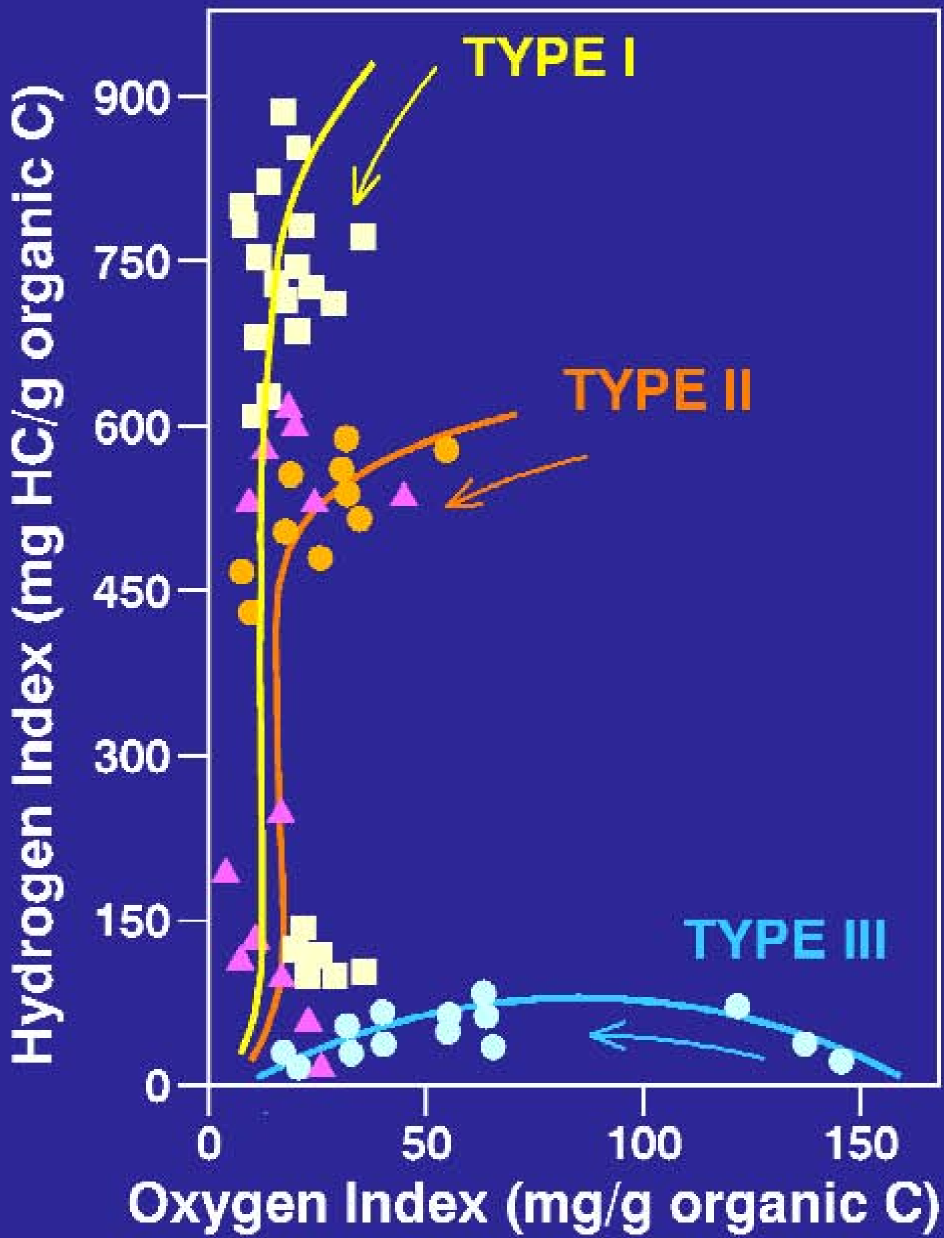
Further characterisation by pyrolysis (Rock-Eval), pyrolysis-GC, pyrolysis GC-MS and laser ablation-MS

Solvent extraction and GC, GC-MS give information on bitumen composition



Van Krevellen diagram of elemental H/C

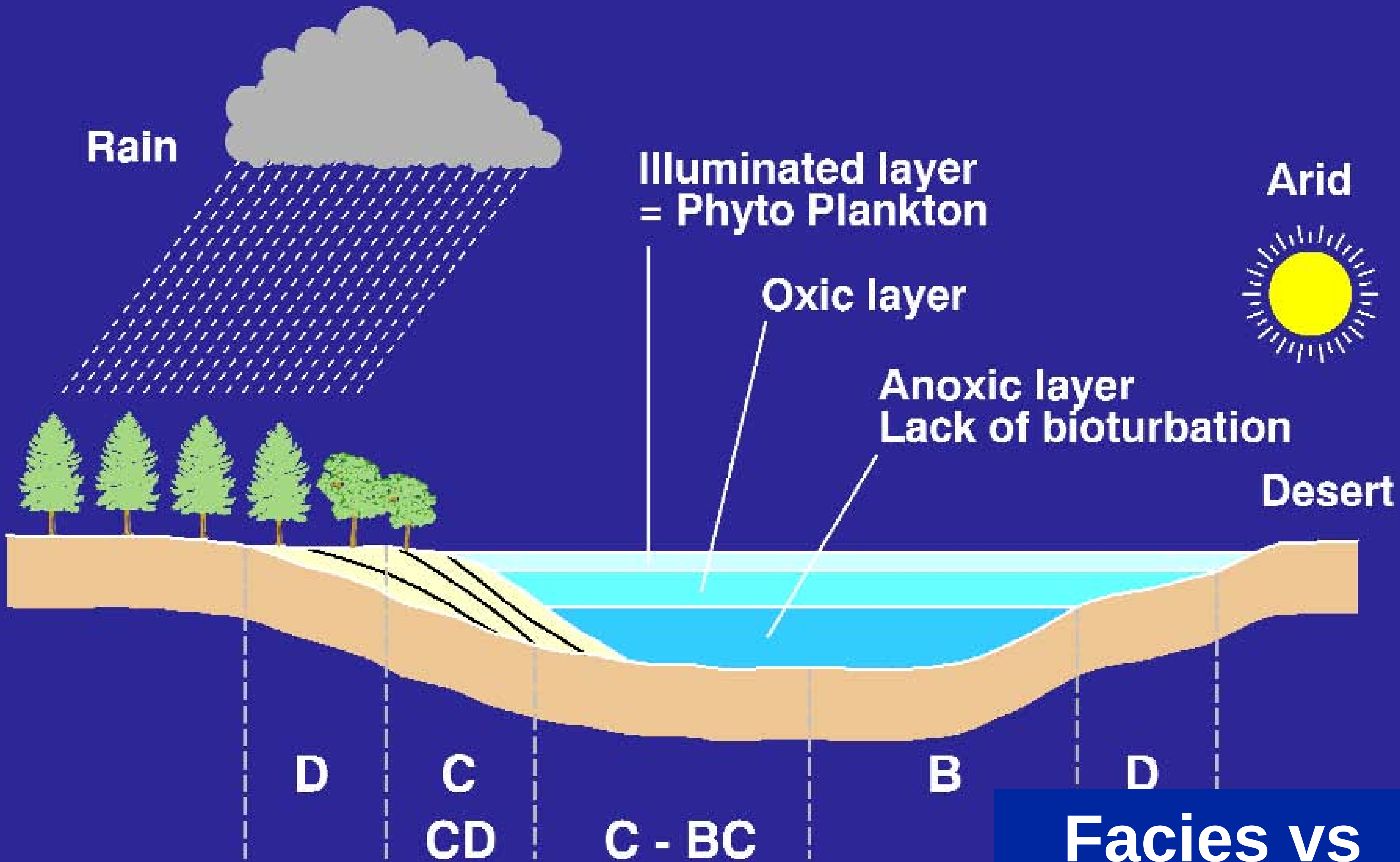
Typical tool to crudely characterize OM



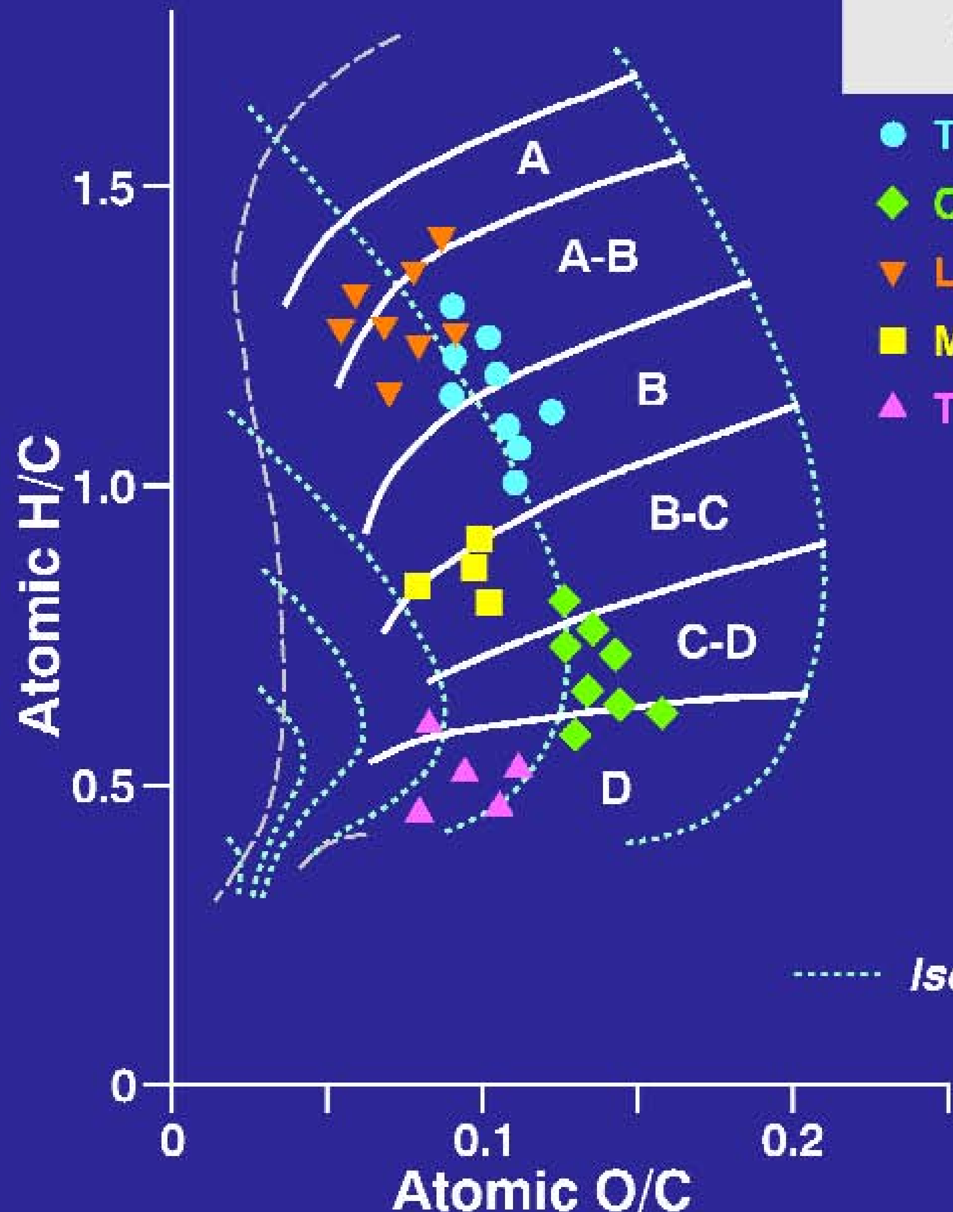
Rock-Eval Pyrolysis

OI vs HI

Facies vs Environment



Facies vs Environment

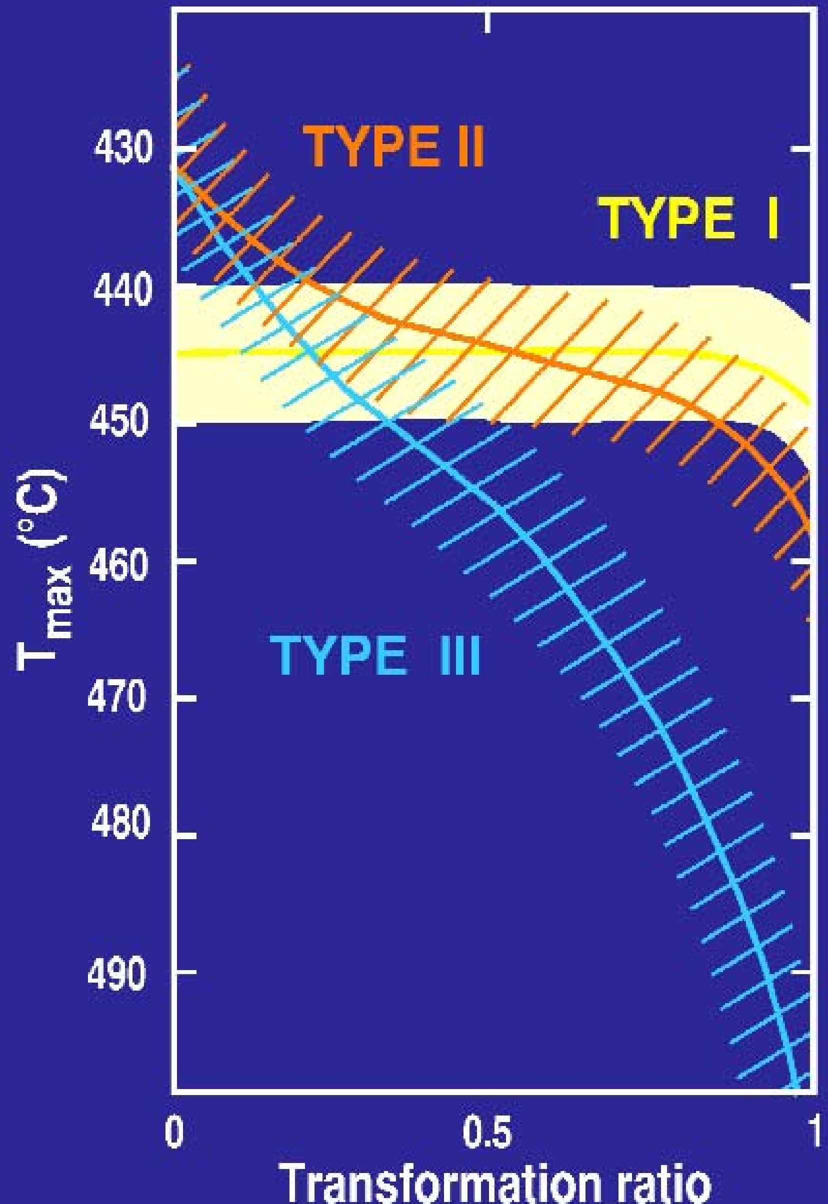


Age	Organic Facies	Depositional Environment
Tertiary	B,BC	*Marine - mixed*
Cretaceous	CD	*Open marine*
L. Jurassic	B	*Restricted marine*
M. Jurassic	C	*Terrestrial - coal*
Triassic	D	*Terrestrial - Red bed*

Isorank, % vitrinite reflectance

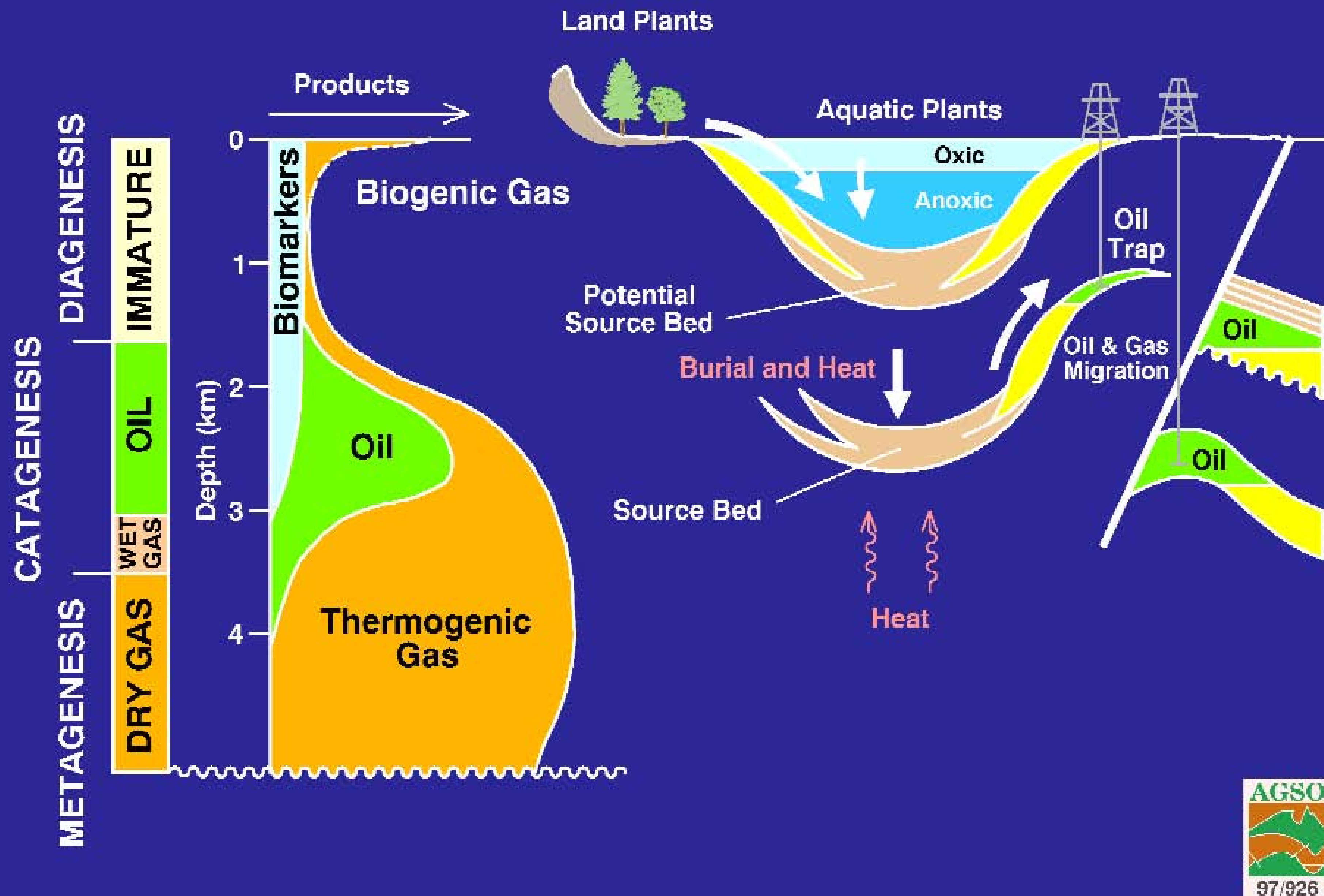
Source Controls on Organic Carbon

	Sapropelic	Humic		
Kerogen	Algal + Amorphous	Herbaceous	Woody	Coaly
Macerals	Liptinite	Exinite	Vitrinite	Inertinite
	Alginite + Amorphous	Sporinite Cutinite Resinite	Telinite Collinite	Fusinite Micrinite
Kerogen	Types I, II	Type II	Type III	Type III/IV
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	.3-0.02
ORGANIC SOURCE	Marine & lacustrine	Terrestrial	Terrestrial	Terrestrial &recycled
FOSSIL FUELS	Oil OIl shales, boghead and cannel coals	Oil and gas	Gas coals	No oil, low gas



MATURATION INDEX / TRANSFORMATION RATIO FOR MAIN KEROGEN TYPES

Kerogen Type vs Burial Response


DIAGENESIS
CATAGENESIS
METAGENESIS
IMMATURE
OIL
WET GAS
DRY GAS
Depth (km)
0
1
2
3
4
Biomarkers
Products
Biogenic Gas
Oil
Thermogenic Gas
Land Plants
Aquatic Plants
Oxic
Anoxic
Oil Trap
Potential Source Bed
Burial and Heat
Oil & Gas Migration
Oil
Oil
Source Bed
Heat
AGSO
97/926

Oils

Bulk Properties

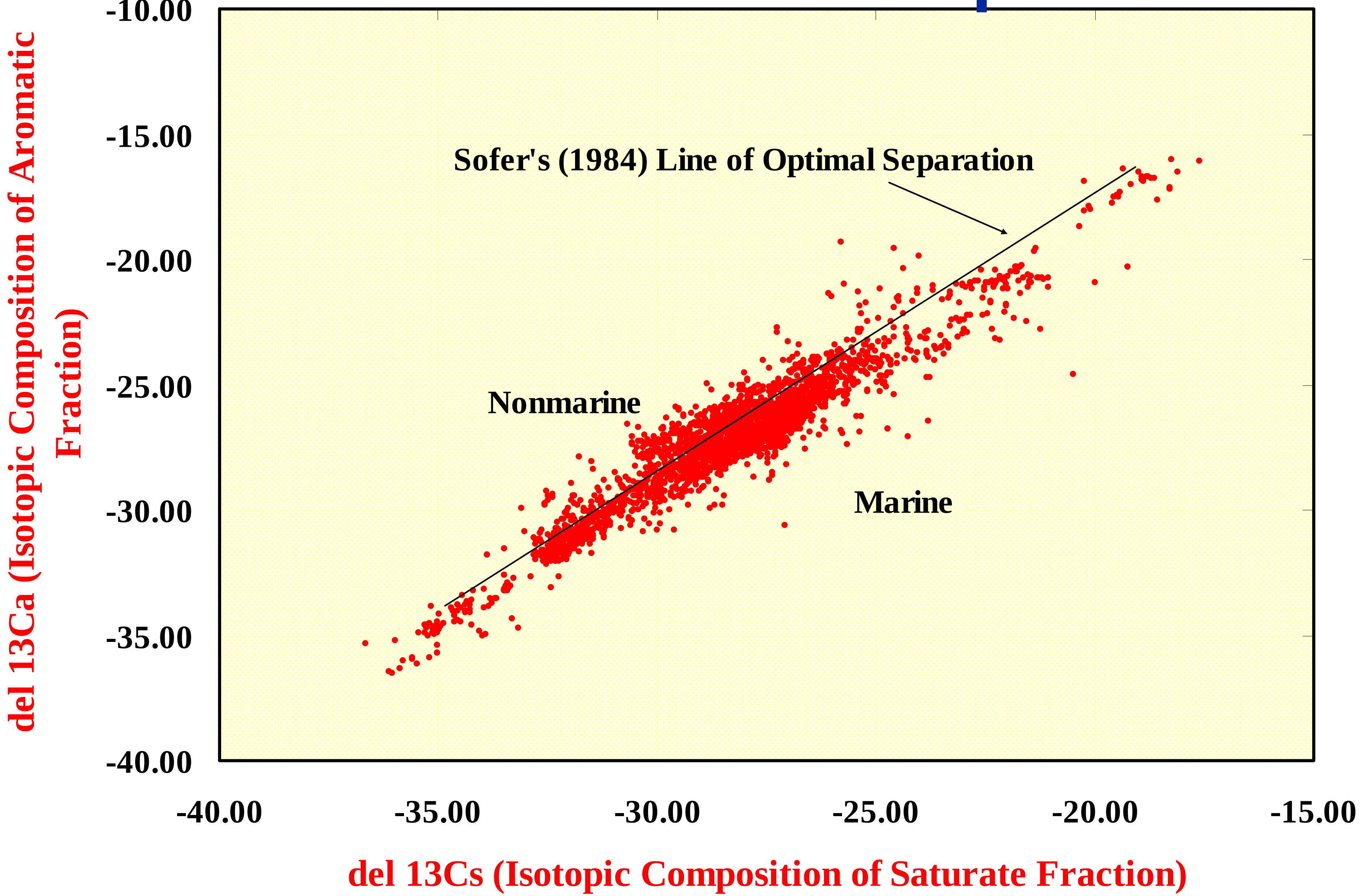
- API gravity. USA measure related to specific gravity

- 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°

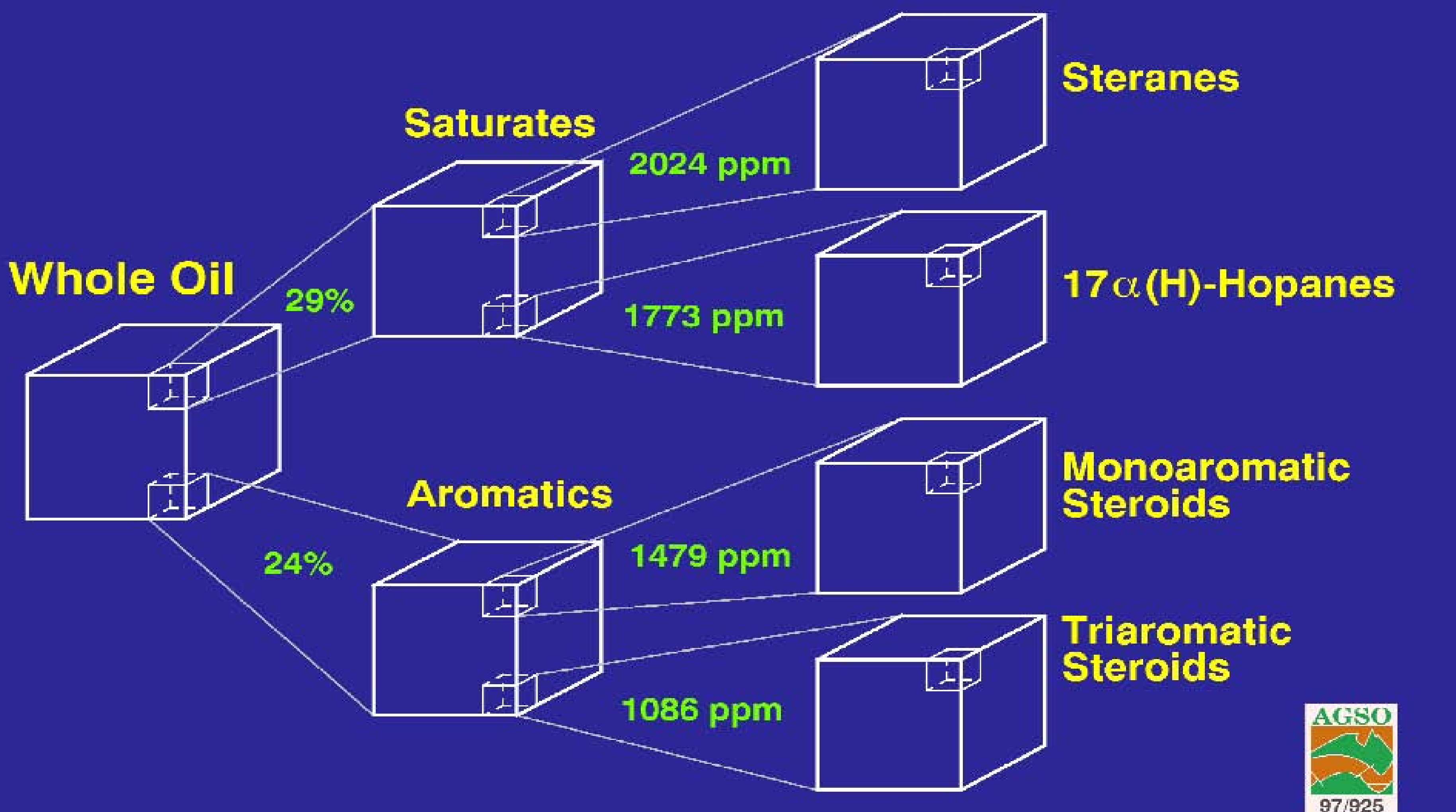
Sulfur, Nickel and Vanadium

- 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.

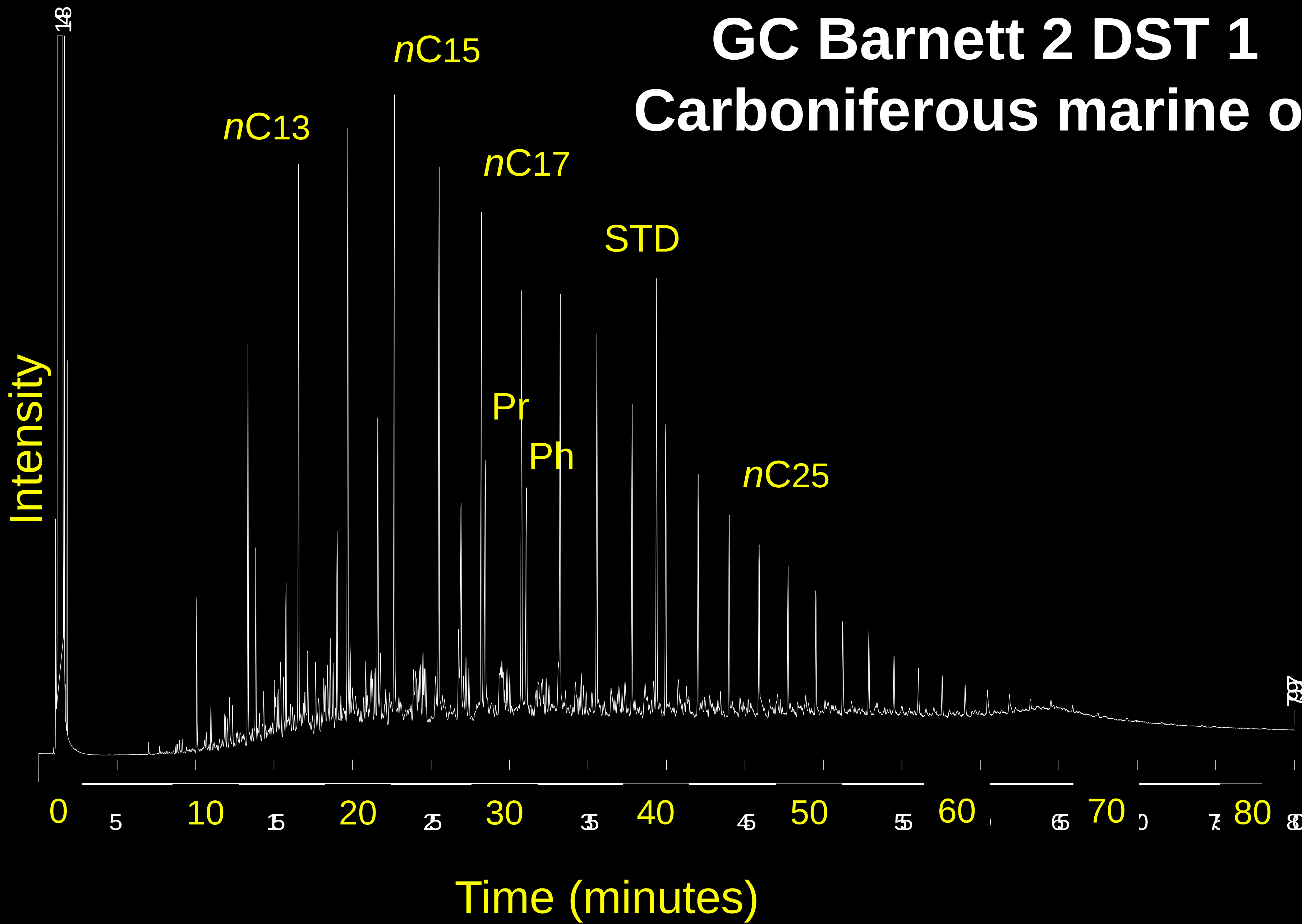
Bulk Stable C-Isotopes



Petroleum Composition



GC Barnett 2 DST 1
Carboniferous marine oil

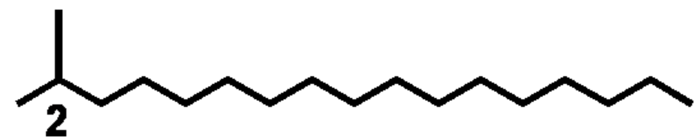


HYDROCARBONS

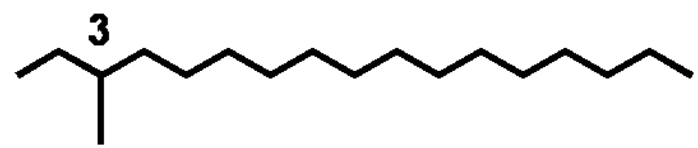
ACYCLIC & MONOCYCLIC ALKANES

n-alkane C_{17}

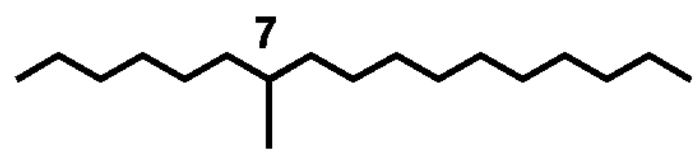
2-methyl- or isoalkane C_{18}



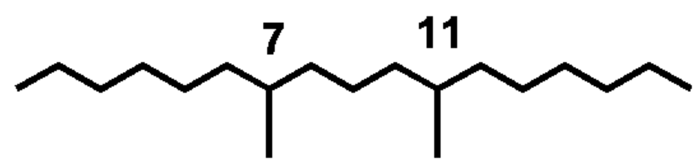
3-methyl- or anteisoalkane C_{18}



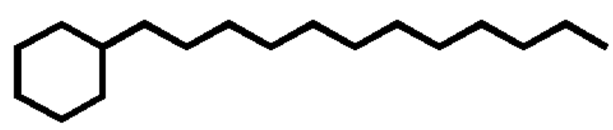
7-methyl alkane C_{18}



7,11-dimethyl alkane C_{19}



cyclohexyl alkane C_{18}



HYDROCARBONS

ACYCLIC ISOPRENOID ALKANES

Regular

Pristane C_{19}

Regular

Phytane C_{20}

Irregular

Botryococcane

HYDROCARBONS

ACYCLIC ISOPRENOID ALKANES

Irregular C_{20} branched

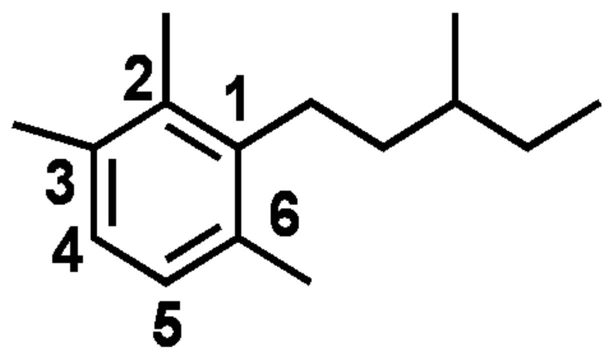
Irregular C_{25} branched

Derived from diatoms

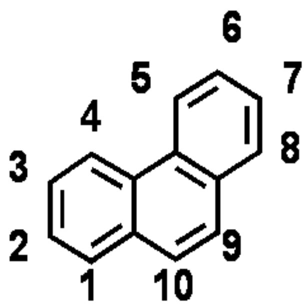
MONOAROMATIC HYDROCARBONS

Toluene

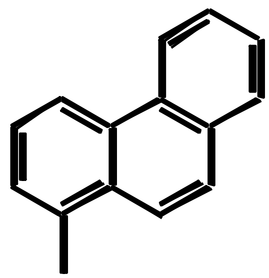
Tri-substituted alkyl benzene



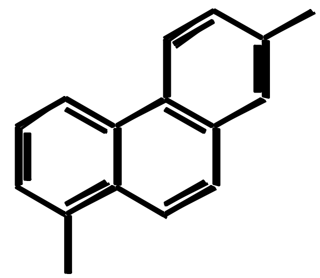
PETROGENIC PAHs



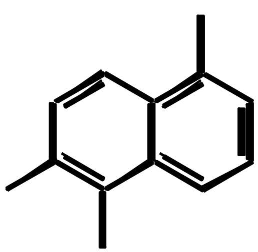
PHENANTHRENE
178 Da



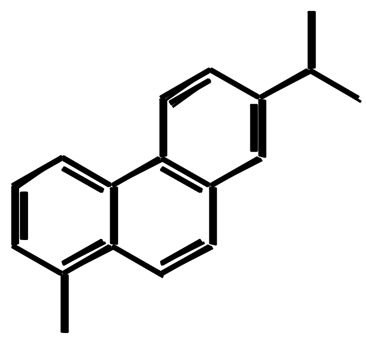
1-METHYL-
PHENANTHRENE 192 Da



1,7-DIMETHYL-
PHENANTHRENE 206 Da

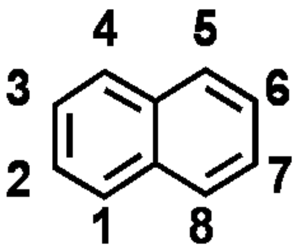


1,2,5-TRIMETHYL-
NAPHTHALENE
156 Da

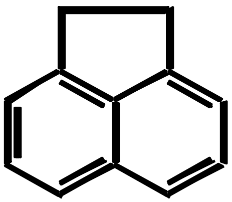


RETENE
234 Da

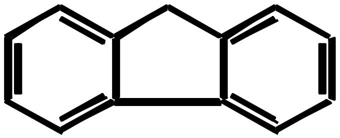
LOW MW PAHs



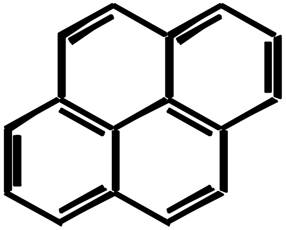
NAPHTHALENE
128 Da



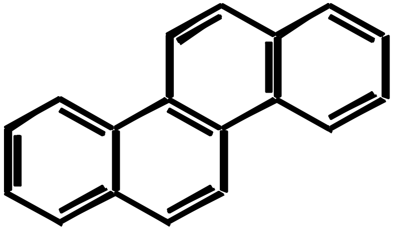
ACENAPTHENE
154 Da



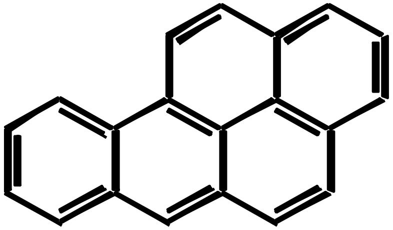
FLUORENE
166 Da



PYRENE
202 Da

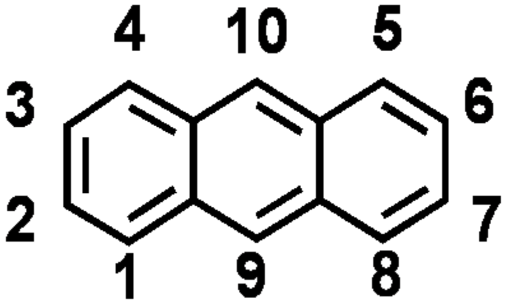


CHRYSENE
228 Da



BENZO(a)PYRENE
252 Da

COMBUSTION PAHs



ANTHRACENE

CORONENE

PENTACENE

Flotsam-Ocean Wandering Oils and Ambers

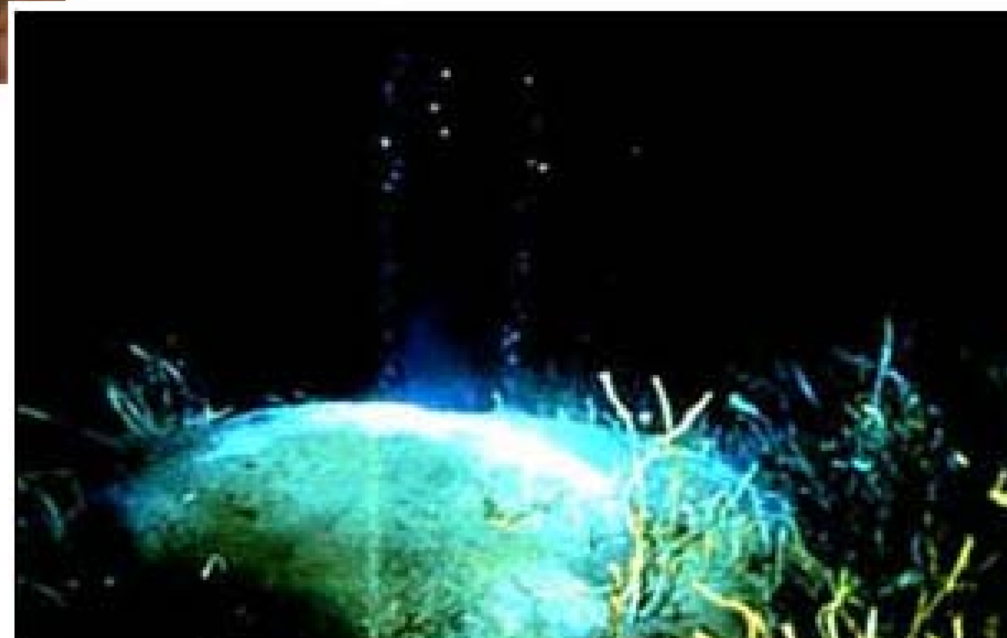
Waxy and asphaltic bitumens

Images courtesy of Dianne Edwards, Geoscience Australia. Used with permission.

http://geology.usgs.gov/connections/images/mms_images/laminae.jpg

Hydrate seams in mud

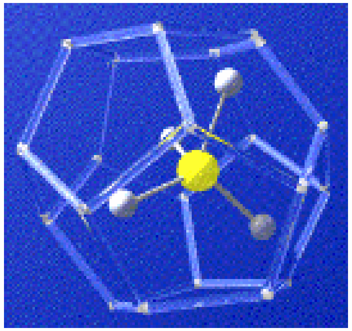
Hydrate outcropping on seafloor and colonised by chemosynthetic ecosystem



Methane actively dissociating from a hydrate mound

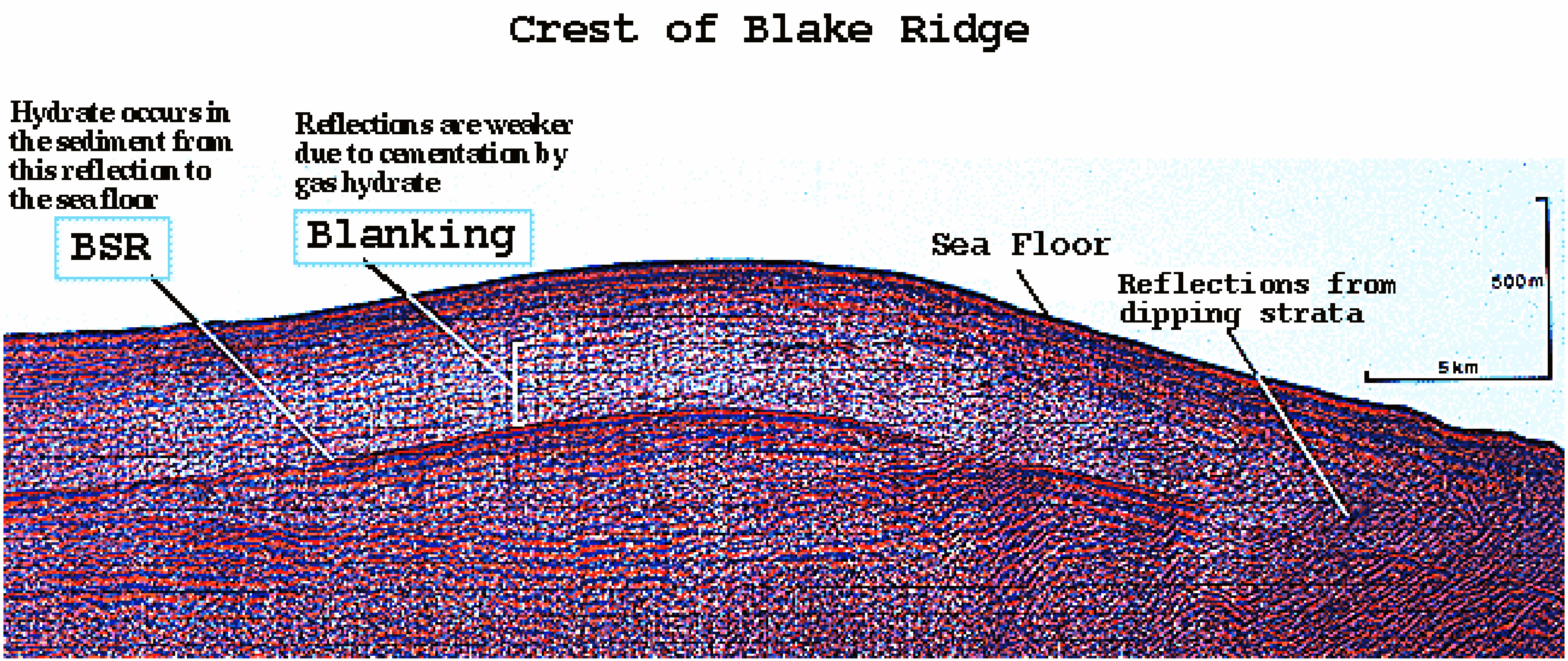
Courtesy USGS

http://geology.usgs.gov/connections/images/mms_images/seafloor_mounds.jpg



A gas hydrate is a crystalline solid; its building blocks consist of a gas molecule surrounded by a cage of water molecules. Thus it is *similar to ice*, except that the crystalline structure is stabilized by the guest gas molecule within the cage of water molecules. Many gases have molecular sizes suitable to form hydrate, including such naturally occurring gases as carbon dioxide, hydrogen sulfide, and several low-carbon-number hydrocarbons, but most marine gas hydrates that have been analyzed are methane hydrates.

Courtesy USGS
http://woodshole.er.usgs.gov/project-pages/hydrates/what.html



Courtesy USGS
http://woodshole.er.usgs.gov/project-pages/hydrates/

Methane

Capacity to Trap Gas

Hydrate forms as cement in the pore spaces of sediment as well as in layers and nodules of pure hydrate. Hydrates also seem to have the capacity to fill sediment pore space and reduce permeability, so that hydrate-cemented sediments act as seals for gas traps.

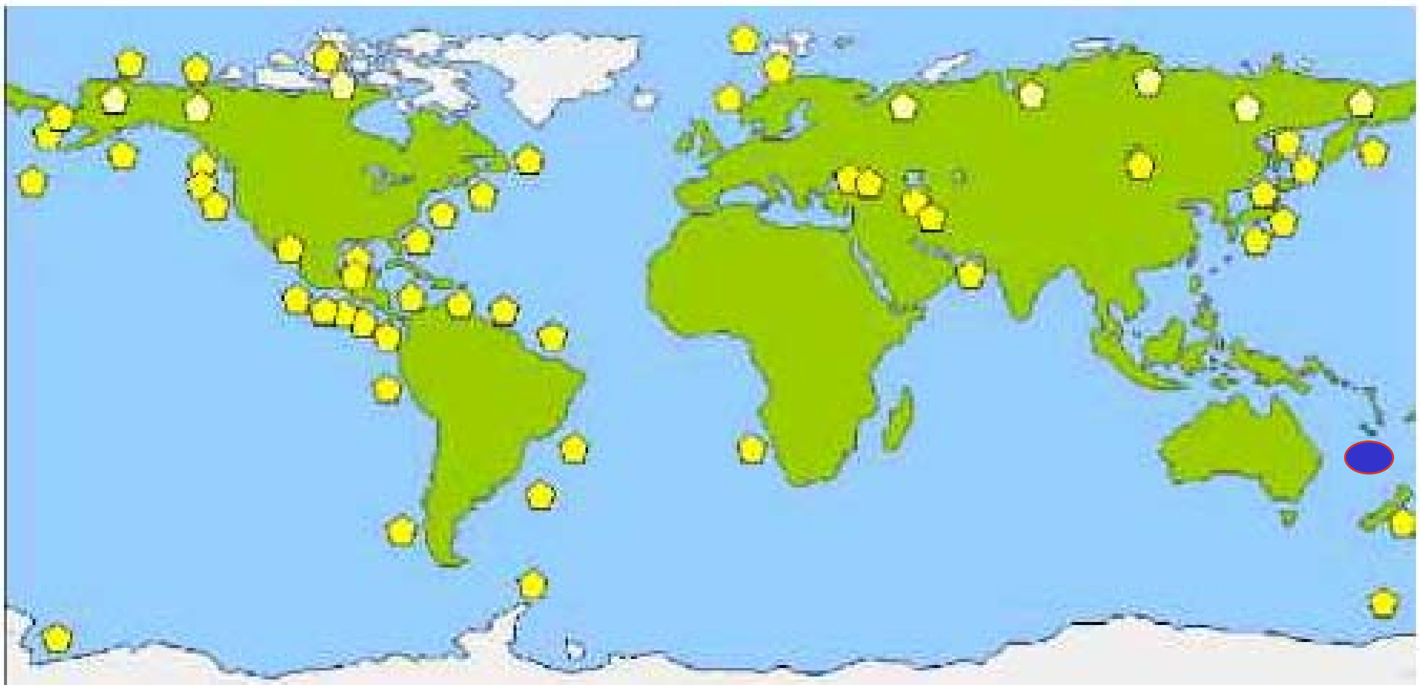
Gas hydrates are stable at the temperatures and pressures that occur in ocean-floor sediments at water depths greater than about 500 m, and at these pressures they are stable at temperatures above those for ice stability. Gas hydrates also are stable in association with permafrost in the polar regions, both in offshore and onshore sediments. Gas hydrates bind immense amounts of methane in sea-floor sediments. **Hydrate is a gas concentrator**; the breakdown of a unit volume of methane hydrate at a pressure of one atmosphere produces about 160 unit volumes of gas. The worldwide amount of methane in gas hydrates is considered to contain at least 1x104 gigatons of carbon in a very conservative estimate). This is *about twice the amount of carbon held in all fossil fuels on earth*.

Gas hydrate concentration occurs at depocenters, probably because most gas in hydrate is from biogenic methane, and therefore it is concentrated where there is a rapid accumulation of organic detritus (from which bacteria generate methane) and also where there is a rapid accumulation of sediments (which protect detritus from oxidation).

Courtesy USGS
http://woodshole.er.usgs.gov/project-pages/hydrates/what.html

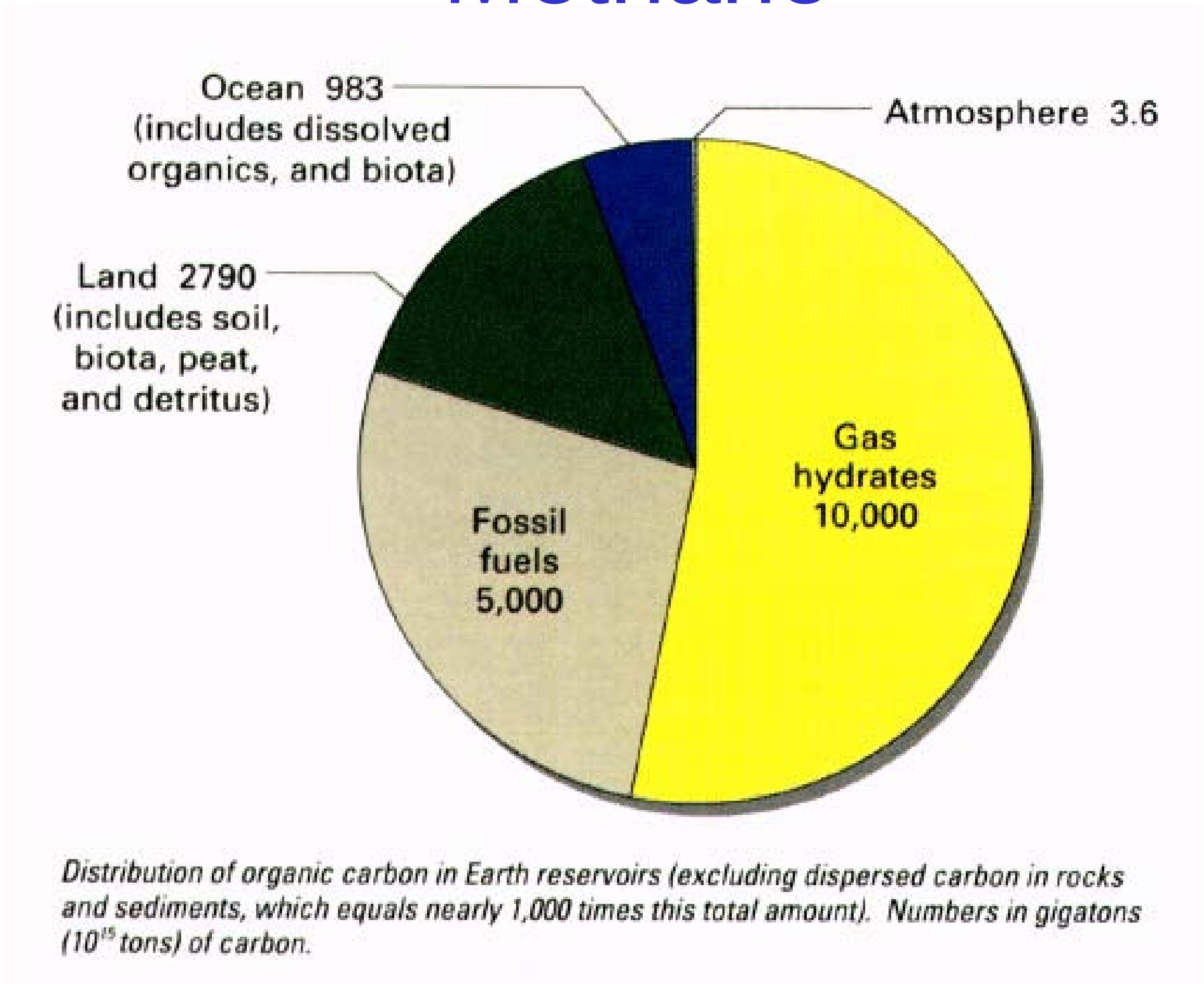
Methane

Gas Hydrate: Where is it found?



Courtesy USGS
http://woodshole.er.usgs.gov/project-pages/hydrates/where.html

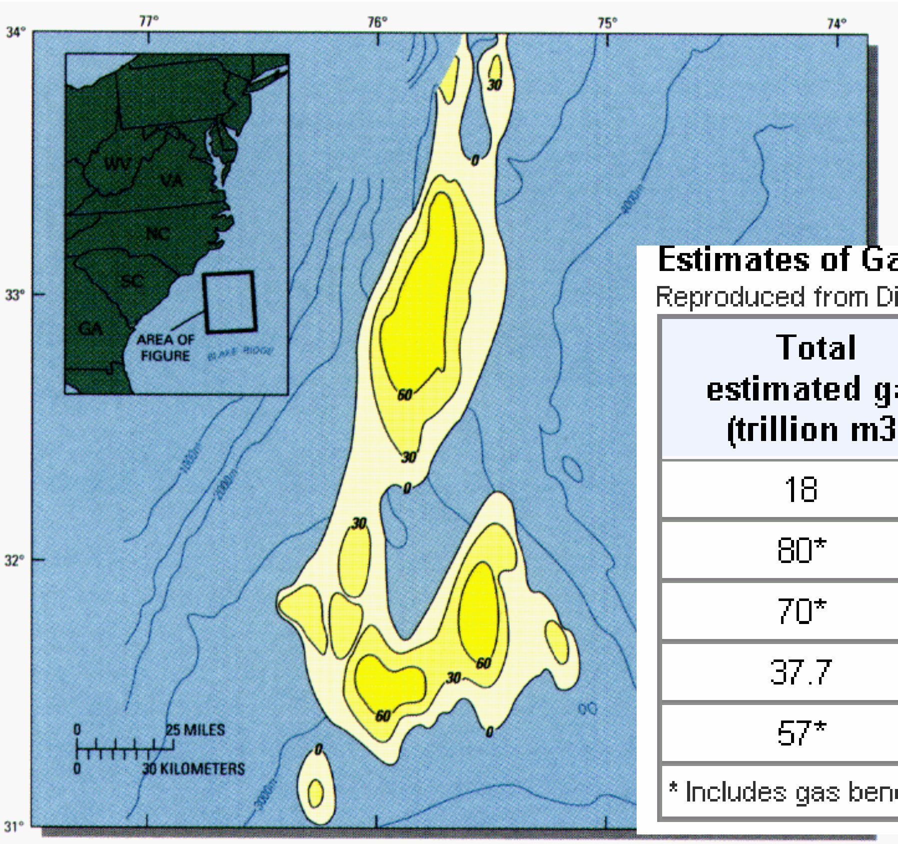
Methane



Courtesy USGS
http://pubs.usgs.gov/fs/gas-hydrates/figures/fig3.html

Methane – Blake Ridge

There is a lot of it out there and all published figures are only estimates



Map showing location and inferred thickness (in meters) of hydrates within sediments in the high concentration area off North Carolina and South Carolina.

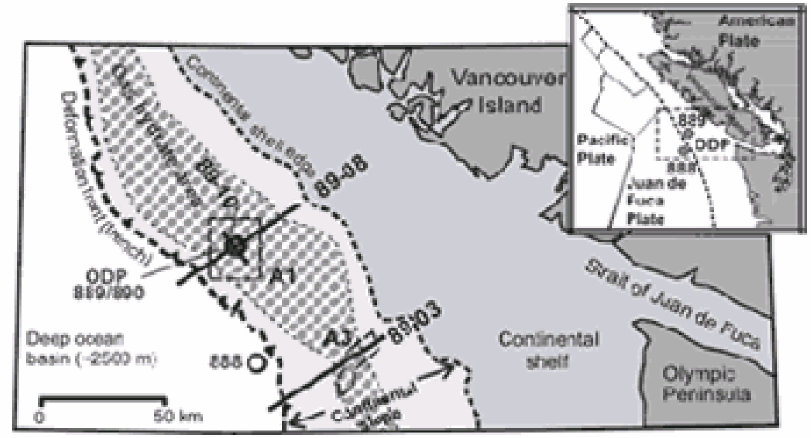
Courtesy USGS
http://pubs.usgs.gov/fs/gas-hydrates/figures/fig2.html

Estimates of Gas Volume for the Blake Ridge Area
Reproduced from Dillon and Max, 2000.

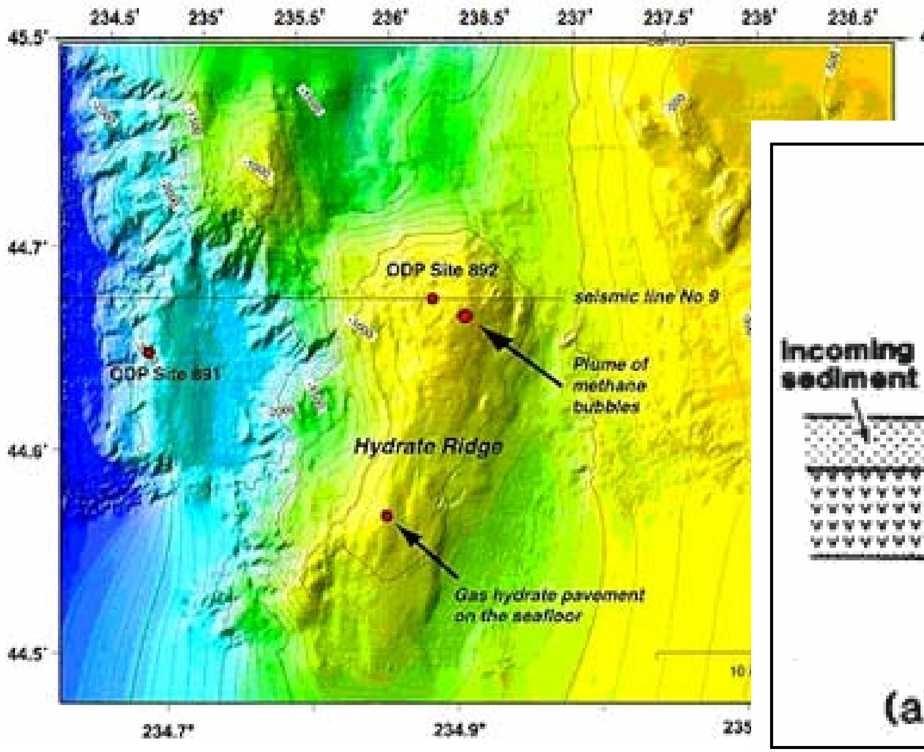
Total estimated gas (trillion m3)	Area (km2)	Volume/Unit Area (billion m3/km2)	Reference
18	3,000	6	Dillon et al. 1993
80*	100,000	0.8	Holbrook et al. 1996
70*	26,000	2.7	Dickens et al. 1997
37.7	26,000	1.5	Collett and Ladd 2000
57*	26,000	2.2	Collett and Ladd 2000

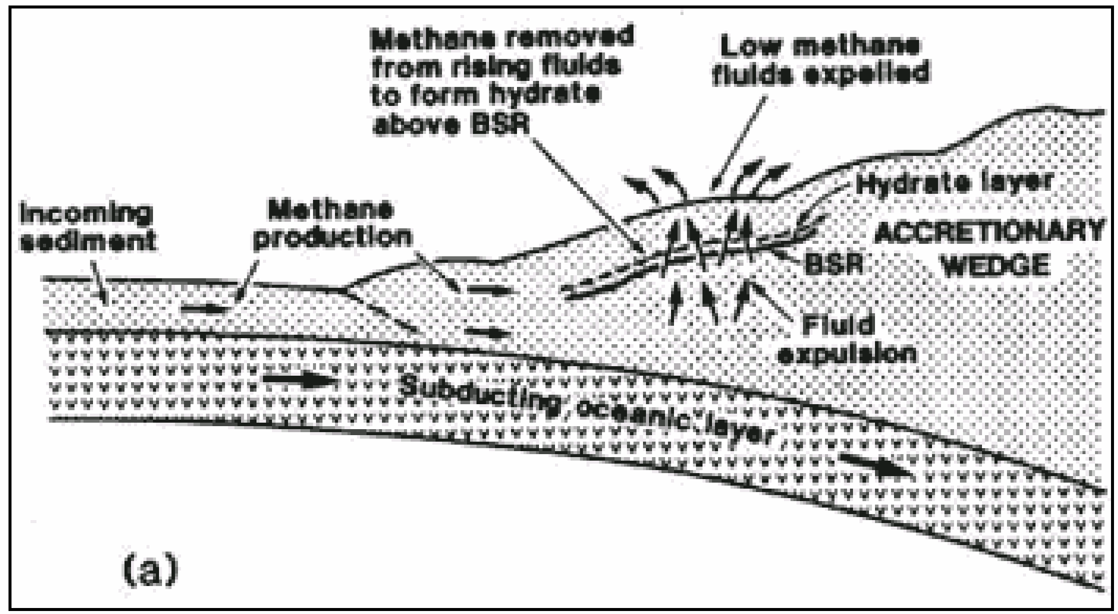
* Includes gas beneath the gas hydrate seal.

Methane – Cascadia Margin



Locations of methane hydrate off the Cascadia Margin



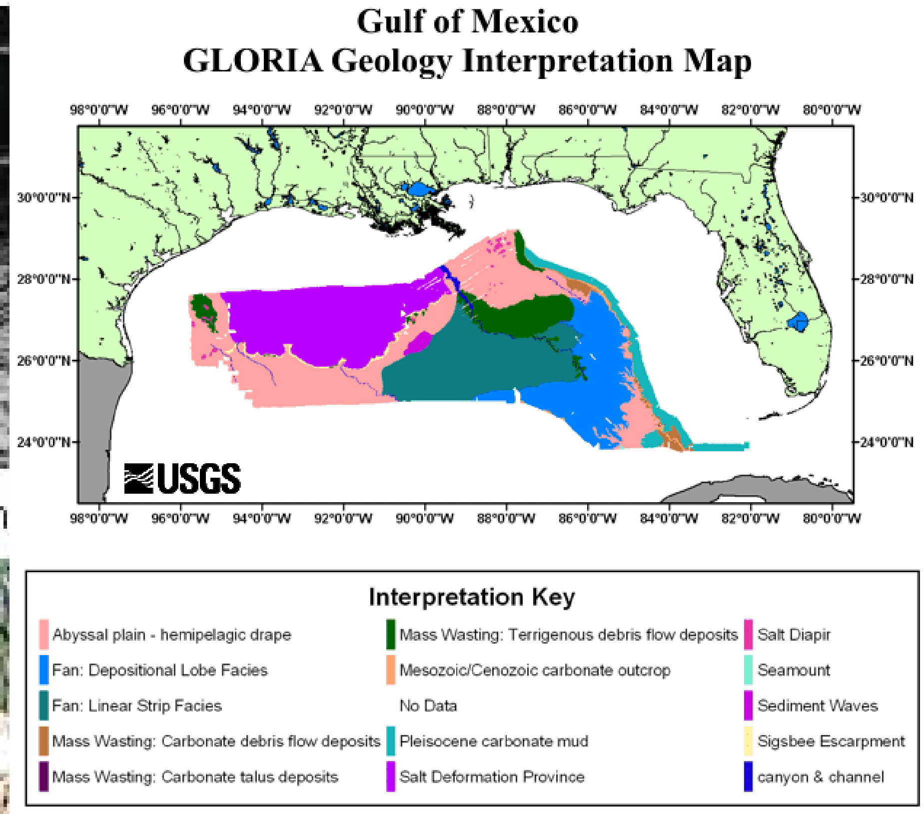


Schematic representation showing the movement of methane and fluids through an accretionary wedge.

Courtesy of Natural Resource Canada and Dr. Roy Hyndman.

Courtesy DOE

Ice Worm



Courtesy USGS
http://coastalmap.marine.usgs.gov/gloria/gomex/images/gomex_geology-map.gif

Tubeworms

Courtesy DOE
http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/about-hydrates/gulf-mexico.htm

GOM hydrates derived from thermogenic methane. They are isotopically distinct and impregnated with oil

Methane Hydrate Act

On May 2, 2000, the President of the United States enacted the Methane Hydrate Research and Development Act of 2000. The bill calls for the Secretary of Energy to commence a methane hydrate R&D program in consultation with the Department of Defense (represented by the U.S. Naval Research Laboratory), the Department of the Interior (represented by the Minerals Management Service and the U.S. Geological Survey), the Department of Commerce (represented by the National Oceanic and Atmospheric Administration), and the National Science Foundation.

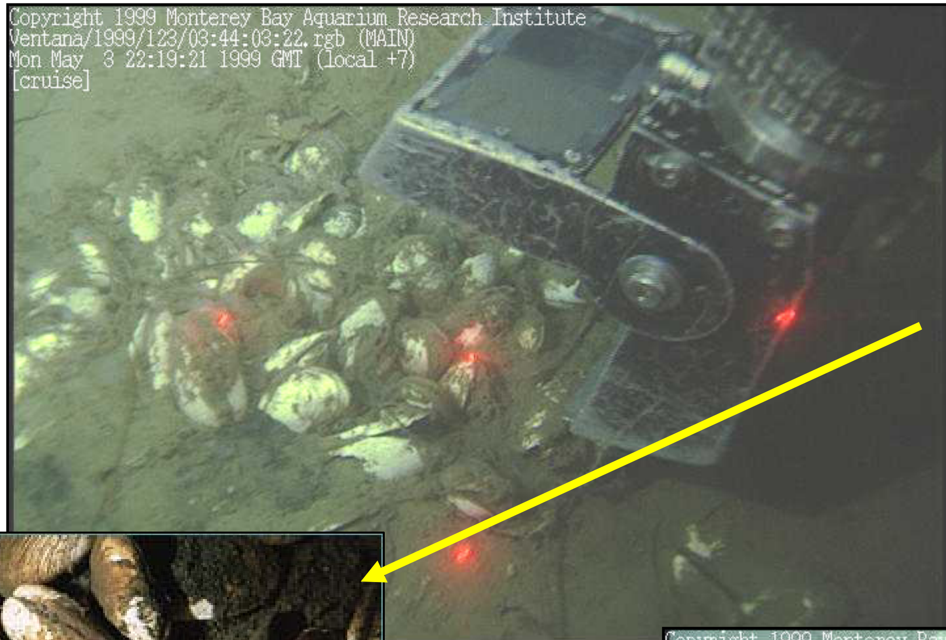
The bill calls for the Secretary of Energy to award grants, contracts, or cooperative agreements with institutions of higher education and industrial enterprises on a competitive, merit-based process to:

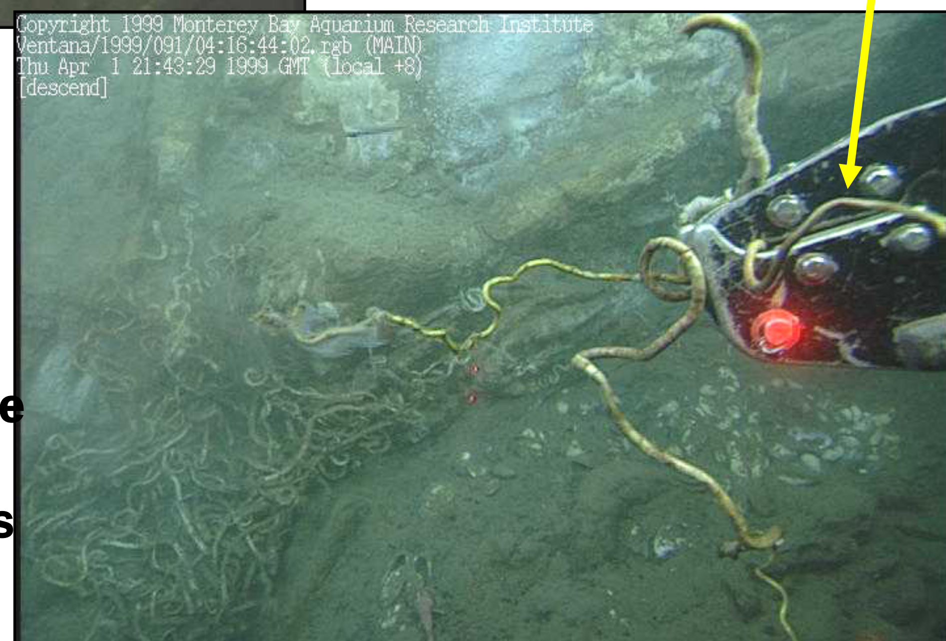
- Conduct basic and applied research to identify, explore, assess, and develop methane hydrates as a source of energy.
- Assist in developing technologies required for efficient and environmentally

Courtesy DOE
http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/rd-program/legislation.htm

Large communities of clams and worms

also use sulfide for energy





MBARI scientists are studying these animals to better understand the physiology, ecology, and energetics of these animal communities.

These clams and worms don't have stomachs or mouths!!

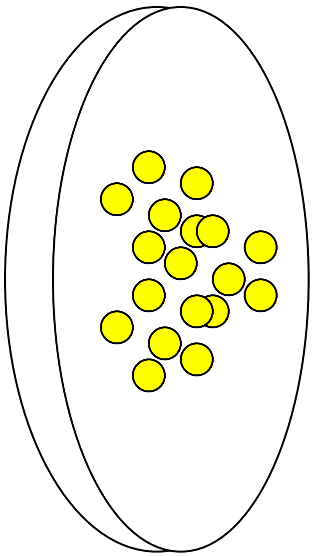
…How do they survive?

It's called "symbiosis"

Living together of organisms of different species.
The term usually applies to a dependent relationship
that is beneficial to both members (also called mutualism).
Symbiosis may occur between plants, animals and/or bacteria

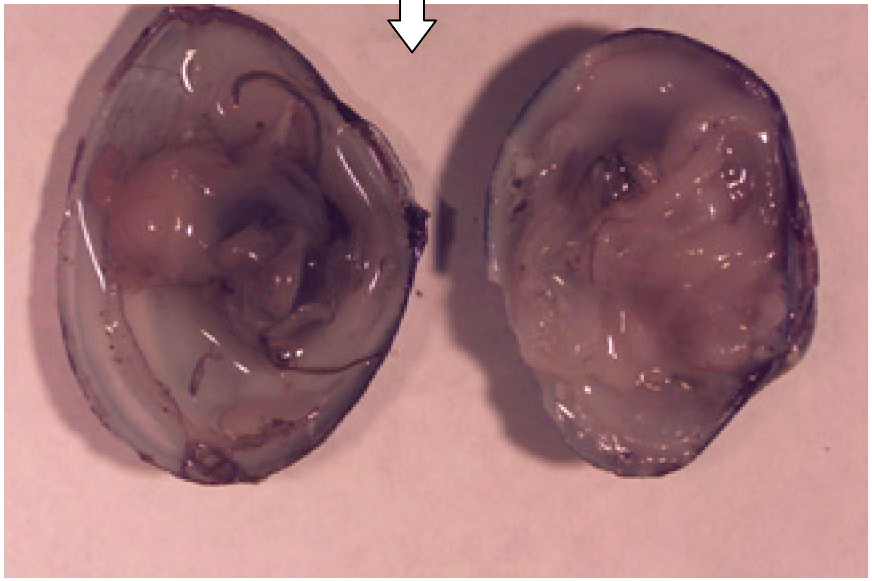
Once inside, the bacteria and animal host become partners. The bacteria multiply within the host, eventually integrating completely.

The animal benefits from food produced by the bacteria and the symbiont benefits from the shelter and stable environment provided by the host.



Seep clams are no ordinary clams!!

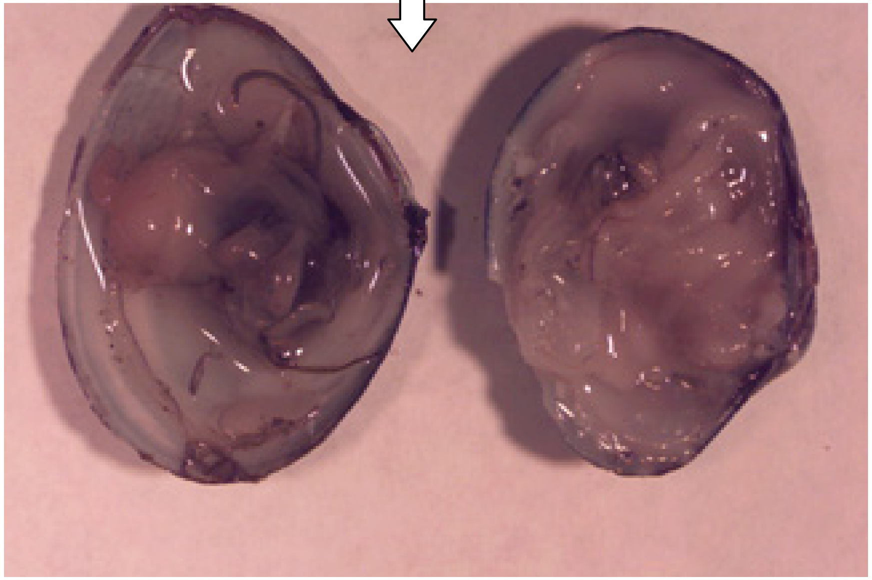
Ordinary clam



Clam chowder
- yum -

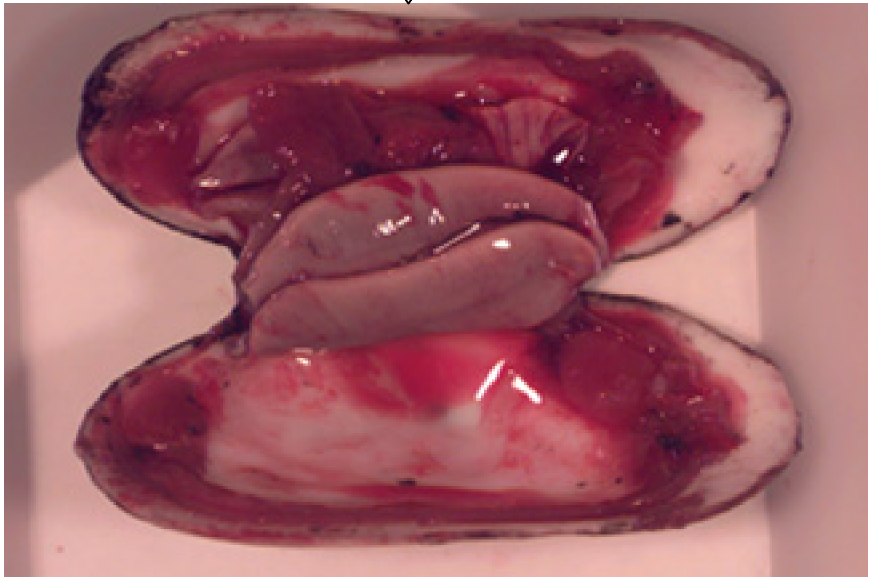
Seep clams are no ordinary clams!!

Ordinary clam



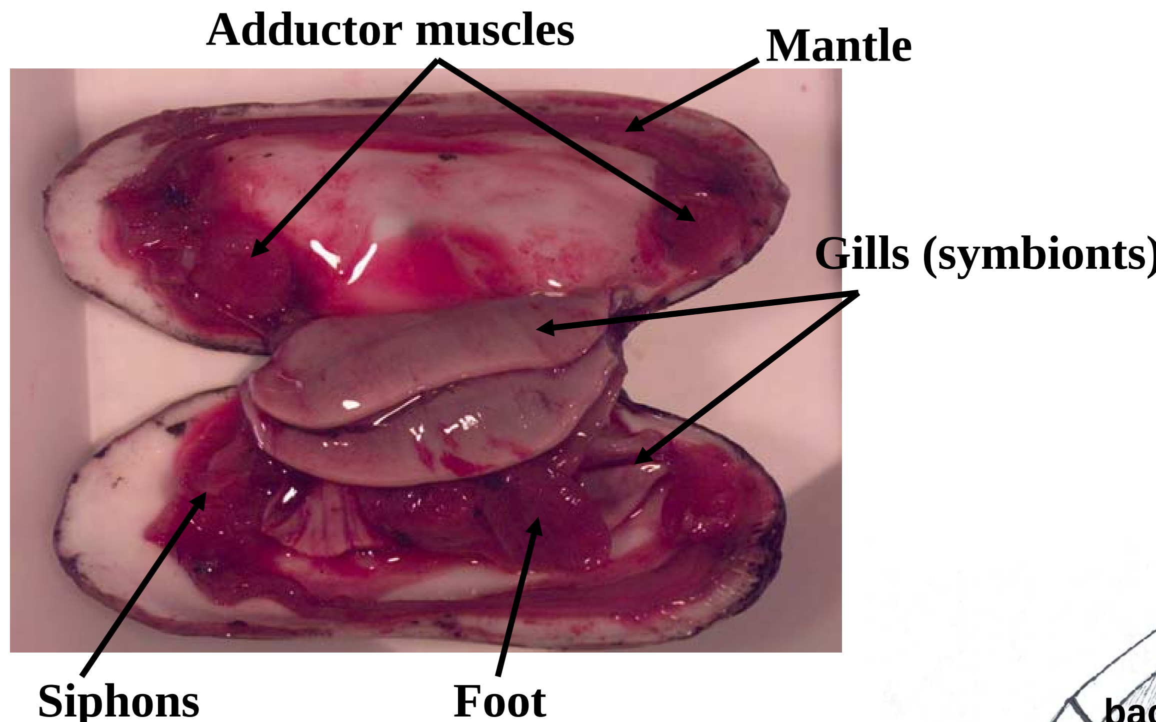
Clam chowder
- yum -

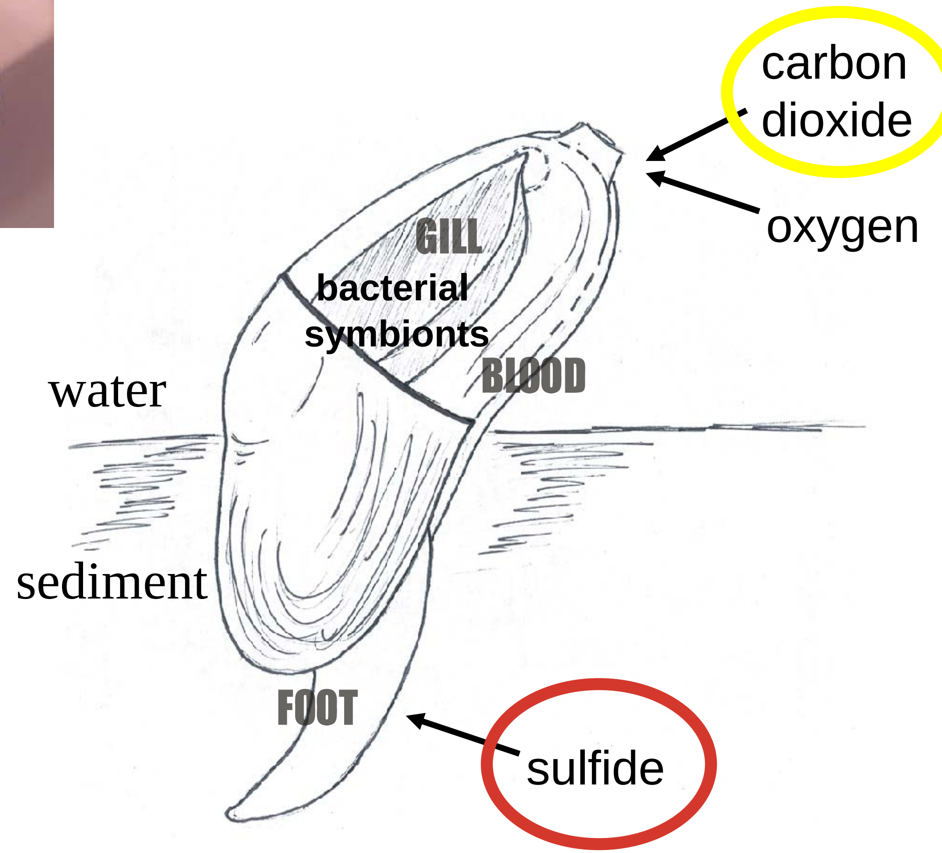
Extraordinary clam



Rotten eggs
- yuck -

Courtesy Victoria Orphan.Used with permission.



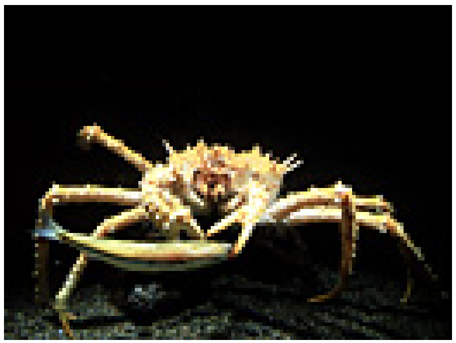


Unlike other animals, these clams must take up carbon dioxide (through their enlarged gills) and sulfide (through their foot) in order meet the needs of their symbionts.

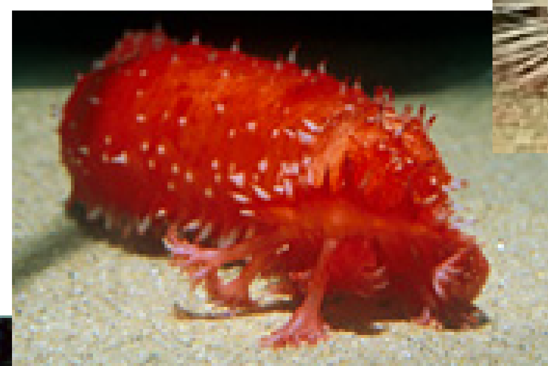
Courtesy Victoria Orphan.Used with permission.

In addition to strictly ‘seep’ animals, a variety of other animals benefit from foraging within seep sites.

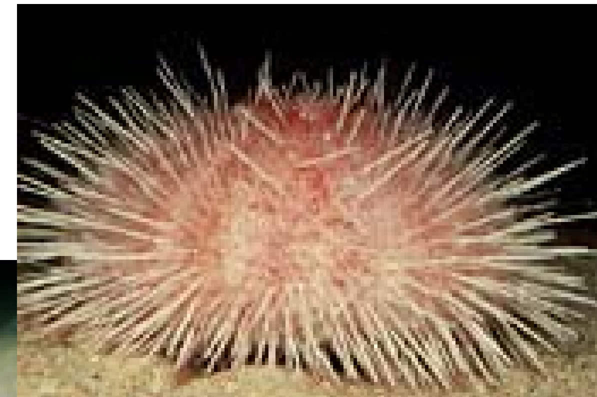
These include....



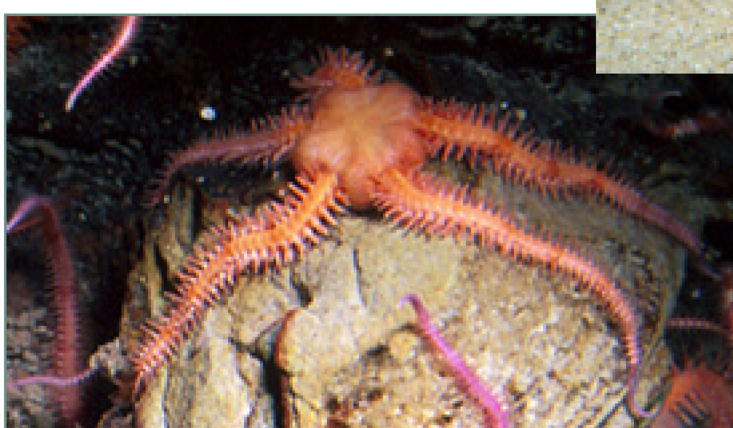
Crabs



Sea cucumbers



Sea urchins



Brittle stars

King crabs

Methane-Dependent Communities in the GOM

Methane hydrates like this one, which is 540 meters deep in the Gulf of Mexico, are crystal structures of methane and water which can form under conditions of low temperature and high pressure. This hydrate mound, which is over 6 feet in diameter, has risen off of the seafloor because the "methane ice" is lighter than the sediment or sea water. Click on the hydrate for a closer look at the inhabitants of the mound