Pyrolysis studies on shales from Damodar Valley, India : Preliminary results

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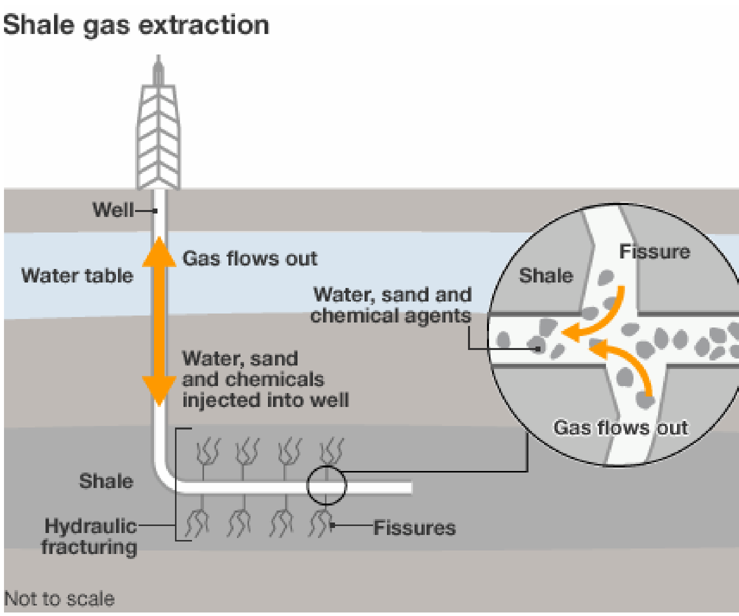
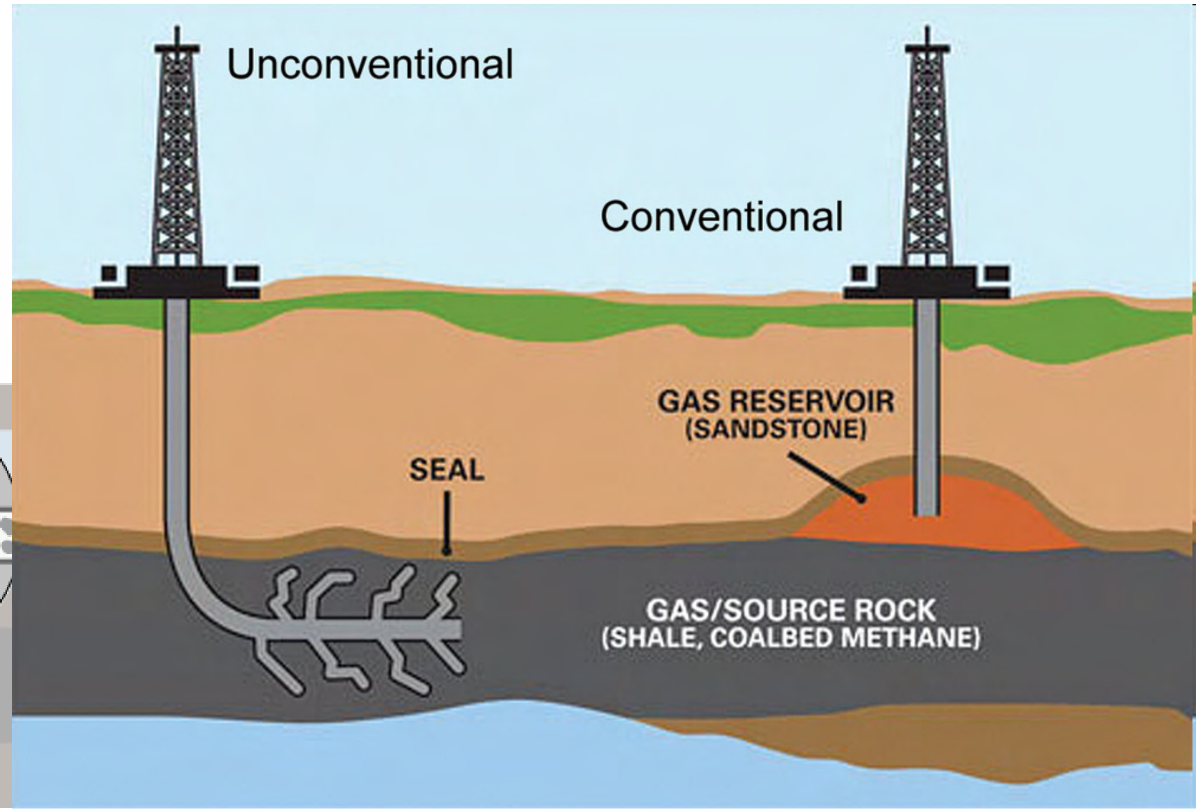
Contents of Talk:

1. What is shale, shale gas and shale system
2. Organic geochemistry of shale
3. Basin method of Rock Eval pyrolysis
4. Evaluation of Geochemical parameters
5. Case Studies
    5a) Damodar Basin
    5b) Jammu and Kashmir Regio

Petroleum and shale gas systems





Unconventional system

-The gas is generated in-situ and stored in shales,
-gas shales are self sourced reservoirs

Conventional System

Essential elements :
- **Source rock**
- Reservoir rock
- Seal rock
- Overburden rock
- Geologic time

Essential processes :
- Formation of basins
- Deposition of reservoir & source rock
- Generation, migration, trapping & preservation of HC's

What is shale:

Shales are usually classified according to the amount of silt, presence and type of lamination, mineralogy, chemical composition and color.

Variations in these properties are related to the type of environment in which the shale was deposited and to the post depositional changes caused by diagenesis and compaction.

Shale exhibits varying degrees of fissility and break into thin layers. These layers are usually parallel to the indistinguishable bedding plane because of parallel orientation of clay mineral flakes.

Shales contain 95 percent of the organic matter. However, this amounts is less than one percent by mass in an average shale.

What is shale gas:

Shale gas is natural gas, primarily methane, trapped in the shales which has low permeability. Shale gas is in-situ gas present in organic rich, fine grained, sedimentary rocks (Shale).

Gas is generated and stored in-situ as sorbed gas in organic matter and free gas in fracture and pores. As such gas shales are self sourced reservoirs.

Low permeable shale requires extensive fractures (natural or induced) to produce commercial quantities of gas.

Shale gas has become an increasingly important source of natural gas in the United States over the past decade.

Shale Gas System:

A shale gas system is self –contained source reservoir.

Shales that generates the gas also function as low matrix permeability and low porosity reservoir rocks, so gas production in commercial quantities requires fractures to provide permeability.

Shale gas has been produced for years from shales with natural fractures. In recent years there is demand of shale gas due to modern technology in hydraulic fracturing to create extensive artificial fractures around well bores.

Horizontal drilling is often used with shale gas wells, with lateral lengths up to 10,000 feet within the shale, to create maximum borehole surface area in contact with the shale.

QUALITATIVE APPROACH FOR SOURCE ROCK CHARACTERIZATION

✓Organic Richness
✓ Kerogen Type
✓ Thermal maturity

Organic Richness - Total Organic Carbon (TOC)

General grouping of source rocks based on TOC(wt%)
✓ < 0.50 Non-source
✓ 0.50-1.0 Fair
✓1.0-2.0 Good
✓ > 2.0 Excellent

Kerogen Type - Oil, Gas, Oil and Gas Prone

Kerogen Typing by
✓ HI versus OI plots
✓HCs generated (volatile & through kerogen cracking) versus TOC plots

Thermal maturity
✓HI versus Tmax.

ROCK EVAL (RE) PYROLYSIS

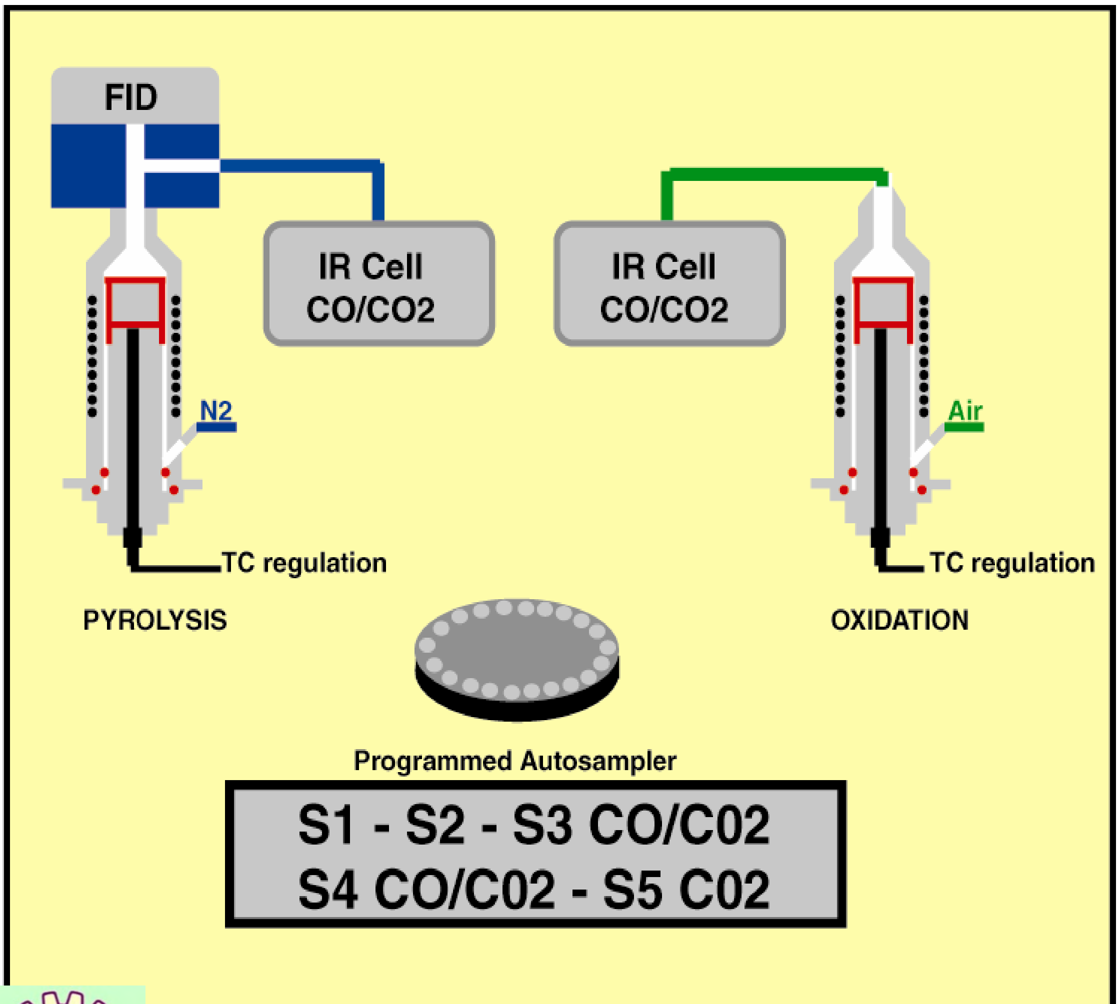
- Most basic organic geochemical methods for characterization of sedimentary organic matter in terms of its abundance, source and properties.

- Used to know the petroleum potential of organic rich rocks

- Pyrolysis technique is based on the steady heating of rock samples so that the total evolved hydrocarbons can be monitored as a function of temperature

- During Pyrolysis, experimental temperatures are set considerably higher than those found naturally in the subsurface, so that appreciable reaction for the generation of hydrocarbons can occur in a reasonably short time and amount of generated hydrocarbons relative to the total potential of the source rock can be estimated

ROCK-EVAL 6 TURBO
COMPLETE ANALYSIS - PARALLEL PROCESS



What is Rock Eval Pyrolysis?

- Rock Eval Pyrolysis consists in estimating petroleum potential of rock samples by pyrolysis according to a programmed temperature pattern.
- Released hydrocarbons are monitored by a FID, forming the so-called peaks **S1 (thermo-vaporized free hydrocarbons)** and **S2 (hydrocarbons from cracking of organic matter).**
- **The CO and CO2 released** during pyrolysis can be monitored in real time by an IR cell.
- This complementary stage allows determination of **Total Organic Carbon and MINeral Carbon content of samples.**

Basic method of RE-6

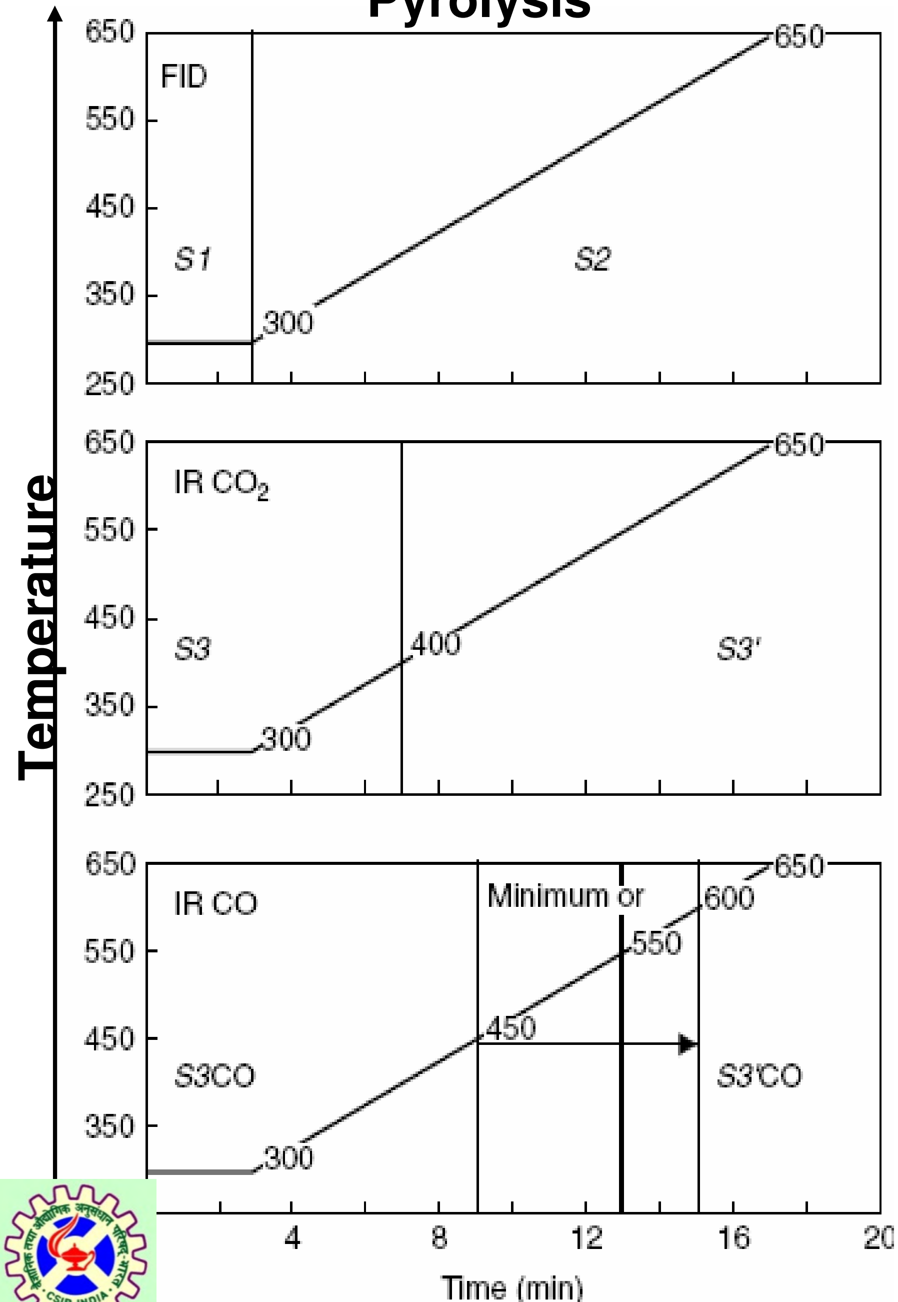
It is the bulk rock method used for screening of all types of samples and allows determination of the full set of available Rock-Eval parameters.

Temperature Program

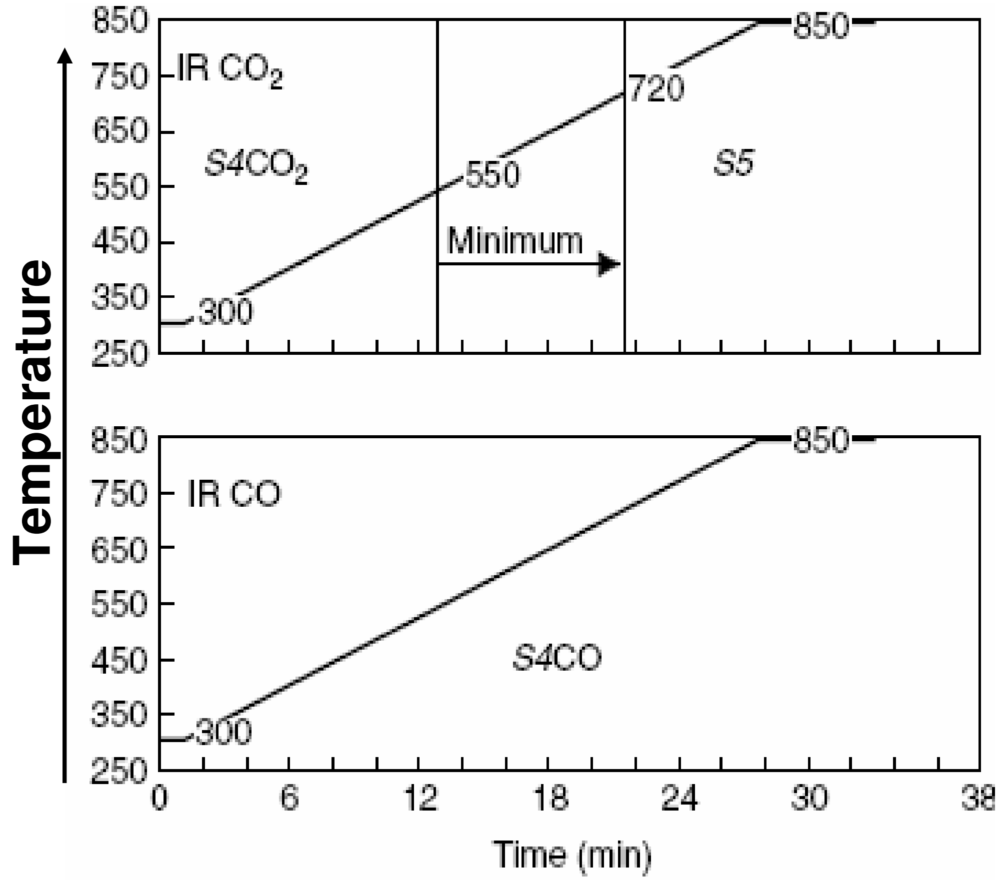
	Initial Temp °C	Final Temp. °C	Rate °/MIN	Initial Step min	Final Step min	Extra Acquisition min
Pyrolysis	300	650	25	3	0	3
Oxidation	300	850	20	1	5	5

Conditions for integration of surfaces for RE 6

Pyrolysis



Oxidation



Calculated Parameters for RE6

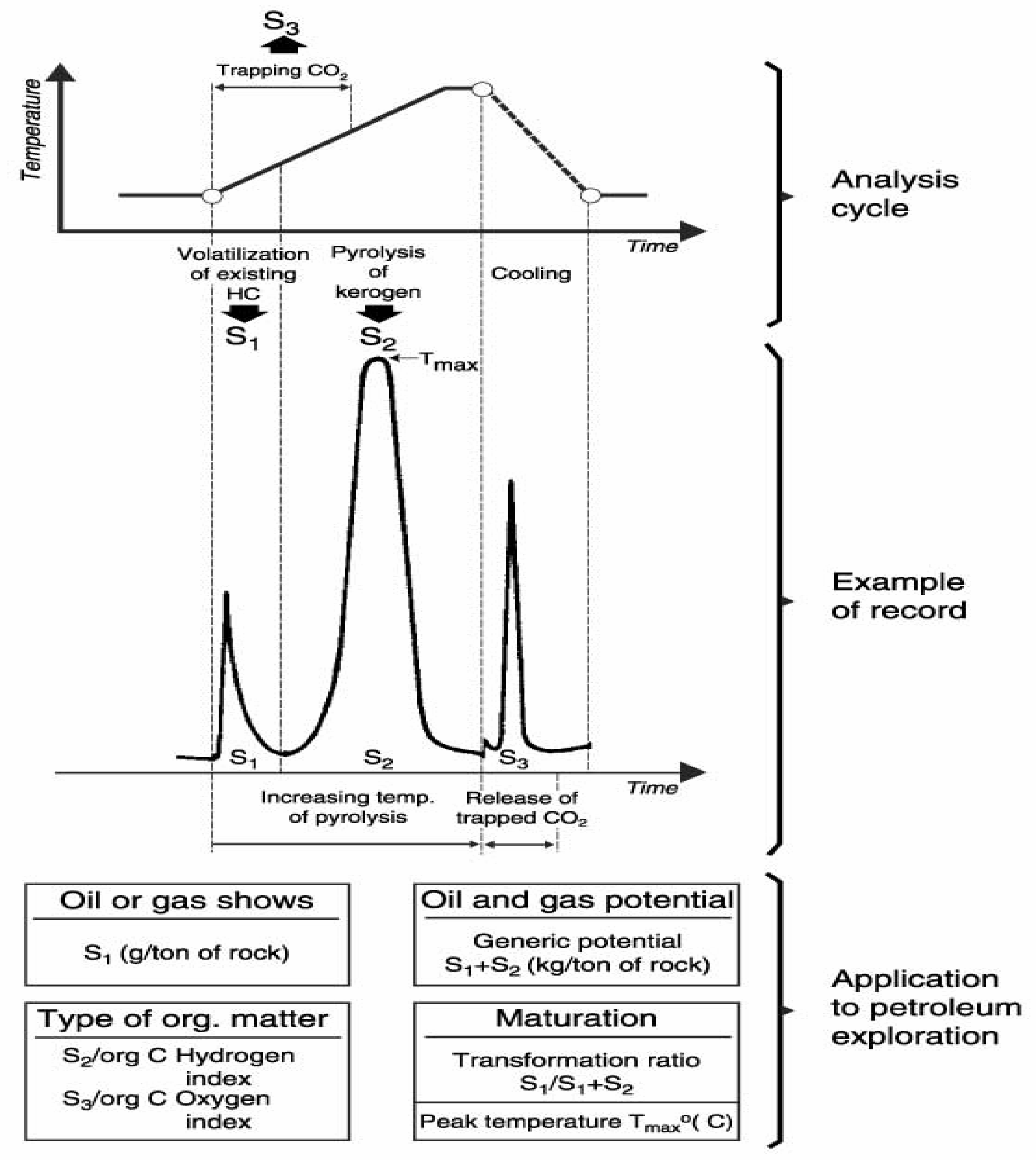
	UNIT	FORMULA	NAME
Tmax	°C	TpS2-ΔTmax(*)	Tmax
PI		S1/(S1+S2)	Production Index
PC	% weight	{[(S1+S2)x0.83]+[S3x12/44]+[(S3CO+S3'CO/2)x12/28]}/10	Pyrolysable Carbon org.
RC CO	% weight	[S4COx12/28]/10	Residual Carbon org. (CO)
RC CO2	% weight	[S4CO$_2$x12/44]/10	Residual Carbon org. (CO2)
RC	% weight	RC CO+ RC CO$_2$	Residual Carbon org.
TOC	% weight	PC+RC	Total Organic Carbon
S1/TOC	mg HC/gTOC	S1x100/TOC	
HI	mg HC/gTOC	S2x100/TOC	Hydrogen Index
OI	mgCO2/gTOC	S3x100/TOC	Oxygen Index
OI CO	mg CO/gTOC	S3COx100/TOC	Oxygen Index CO
PyroMinC	% weight	{[S3'x12/44]+[(S3'CO/2) x12/28]}/10	Pyrolysis Mineral Carbon
OxiMinC	% weight	[S5x12/44]/10	Oxidation Mineral Carbon

Acquisition Parameters of RE6

	Detector/Oven	Unit	Name
S1	FID/Pyrolysis	mgHC/g rock	Free Hydrocarbons
S2	FID/Pyrolysis	mgHC/g rock	Oil Potential
TpS2	Pyrolysis TC(*)	°C	Temperature for maximum of surface S2
S3	IR/Pyrolysis	$mgCO_2$/g rock	CO_2 from organic source
S3’	IR/Pyrolysis	$mgCO_2$/g rock	CO_2 from mineral source
TpS3’	Pyrolysis TC(*)	°C	Temperature for maximum of surface S3’
S3CO	IR/Pyrolysis	$mgCO_2$/g rock	CO_2 from organic source
TpS3CO	Pyrolysis TC(*)	°C	Temperature for maximum of surface S3CO
S3’CO	IR/Pyrolysis	$mgCO_2$/g rock	CO_2 from organic and mineral sources
S4CO2	IR/Oxidation	$mgCO_2$/g rock	CO_2 from organic source
S5	IR/Oxidation	$mgCO_2$/g rock	CO_2 from mineral source
TpS5	Oxidation TC(*)	°C	Temperature for maximum of surface S5
S4CO	IR/Oxidation	$mgCO_2$/g rock	CO_2 from organic source

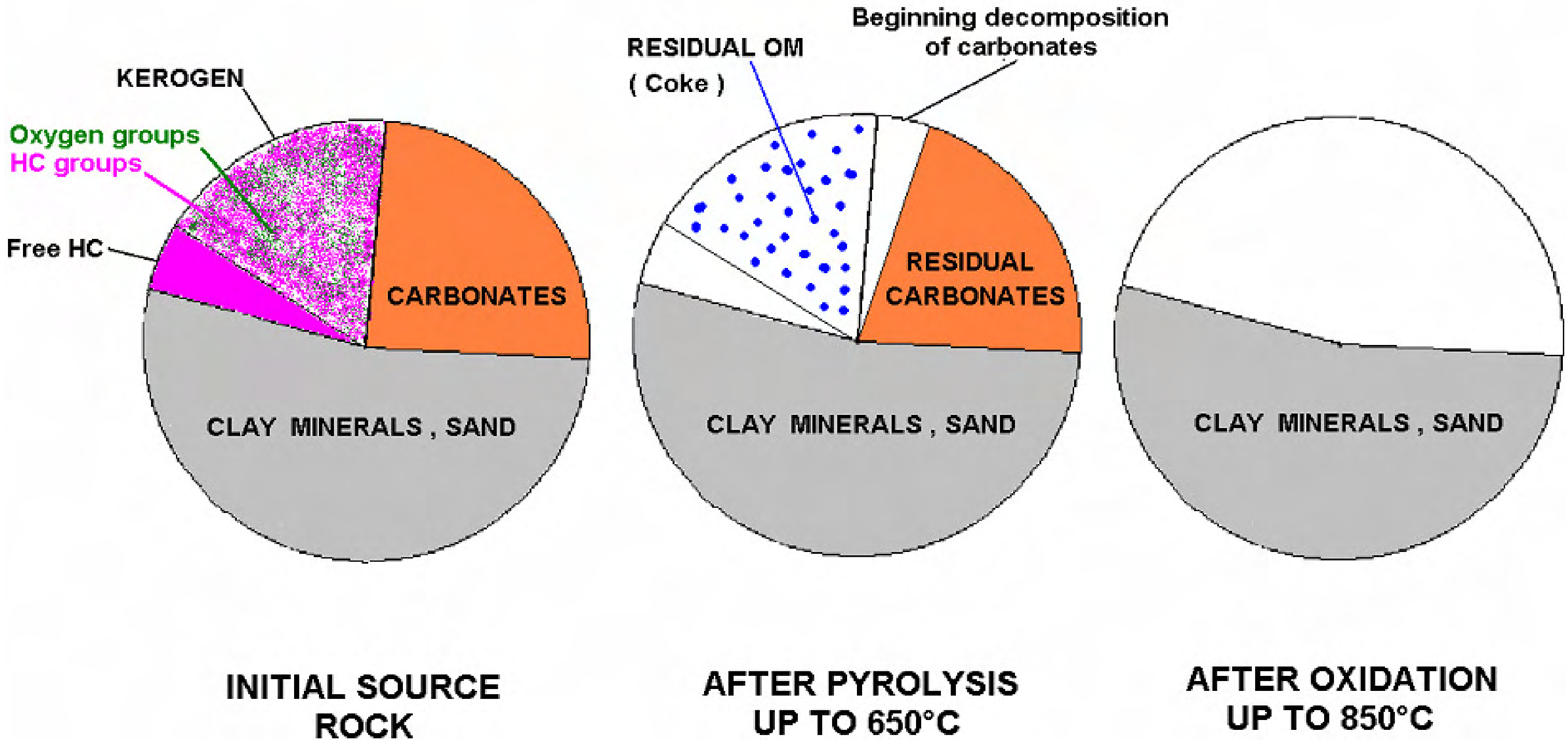
(*) TC Thermo-Couple

Pyrogram



S_3
Trapping CO_2
Temperature
Time
Volatilization of existing HC
Pyrolysis of kerogen
Cooling
S_1
S_2
T_{max}
S_1
S_2
S_3
Time
Increasing temp. of pyrolysis
Release of trapped CO_2
Analysis cycle
Example of record
Oil or gas shows
S_1 (g/ton of rock)
Oil and gas potential
Generic potential
S_1+S_2 (kg/ton of rock)
Type of org. matter
S_2/org C Hydrogen index
S_3/org C Oxygen index
Maturation
Transformation ratio
S_1/S_1+S_2
Peak temperature T_{max}°(C)
Application to petroleum exploration

EVOLUTION OF A BULK ROCK DURING PYROLYSIS AND OXIDATION



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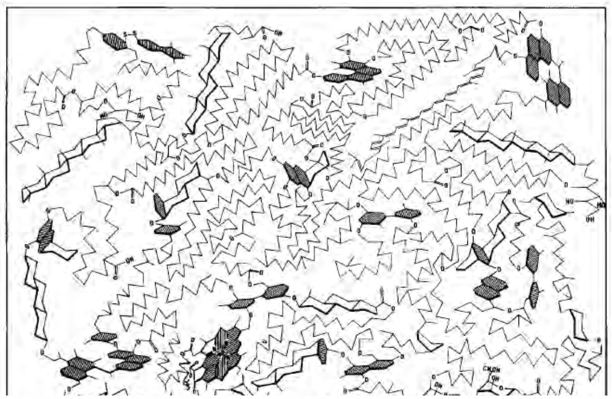

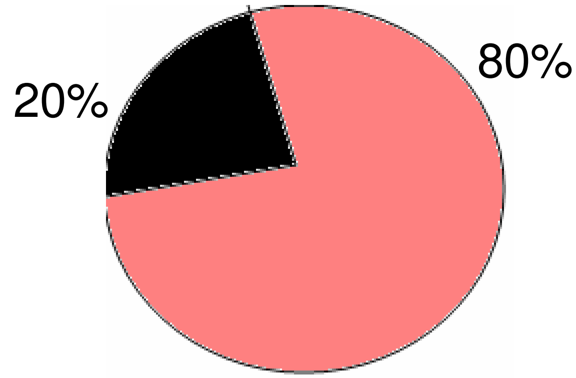

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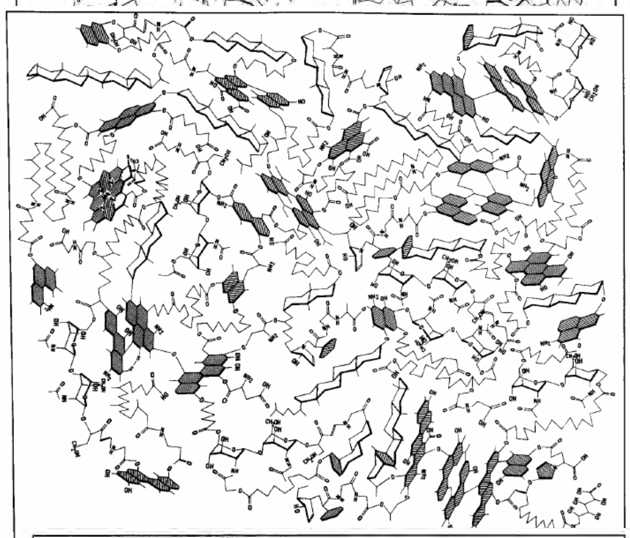

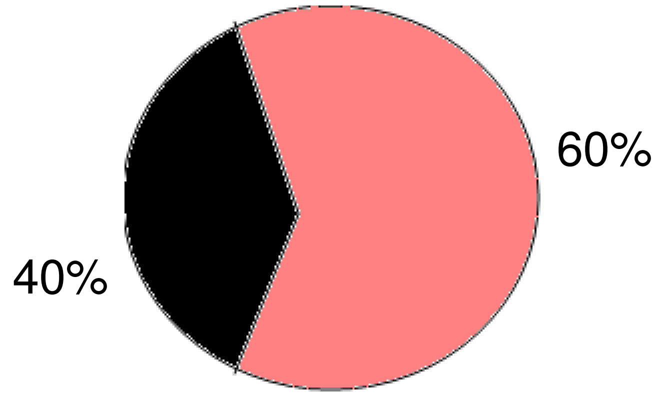

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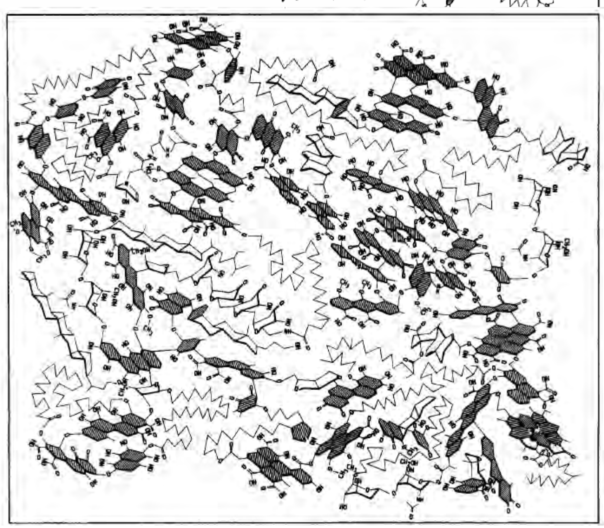
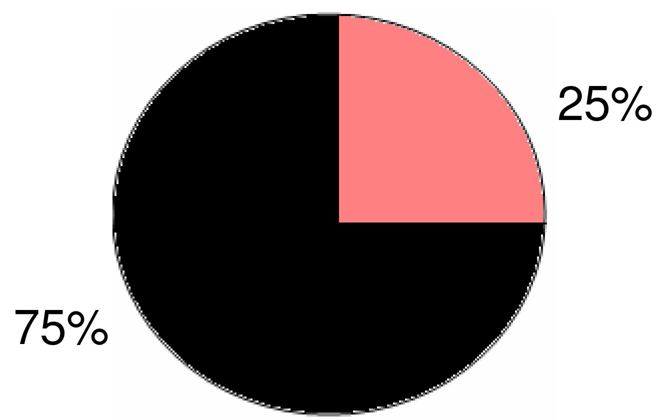
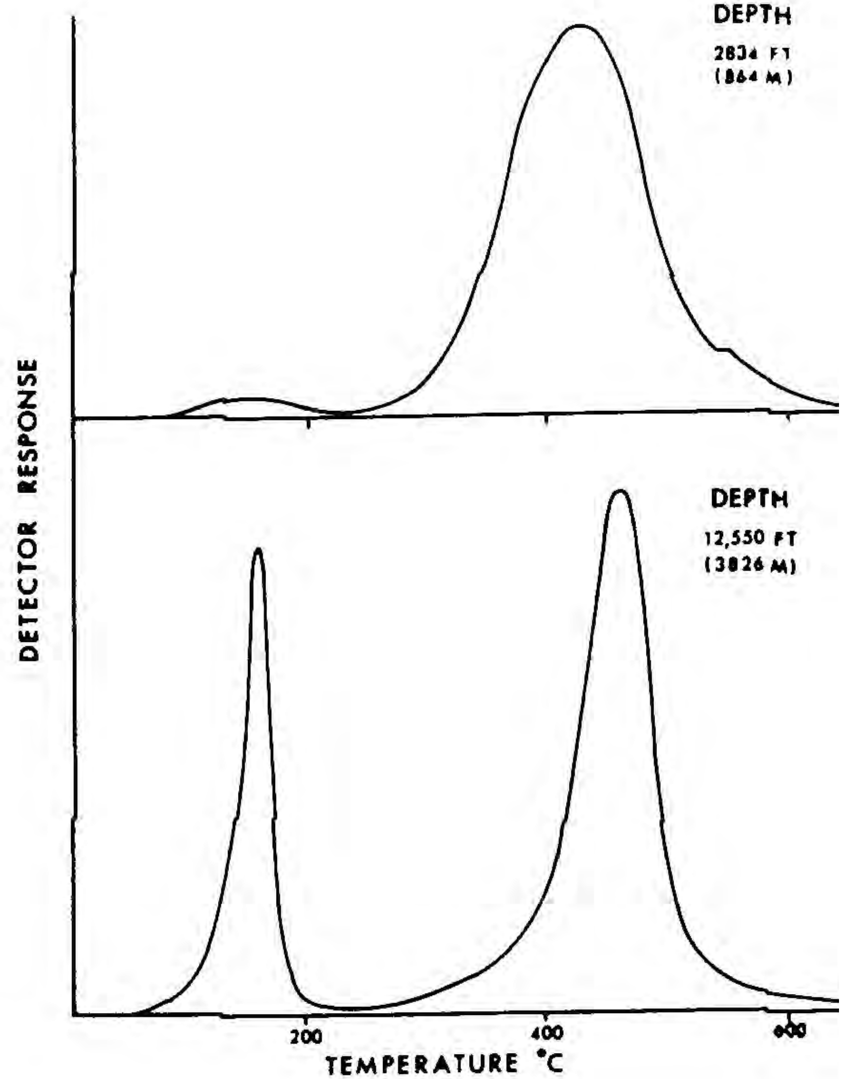
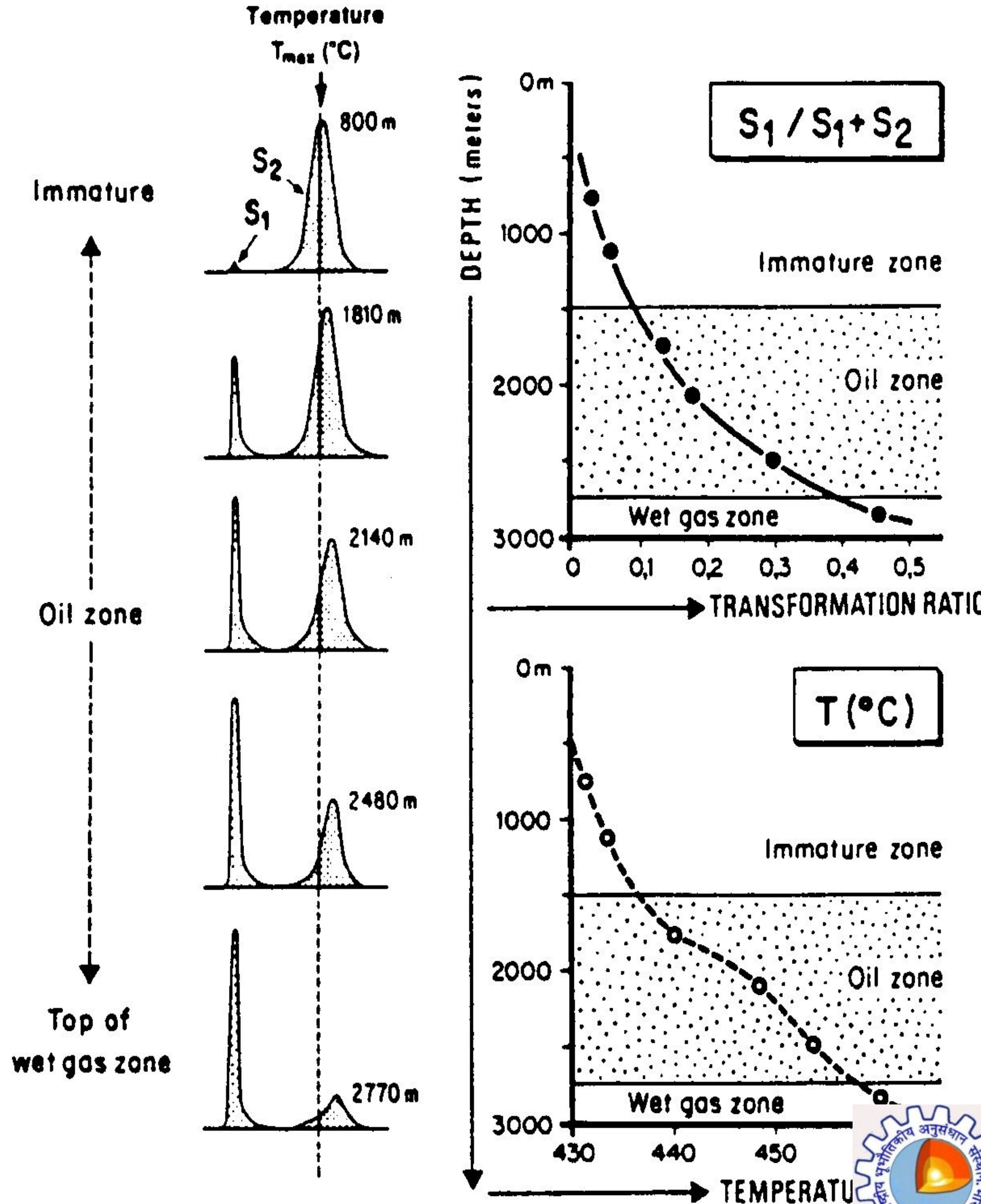




Yield of Hydrocarbons with Increasing Temperature



Changes in TR and Tmax



Evaluation of Geochemical Parameters

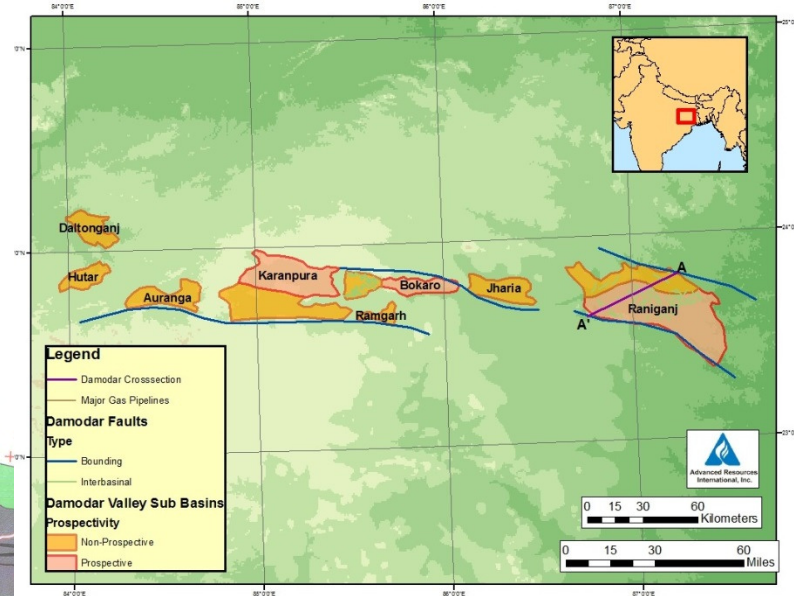
GENERATING POTENTIAL	TOC (wt%)	S1 mg HC/g rock	S2 mg HC/g rock
Poor	0.0 - 0.5	0.0 - 0.5	0.0 - 2.5
Fair	0.5 - 1.0	0.5 - 1.0	2.5 - 5.0
Good	1.0 - 2.0	1.0 - 2.0	5.0 - 10
Very good	>2.0	>2.0	>10

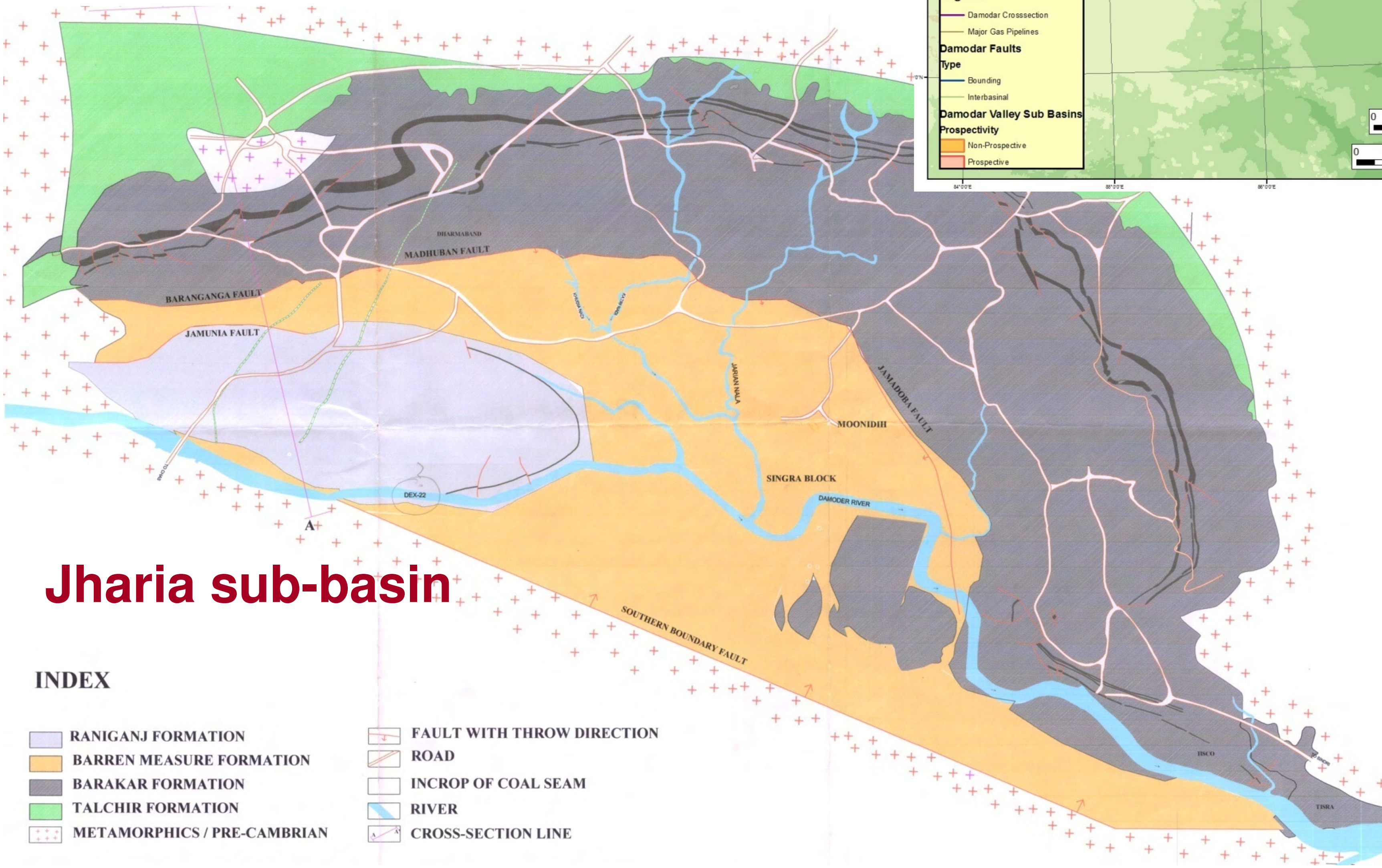
TYPE	HI	S2 / S3
Gas	0 - 150	0 - 3
Gas and oil	150 - 300	3 - 5
Oil	>300	>5

MATURATION	TR	Tmax	Ro
Top of oil window	~0.1	~435 - 445	~0.6
Bottom of oil window	~0.4	~470	~1.4

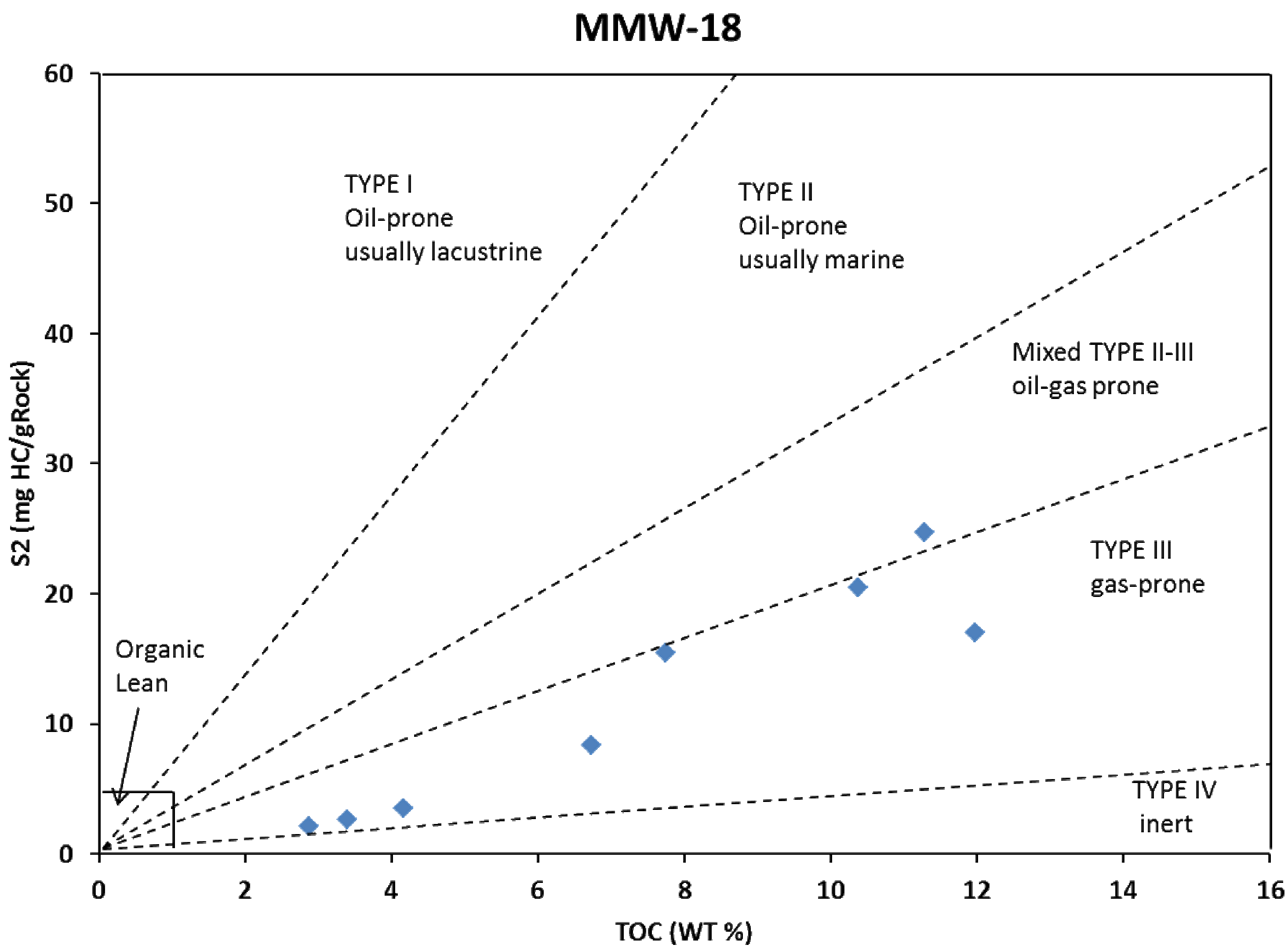
Damodar Valley basins

- Gondwana basins of India
- there is a significant thickness of a marine shale 'Barren measures'

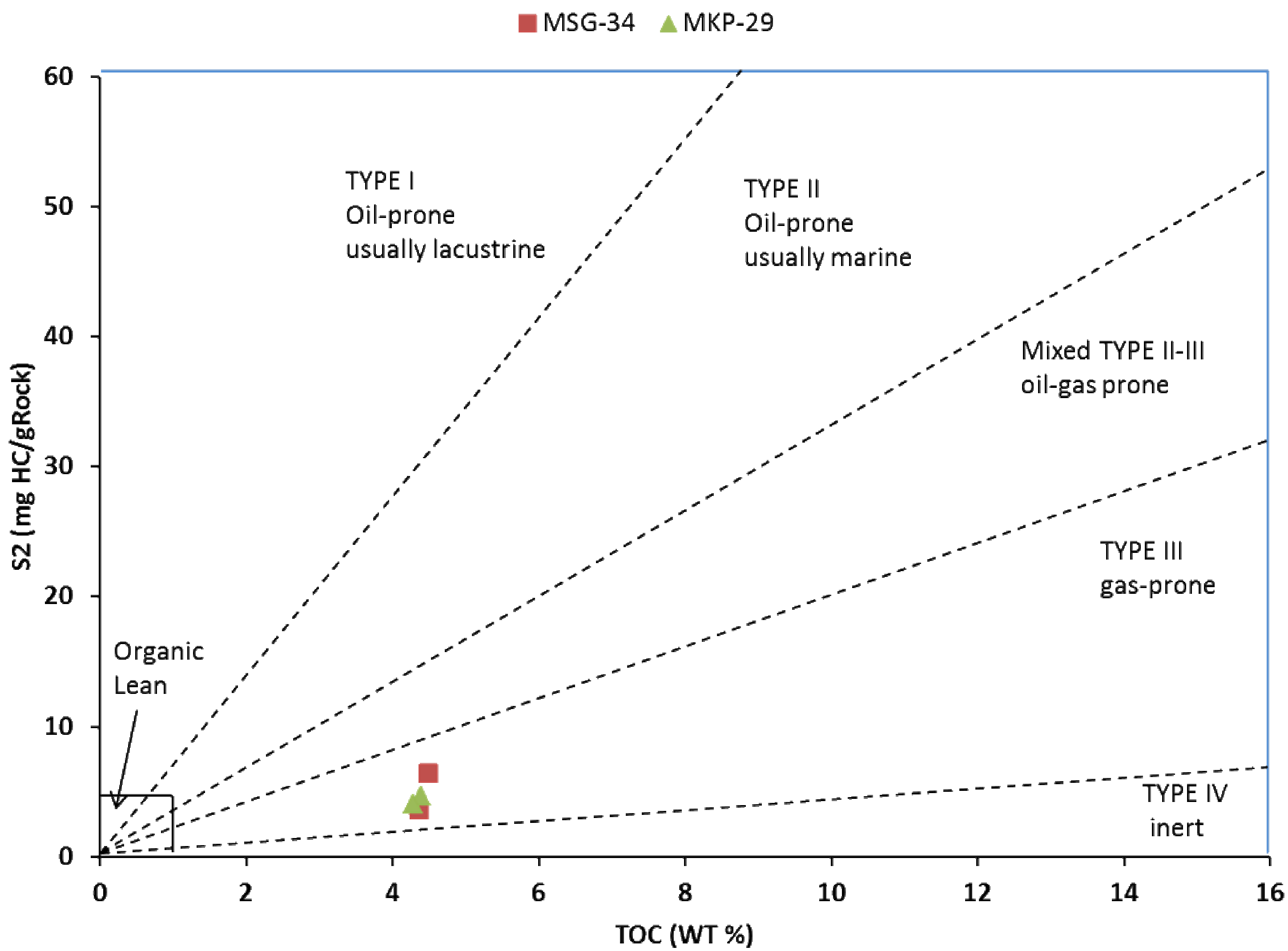




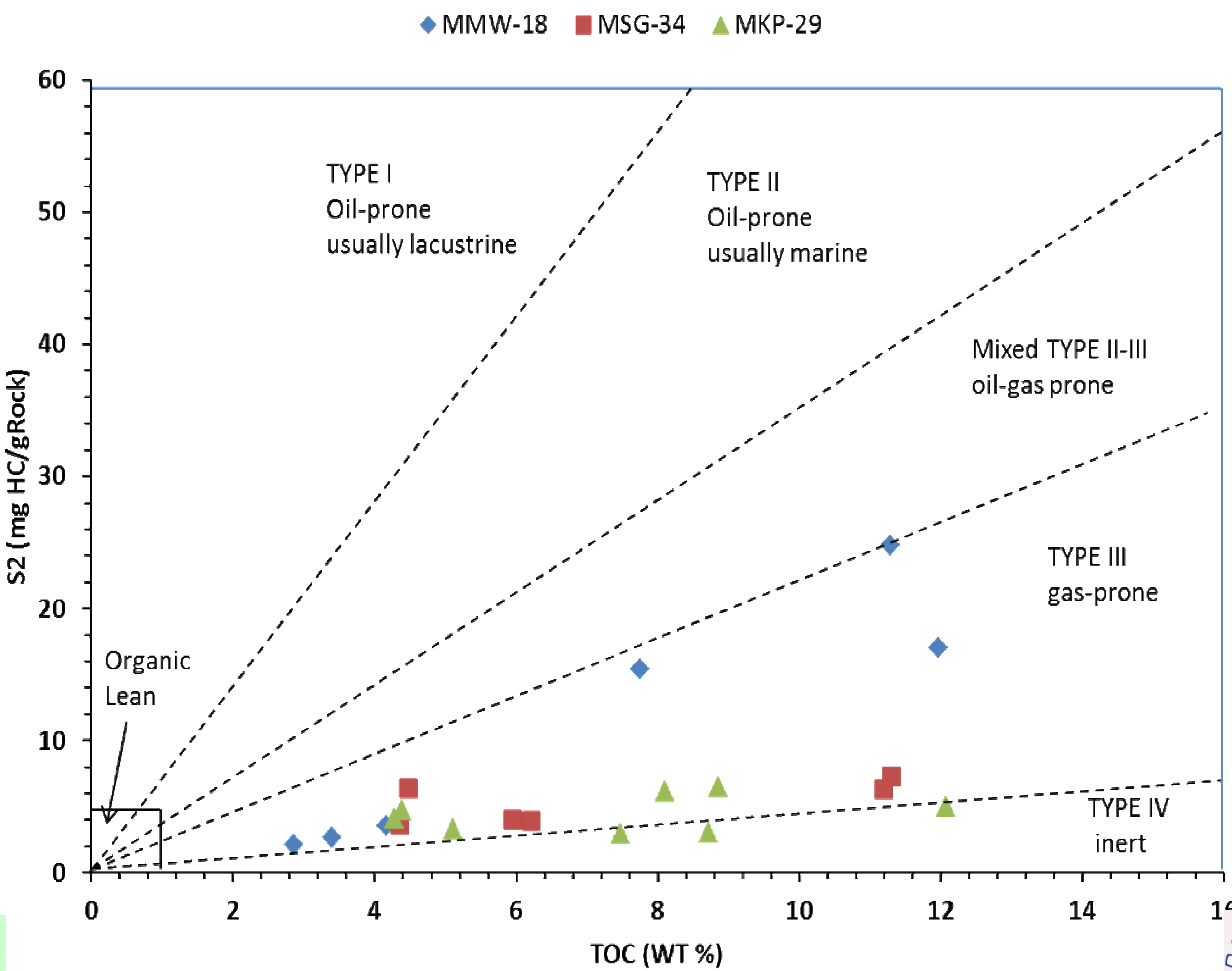
Jharia sub-basin



TOC versus S2 diagram of shale samples from Raniganj Formation, MMW-18 well Jharia Block



TOC versus S2 diagram of shale samples from Barren Measures Formation, Jharia Block


MMW-18
MSG-34
MKP-29
60
50
40
30
20
10
0
S2 (mg HC/gRock)
TYPE I
Oil-prone
usually lacustrine
TYPE II
Oil-prone
usually marine
Mixed TYPE II-III
oil-gas prone
TYPE III
gas-prone
TYPE IV
inert
Organic
Lean
0
2
4
6
8
10
12
14
16
TOC (WT %)

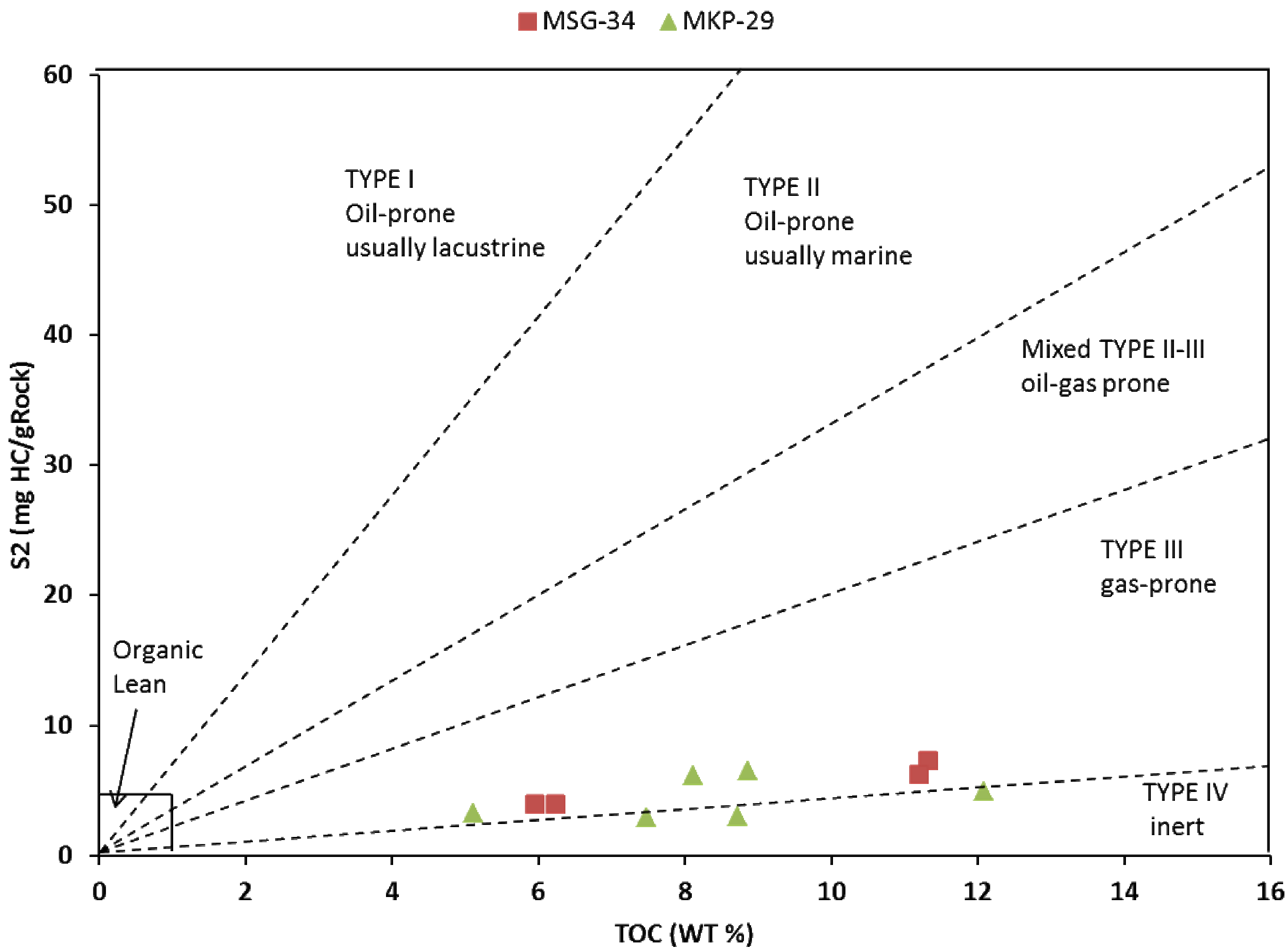
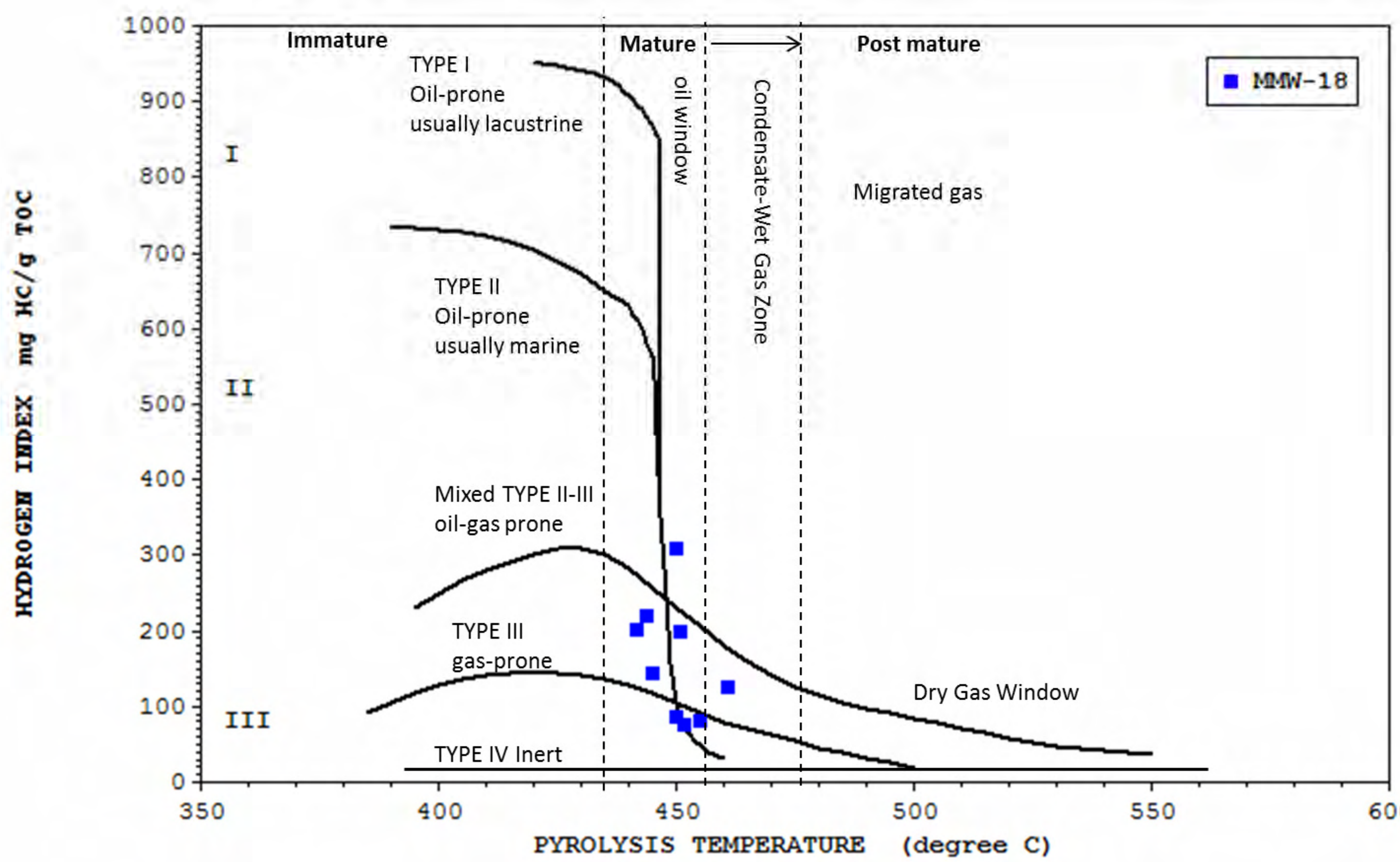
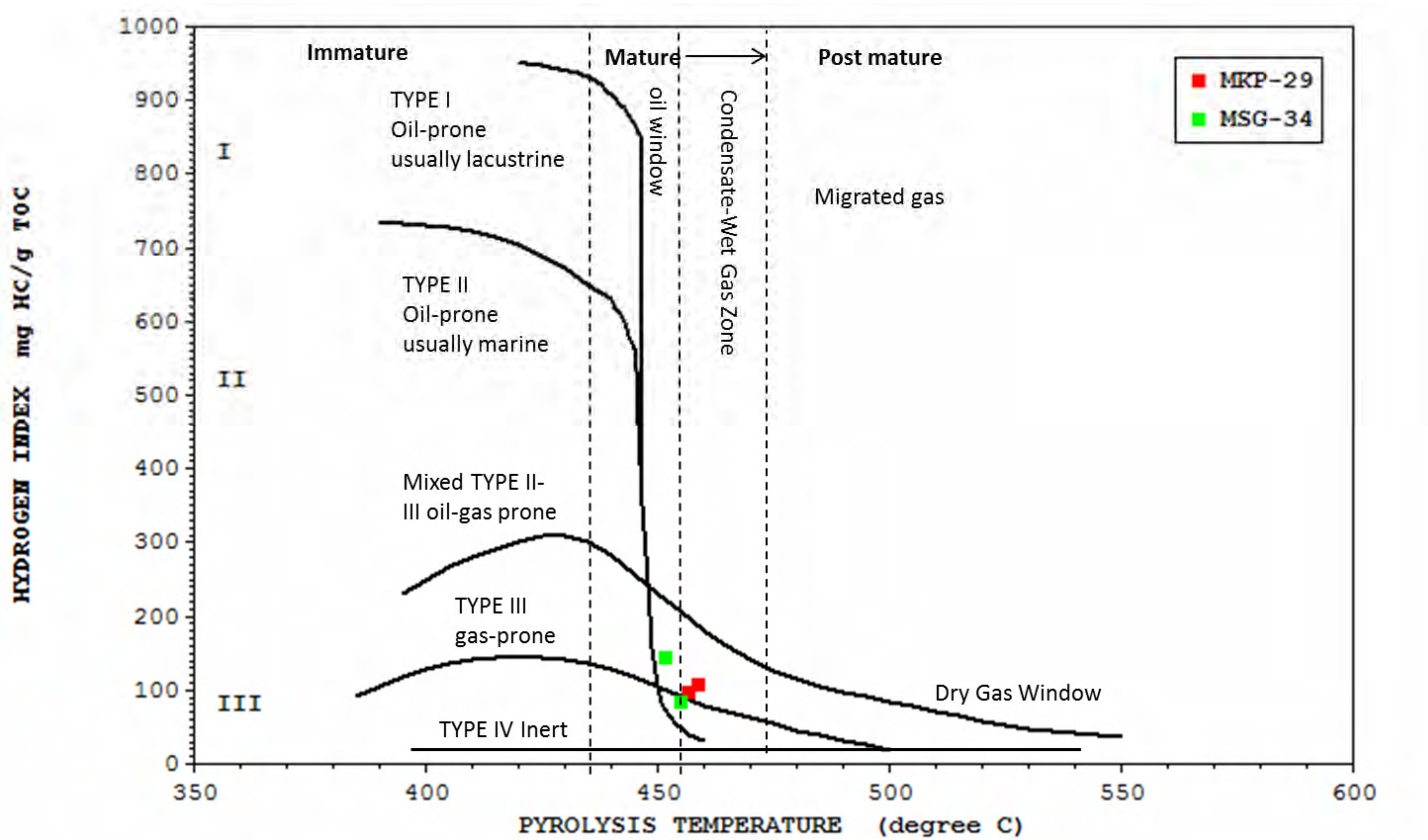


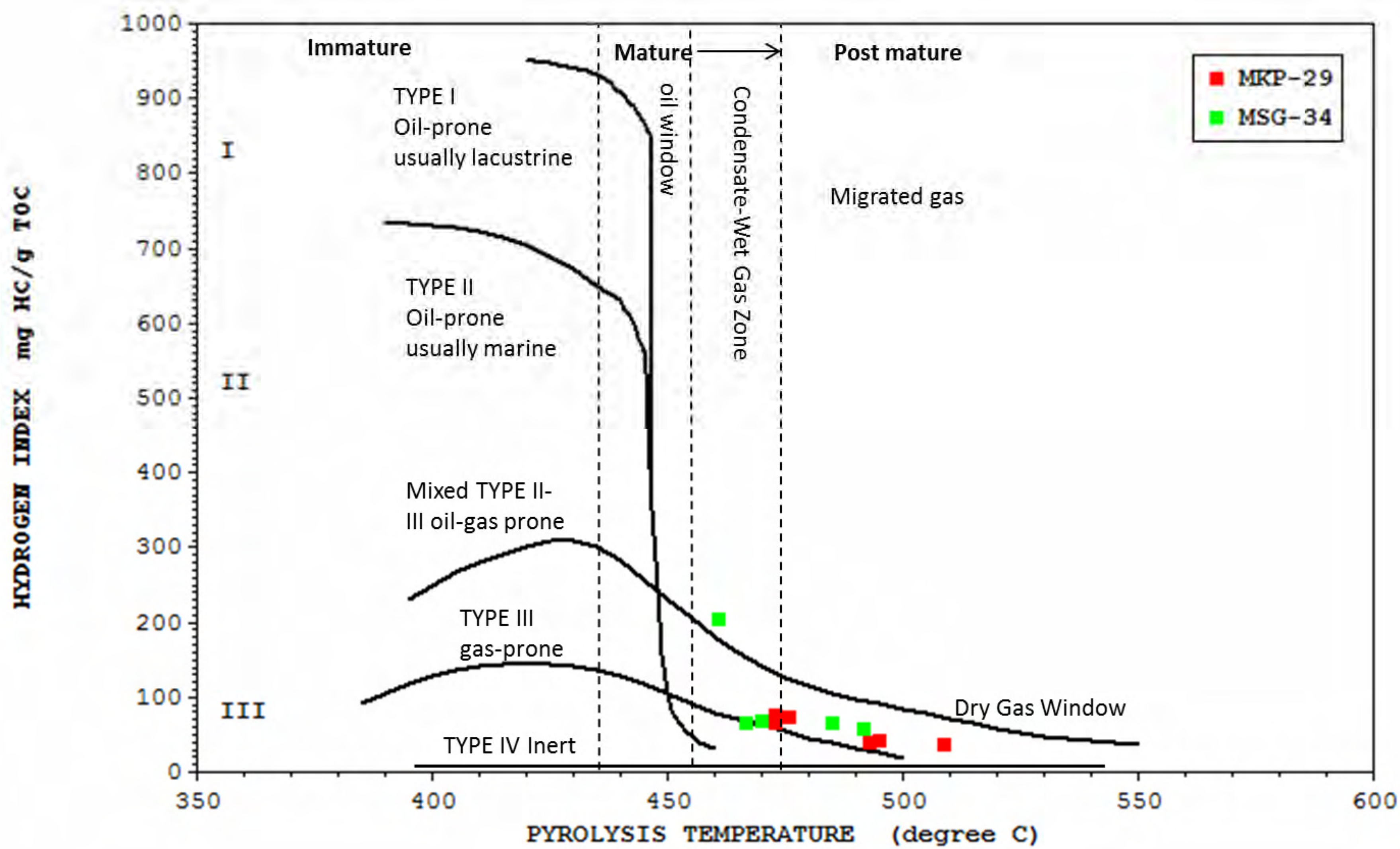
Fig 4. TOC versus S2 diagram of shale samples from Barakar Formation, Jharia Block



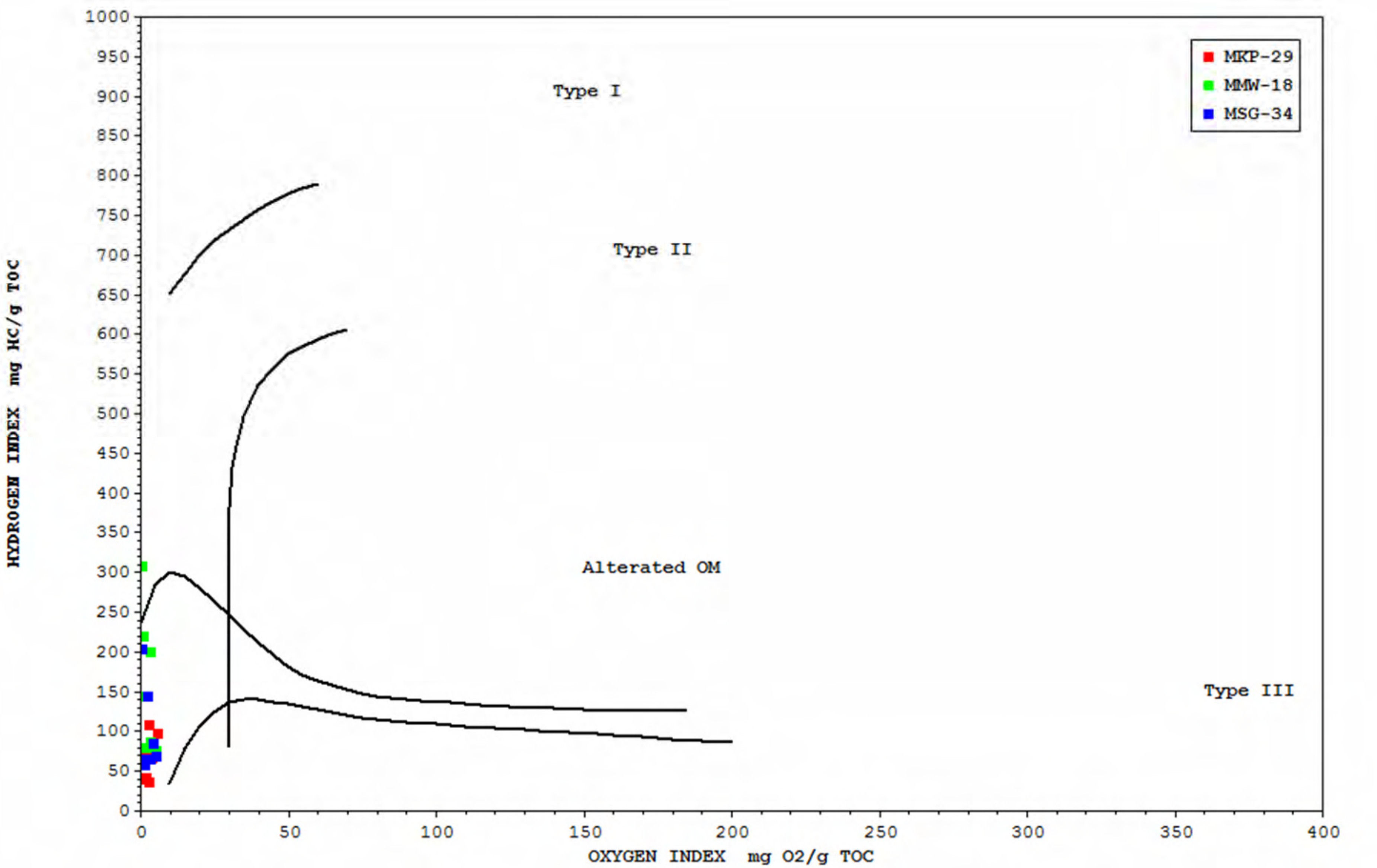
HI versus T max diagram of shale samples from MMW-18 well.



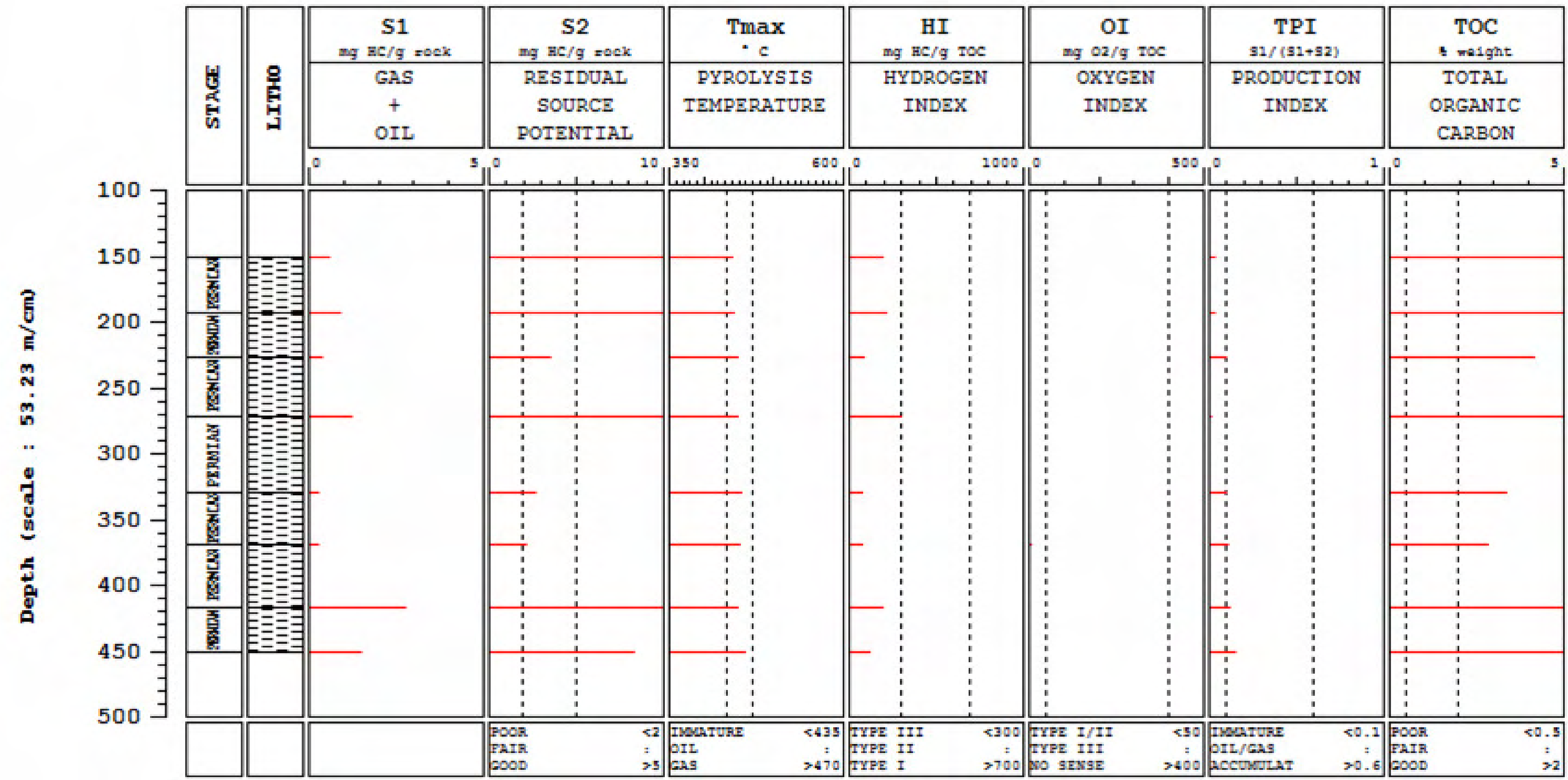
HI versus T max diagram of shale samples from Barren measures Formation.



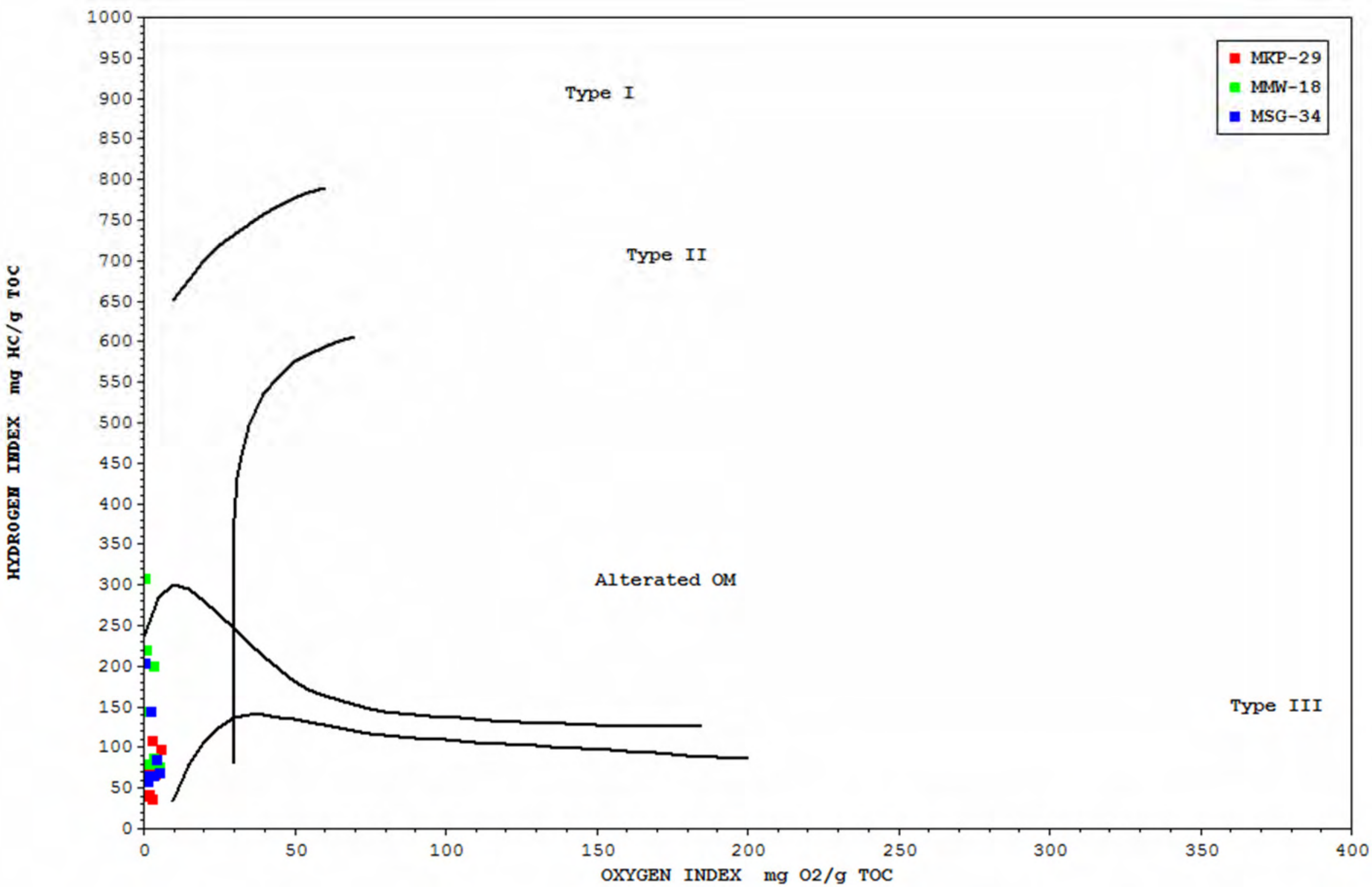
HI versus T max diagram of shale samples from Barakar Formation.



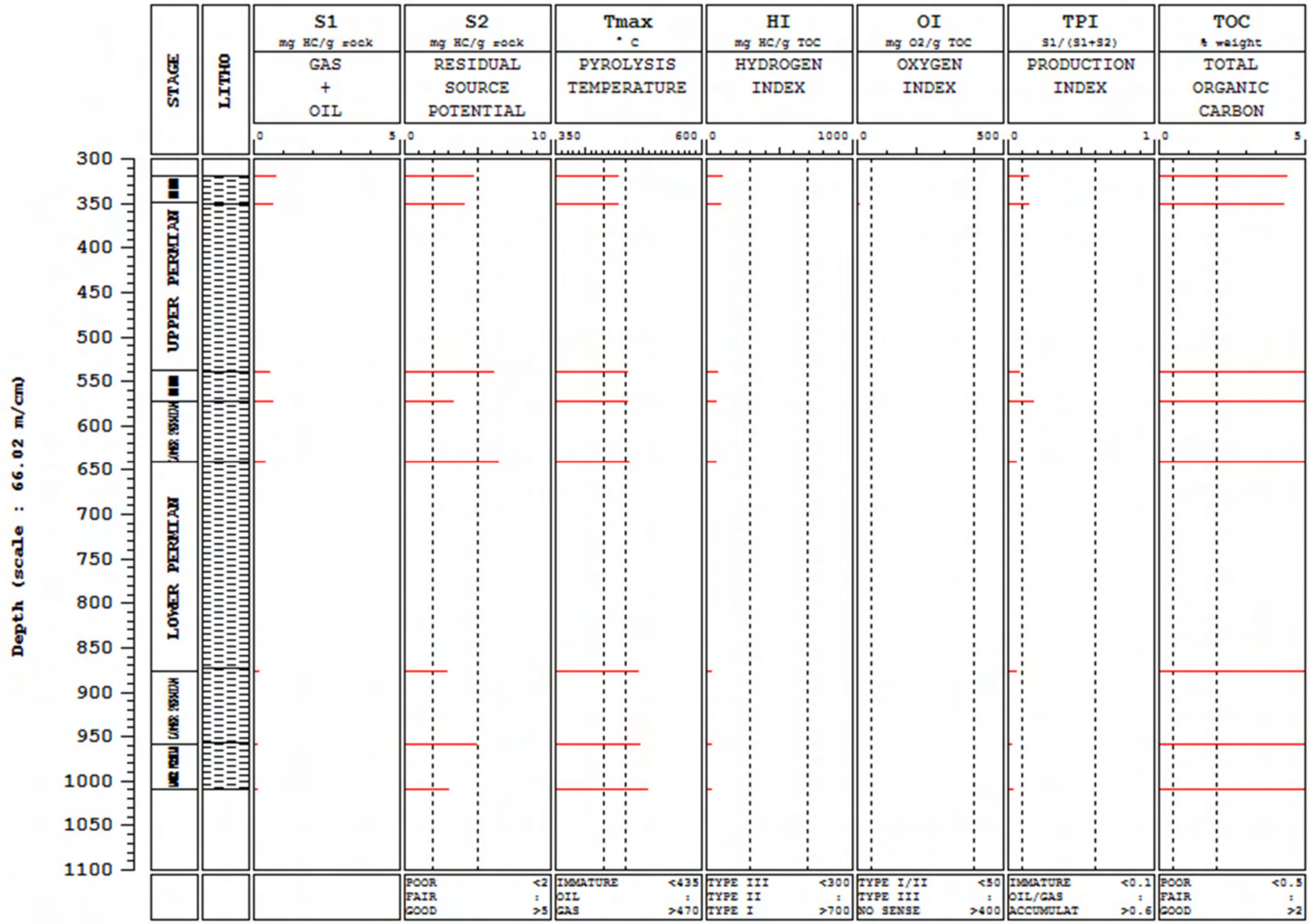
HI versus OI diagram of shale samples from MMW-18, MSG-34, MKP-29 wells, Jharia Block



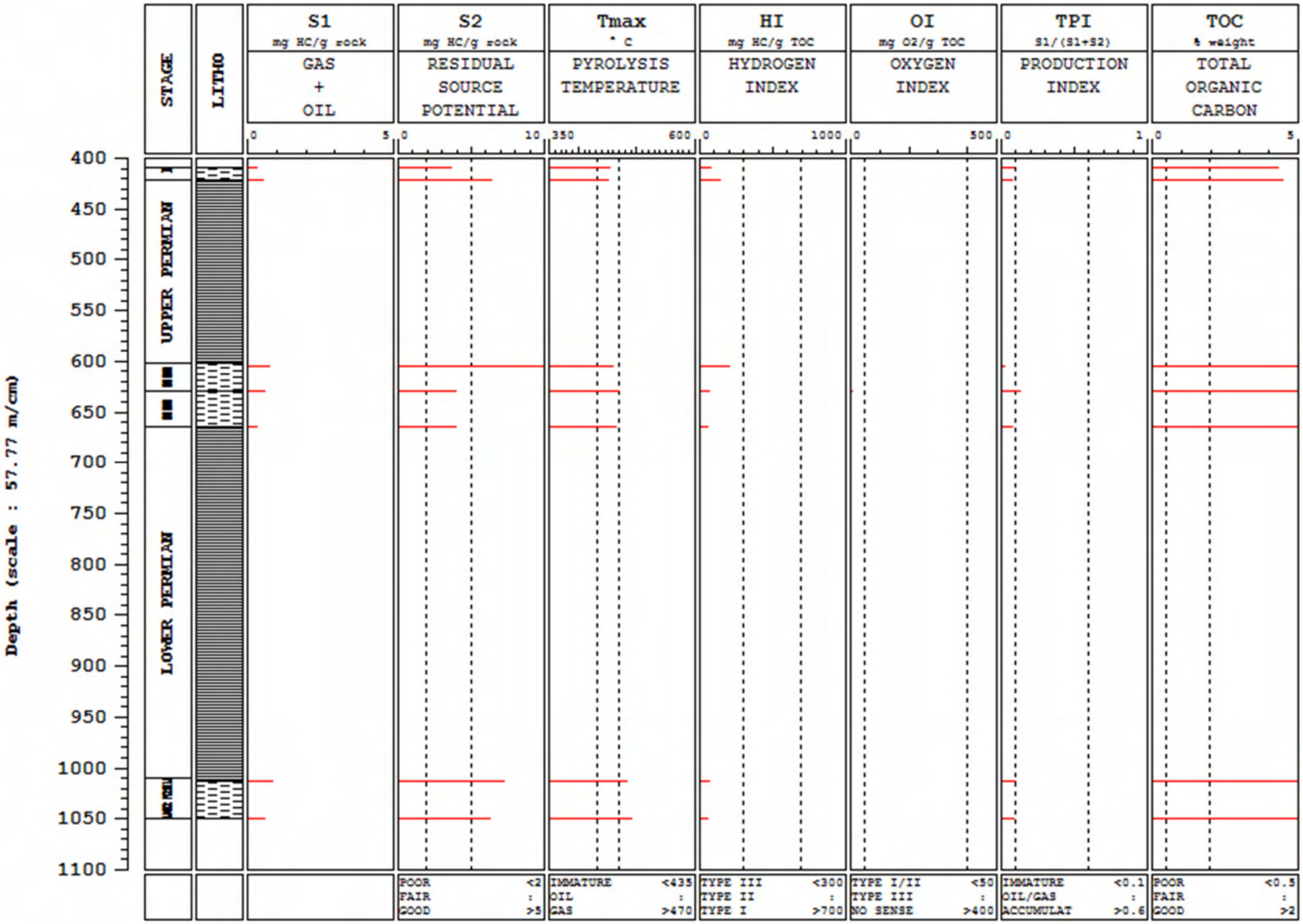
Geochemical Log of MMW-18, Jharia Field:
S1, S2, Tmax, HI, OI, TPI, TOC, versus Depth.



HI versus OI diagram of shale samples from MMW-18, MSG-34, MKP-29 wells, Jharia Block

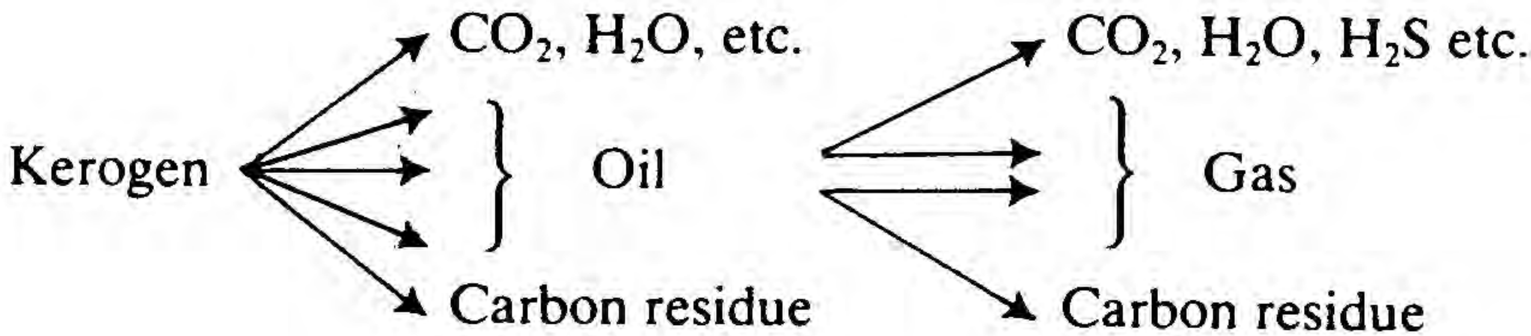


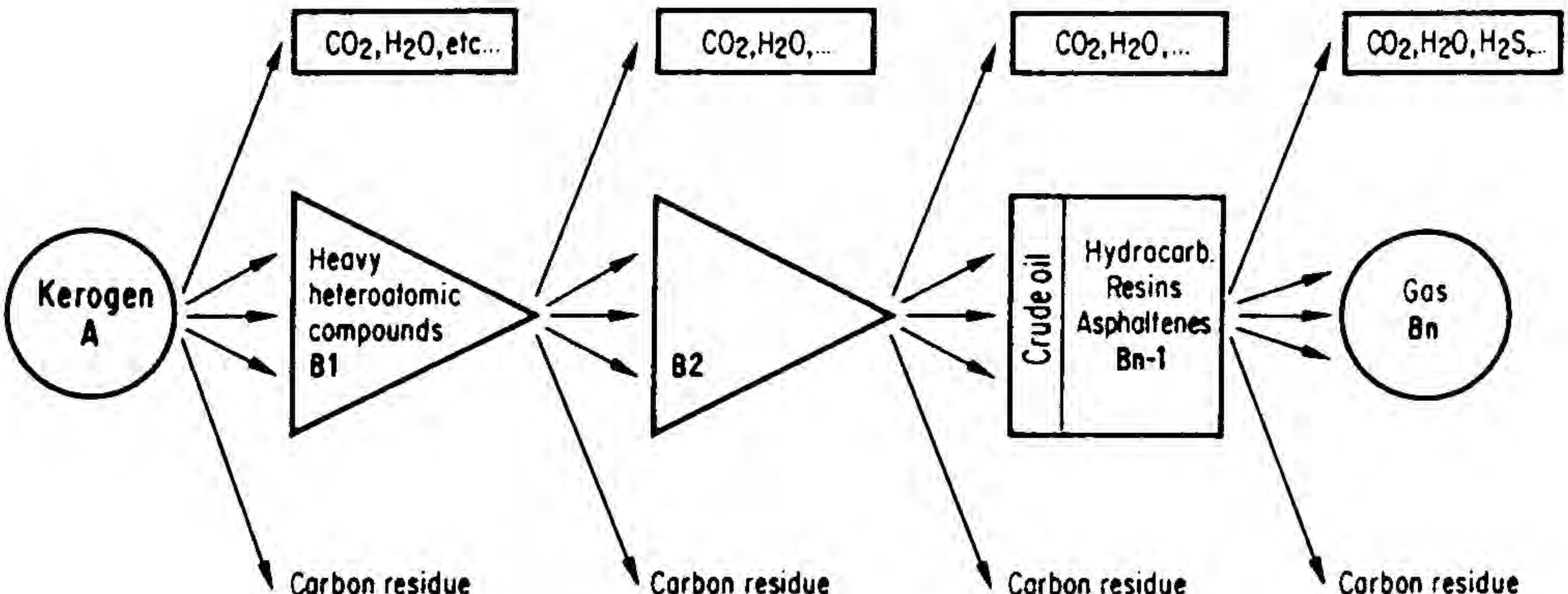
Geochemical Log of MKP-29, Jharia Field: S1, S2, Tmax, HI, OI, TPI, TOC, versus Depth



Geochemical Log of MSG-34, Jharia Field:
S1, S2, Tmax, HI, OI, TPI, TOC, versus Depth.

Hydrocarbon cracking



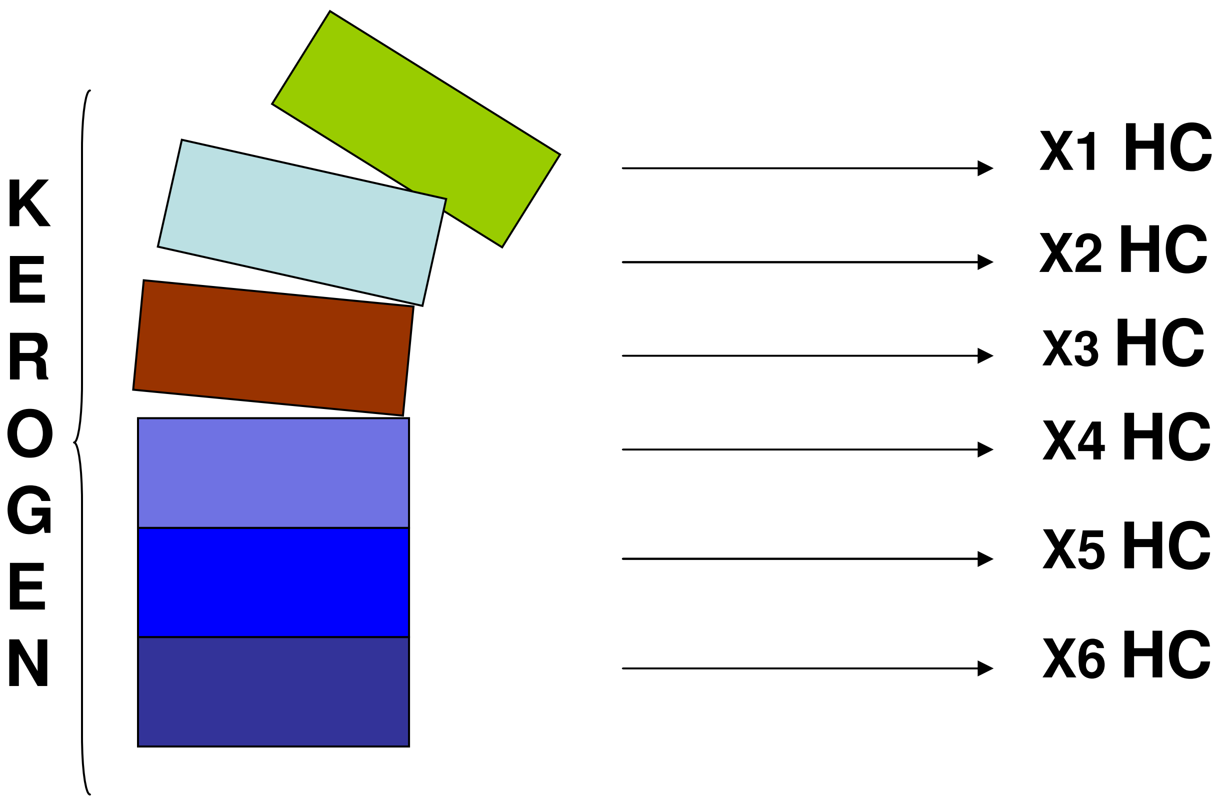


(Tissot & Welte, 1984)

Kinetic model for hydrocarbon cracking

- The amount of hydrocarbons (oil and gas) generated by primary cracking of kerogen when temperature increases through time.

- The degradation of kerogen into hydrocarbons is described by series of n parallel chemical reactions.



$\sum X_i$ = HC potential

- Each of reaction obeys a first order kinetics, characterized by Arrhenius Law

$dXi/dt = -ki. -Xi$ ——— 1.

dXi/dt = hydrocarbon generation rate
Xi= residual petroleum potential
t=time (sec)

$ki=A \exp(-Ei/RT)$ ——— 2.

A= Arrhenius constant
Ei=activation energy
R= molar gas constant
T= absolute temperature
Xi= residual petroleum potential

- Complete Arrhenius law for each reaction i may be defined as:

$dXi/dt = A\exp(-Ei/RT). Xi$

- Total initial petroleum potential of kerogen (Hydrogen Index) HI in mg HC/gTOC is

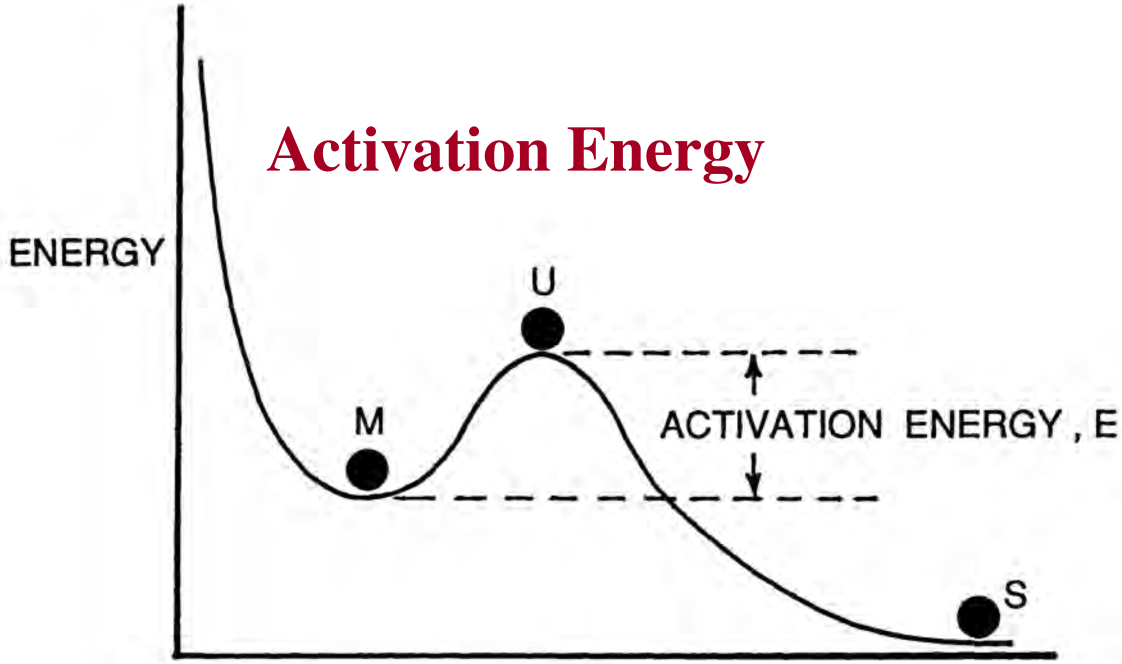
$$HI = \Sigma^{n}_{i=1} xi_o$$

Xio = initial petroleum potential of the kerogen

- The amount Q of generated hydrocarbons is (mg HC/gTOC)

$$\boxed{Q = \sum_{i=1}^{n} (Xi_o - Xi)}$$

Activation Energy

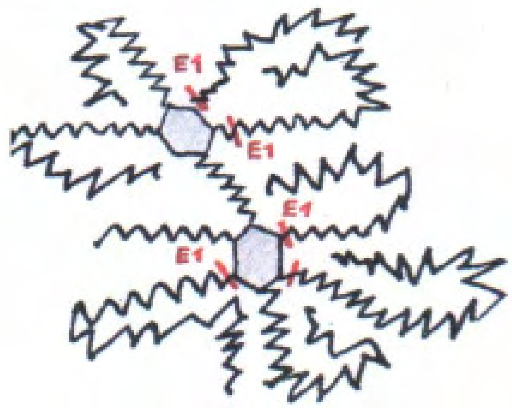


Bond Energies

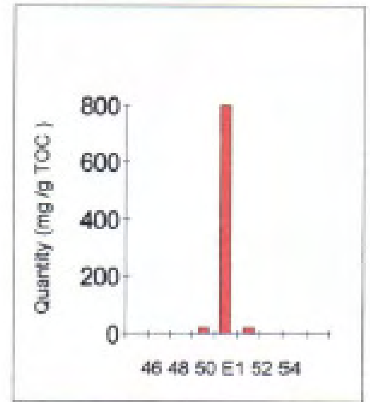
BOND	kcal/mol	kJ/mol
C – H	96 - 99	401 - 414
C – C	83 - 85	347 - 356
C – N	69 - 75	289 - 314
C – O	85 - 91	356 - 381
C – S	66	276
C = C	146 - 151	460 - 464
N – H	93	389
S – H	82	343

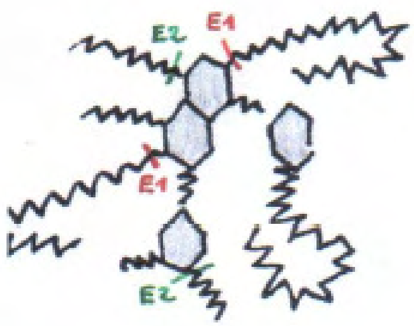
SCHEME OF CHEMICAL STRUCTURES OF THE THREE MAIN TYPES OF IMMATURE KEROGEN

DISTRIBUTION OF ACTIVATION ENERGIES



TYPE I
HIo=820





TYPE II
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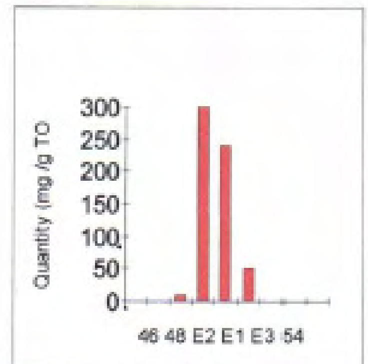
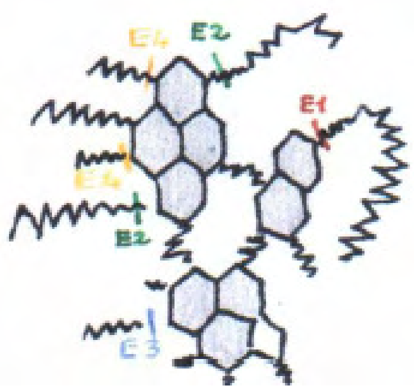
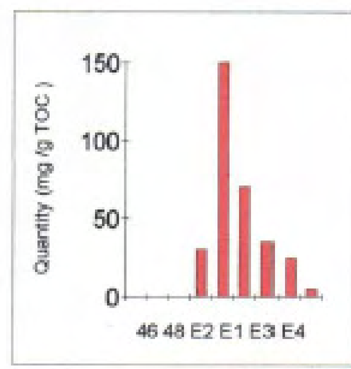
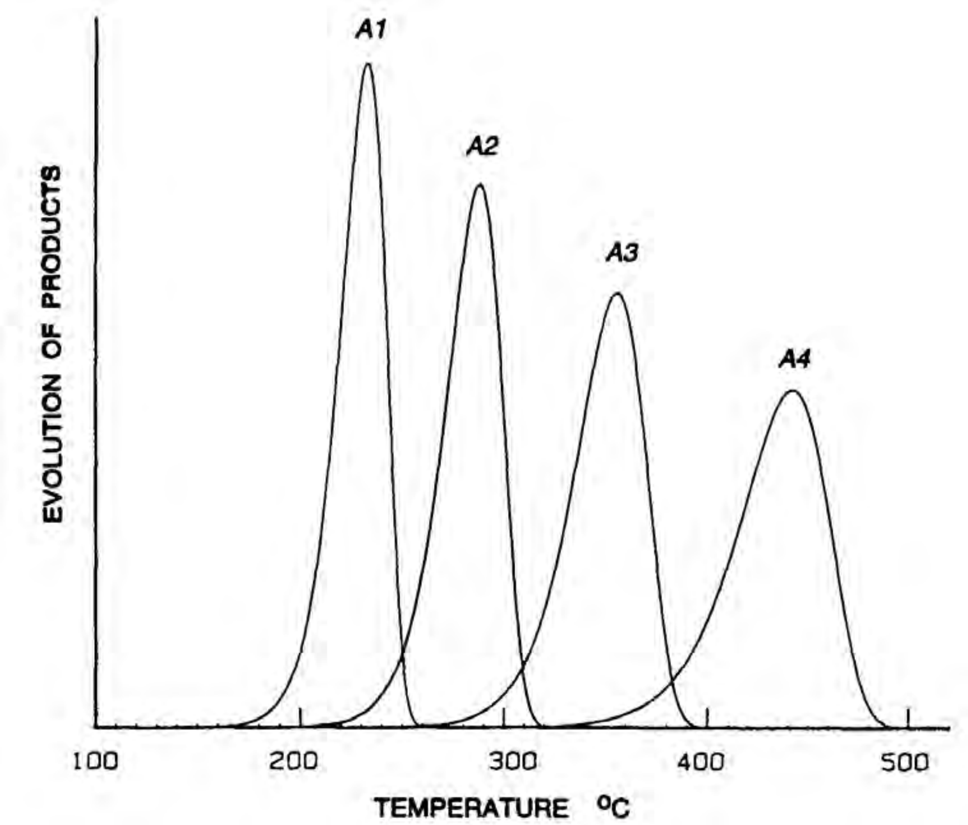


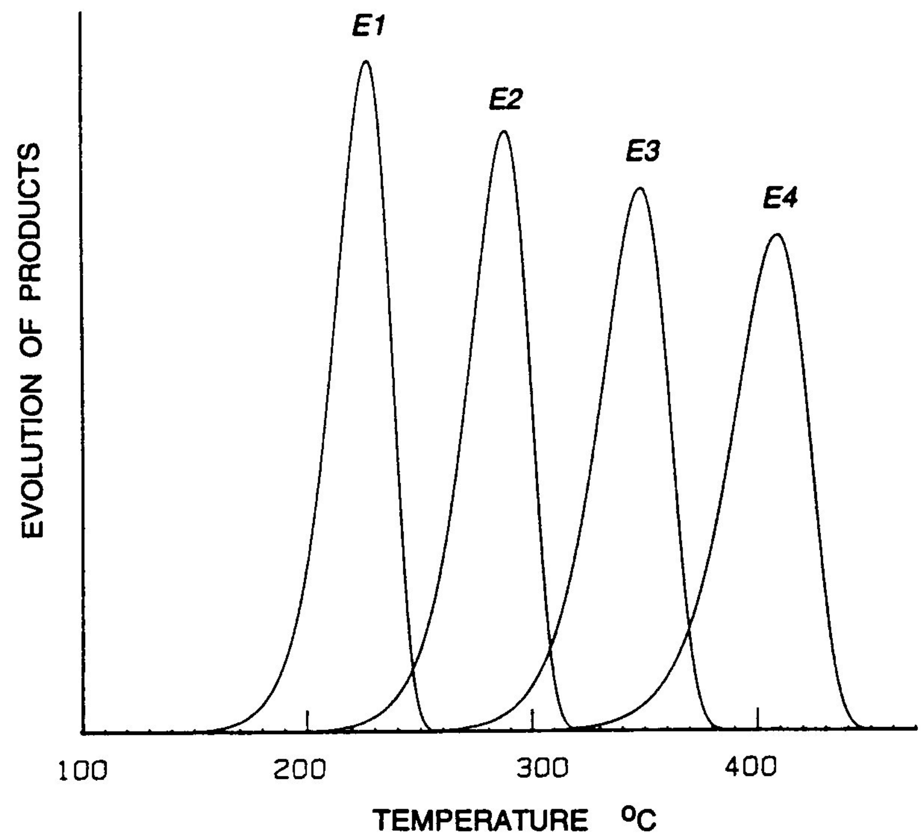


TYPE III
HIo=275



Bitumen Release Curves with Different



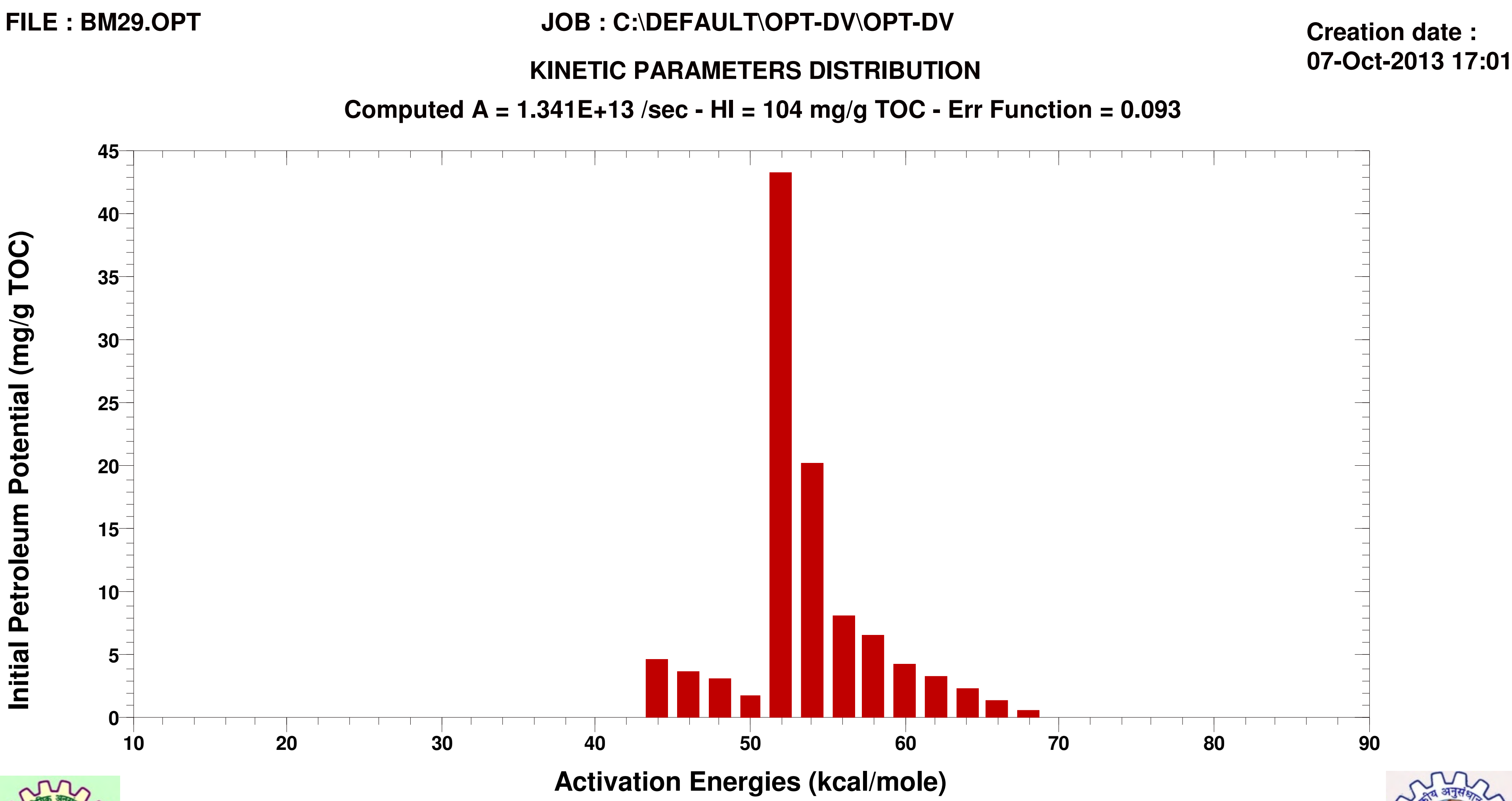


Barker, 1996

Frequency Factors

Activation Energies

Kinetic parameter distribution for the Barren Measures Formation



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HYDROCARBON GENERATION RATE

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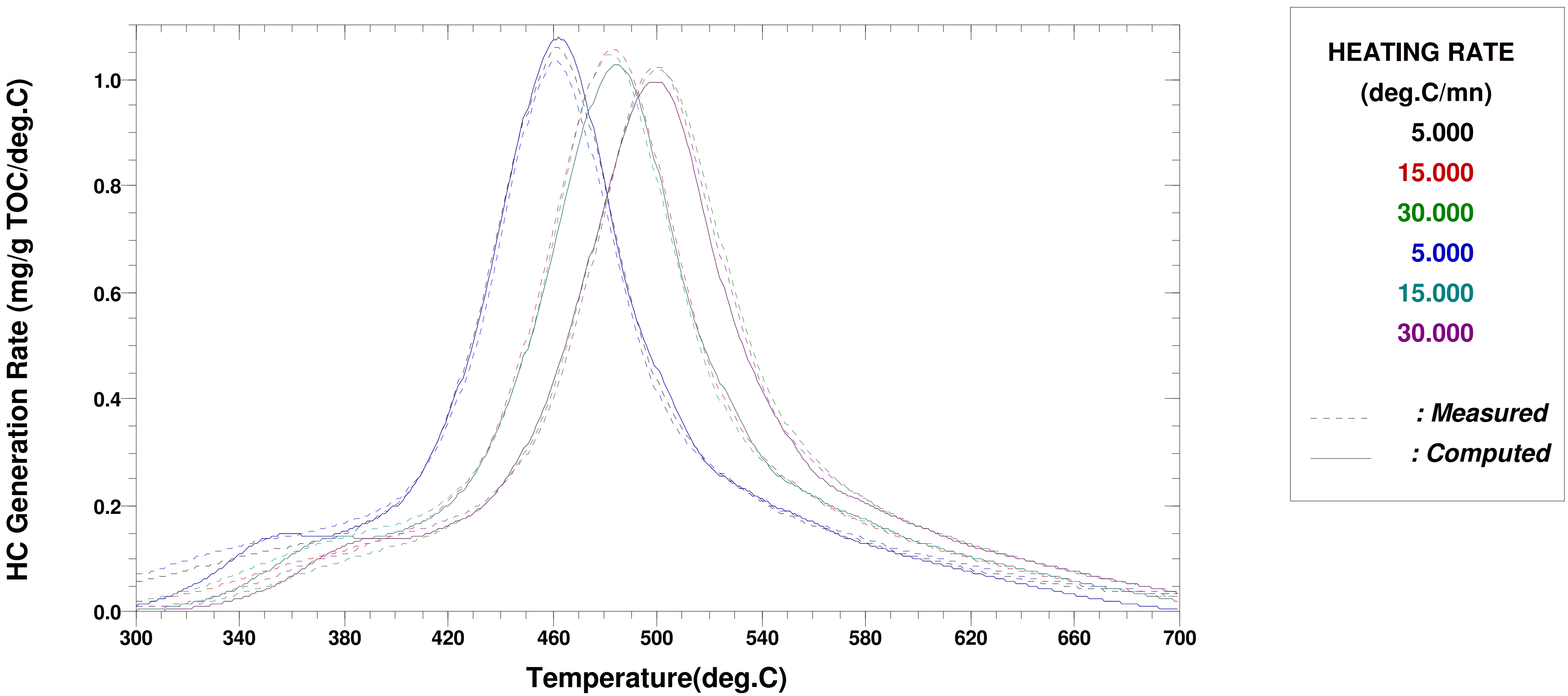

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GENERATED HYDROCARBON

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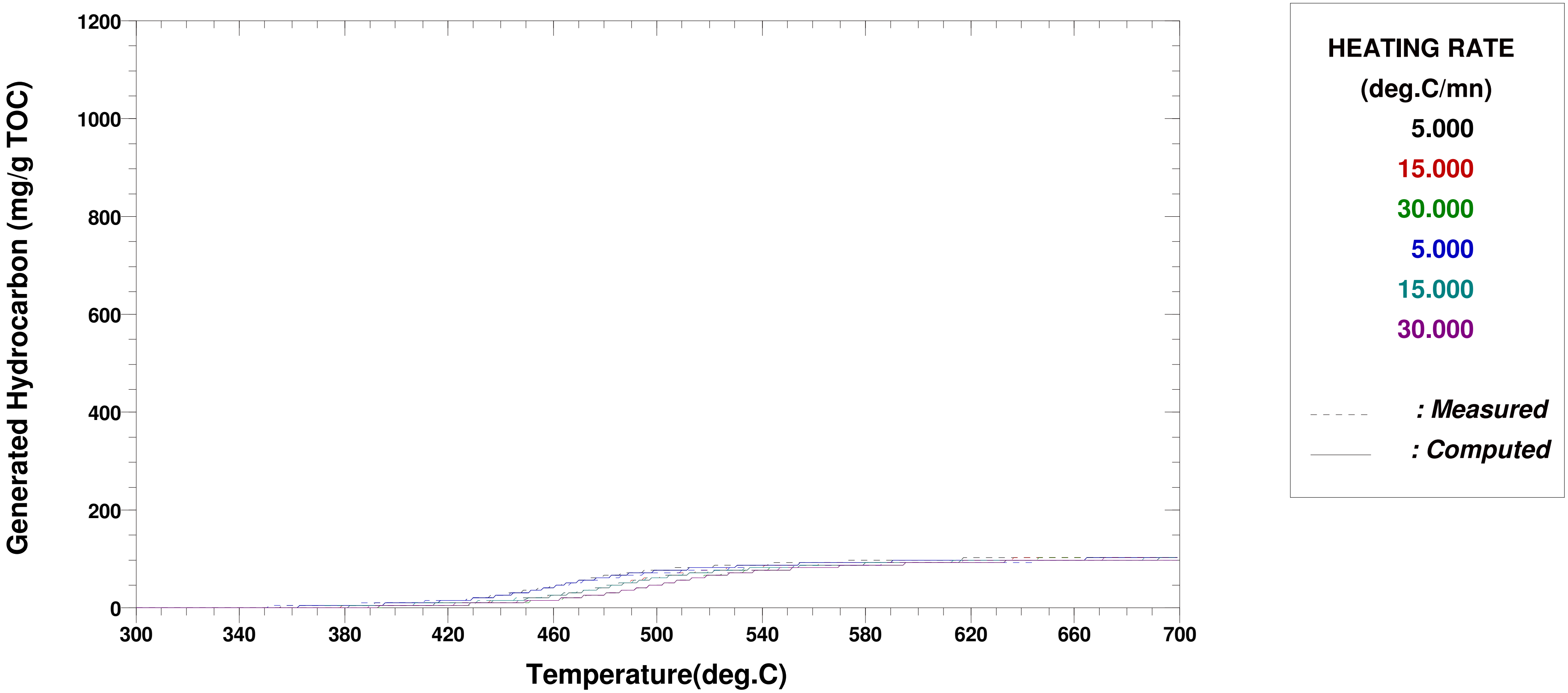

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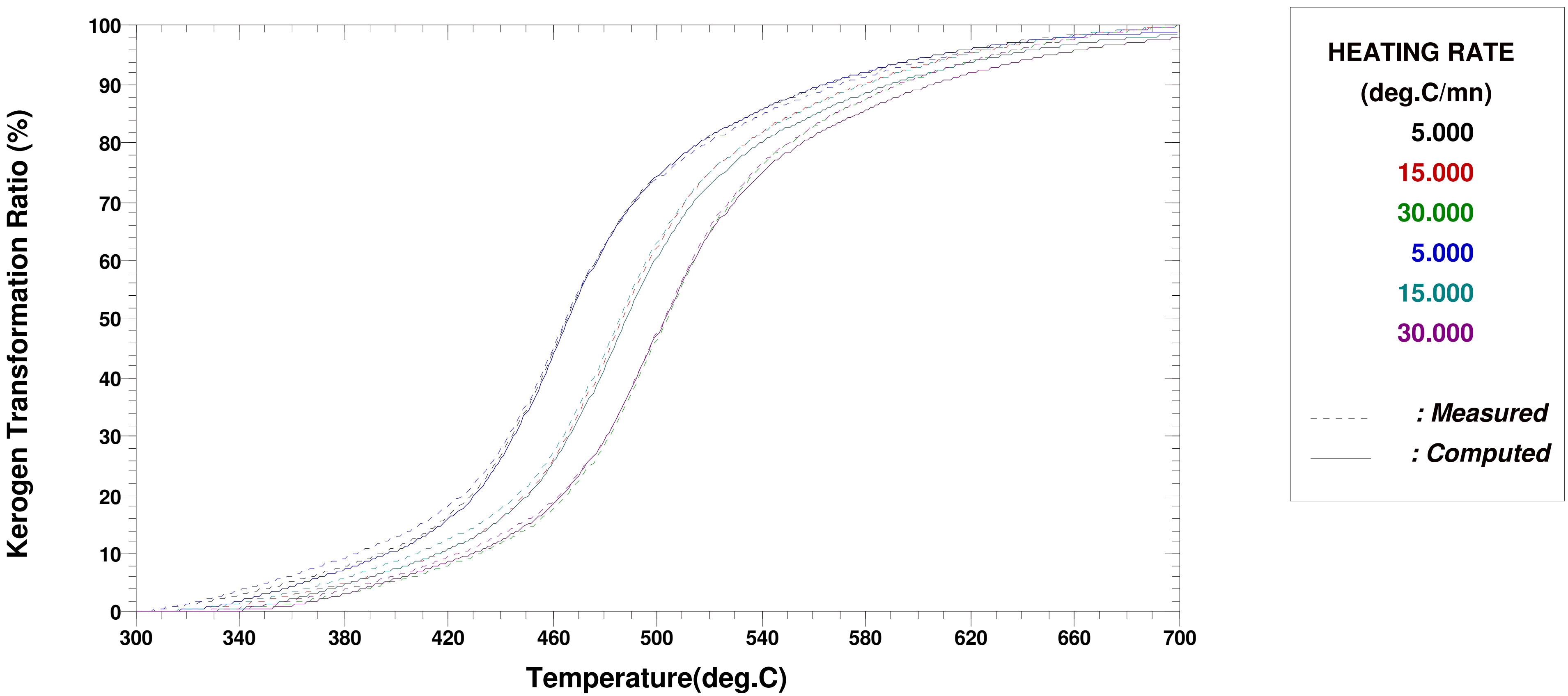
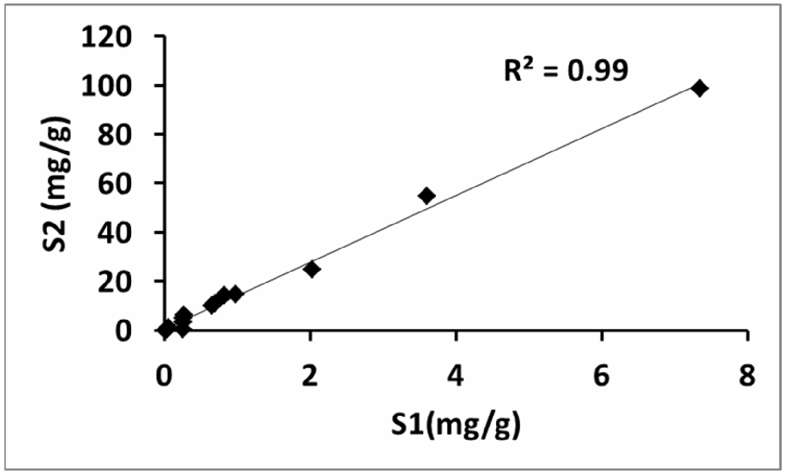
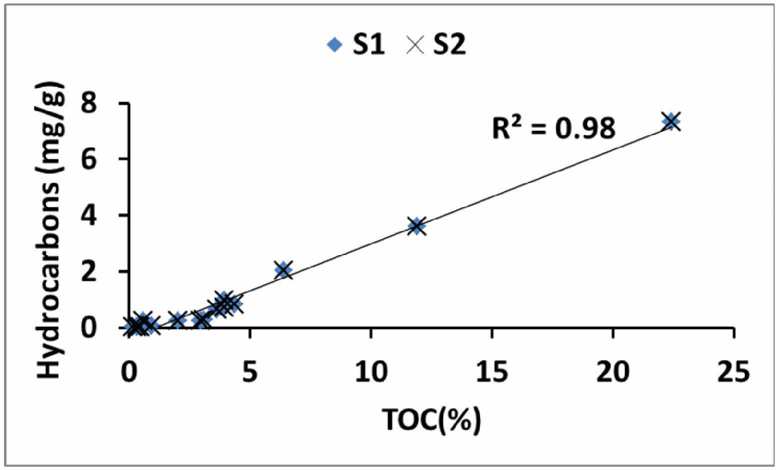
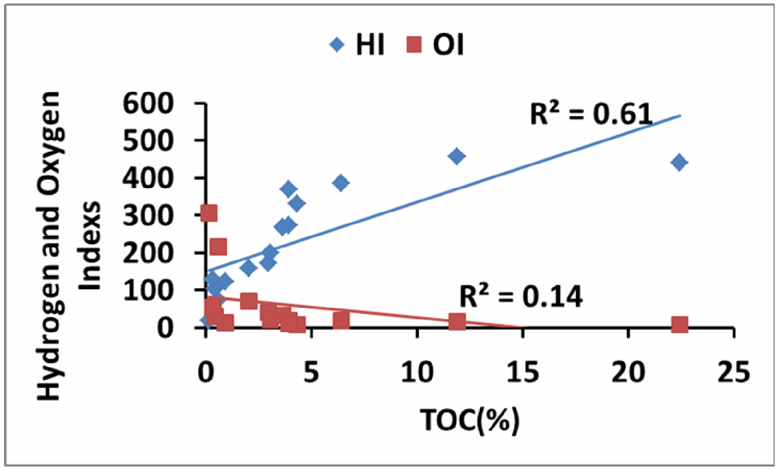
KEROGEN TRANSFORMATION RATIO

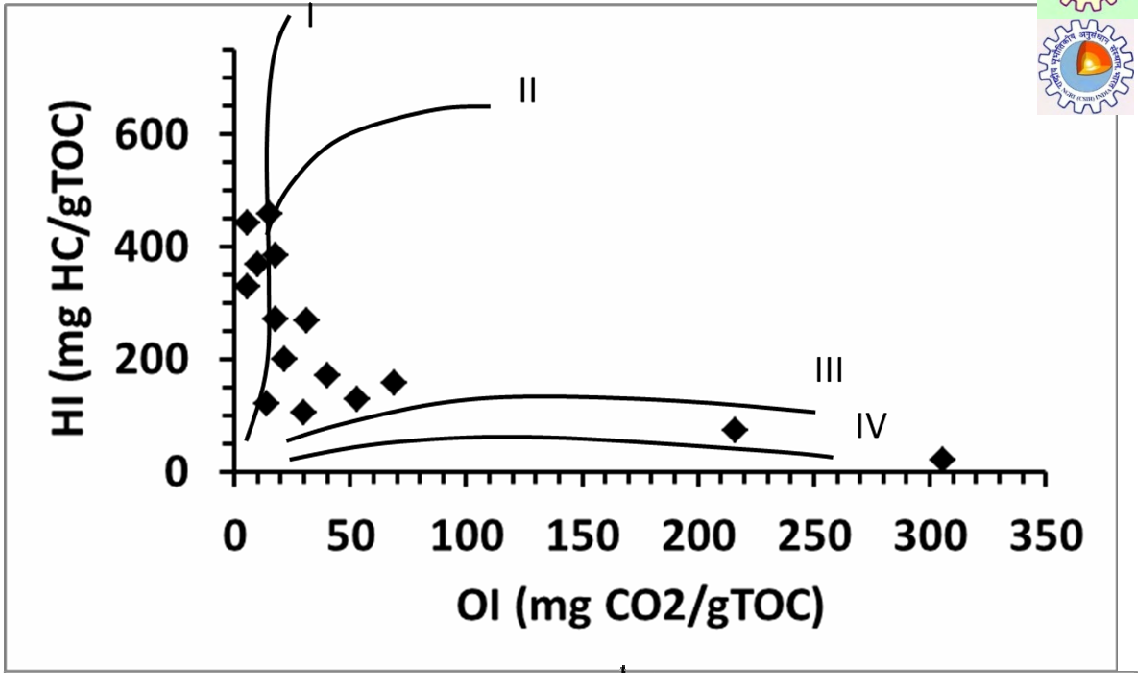


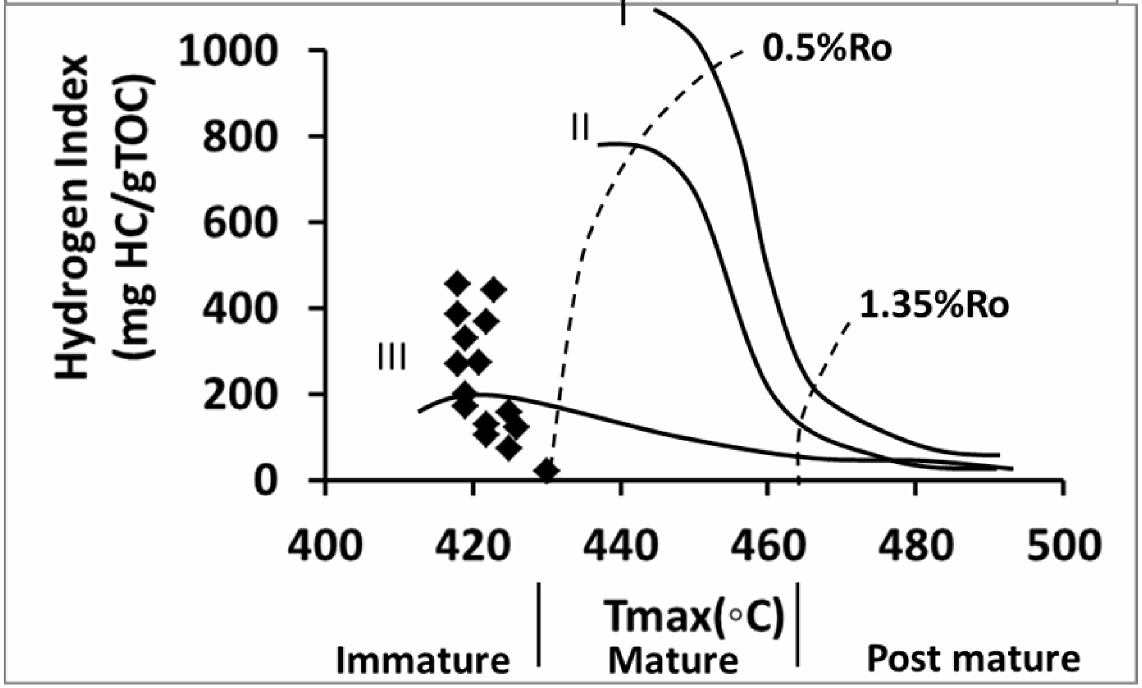
Well BRK- ASSAM ARAKAN











Geochemical Evaluation of the Subathu Group Shales from the Jammu Region for the Shale Gas Prospect

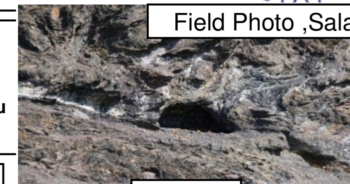
Chakkar Coal Mine

Underground Mines

Subathu Shales

Abstract

Natural gas, primarily methane, from the shale rock formations is emerging rapidly as an unconventional energy resource globally and also in India. Geochemical attributes of the shale source rocks, namely total organic carbon (TOC) content, thermal maturity and kerogen type are controlling parameters in generation of shale gas. In the present work, carbonaceous shales from the Subathu Group of Jammu & Kashmir (J&K) have been studied for their organic richness and maturity based on the programmed pyrolysis method of Rock Eval (RE) VI.

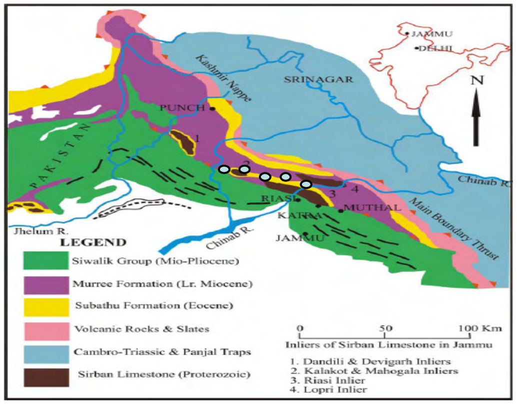


Field Photo ,Salal

Outcrops

Subathu Shales

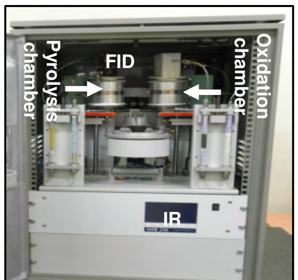
1. Field Study



Formations	Age
Alluvium & Terrace Deposits	Recent & Sub Recent
Siwalik Group	Mio-Plio-Pleistocene
Murree Group	Upper Eocene-Lower Miocene
Subathu Group	Eocene
------------------------------Back thrust----------------------------------- (Marked by Brecciated unit & Bauxite beds)	
Sirban Limestone	Proterozoic
---------------------------Base not exposed-----------------------------	

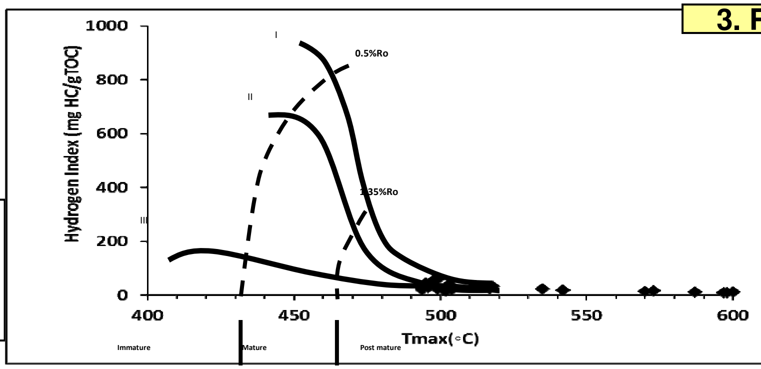
- The Upper Palaeocene to Eocene Subathu Group consists of olive green to dark green shales interbedded with thin limestone bands and coal seams
- It is considered as source rock for the hydrocarbons in the Himalayan Foreland basin in analogy with the adjoining petroliferous Kohat-Potwar basin of Pakistan
- .The shales were sampled from outcrops around Kalakot, Kotla, Mahogala, Salal, Kanthan & Kalimitti areas of Jammu

2. Analytical Method



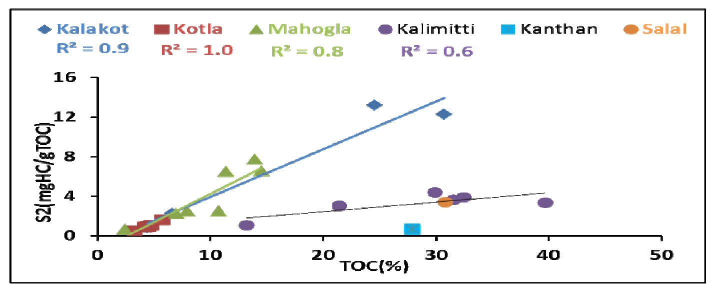
Rock Eval VI

RE VI is calibrated in standard mode using the IFP standard, (Tmax = 416℃; S2= 12.43). Powered samples (~ 50-70 mg) were weighed in pre-oxidized crucibles and run under analysis mode using the bulk rock method and basic cycle of RE 6.



3. Results

Parameters	Range of Values
Total Organic Carbon (TOC)	3-65%
S_1(thermally liberated HC)	0.1-2.6 mg HC/g Rock
S_2(HC from kerogen cracking)	0.5-15.5 mg HC/g Rock
Tmax (temp. at high. yield of S_2)	490-515 ℃
Hydrogen index (HI)	10-50 mg HC/g TOC
Oxygen index (OI)	0-30 mg HC/g CO_2

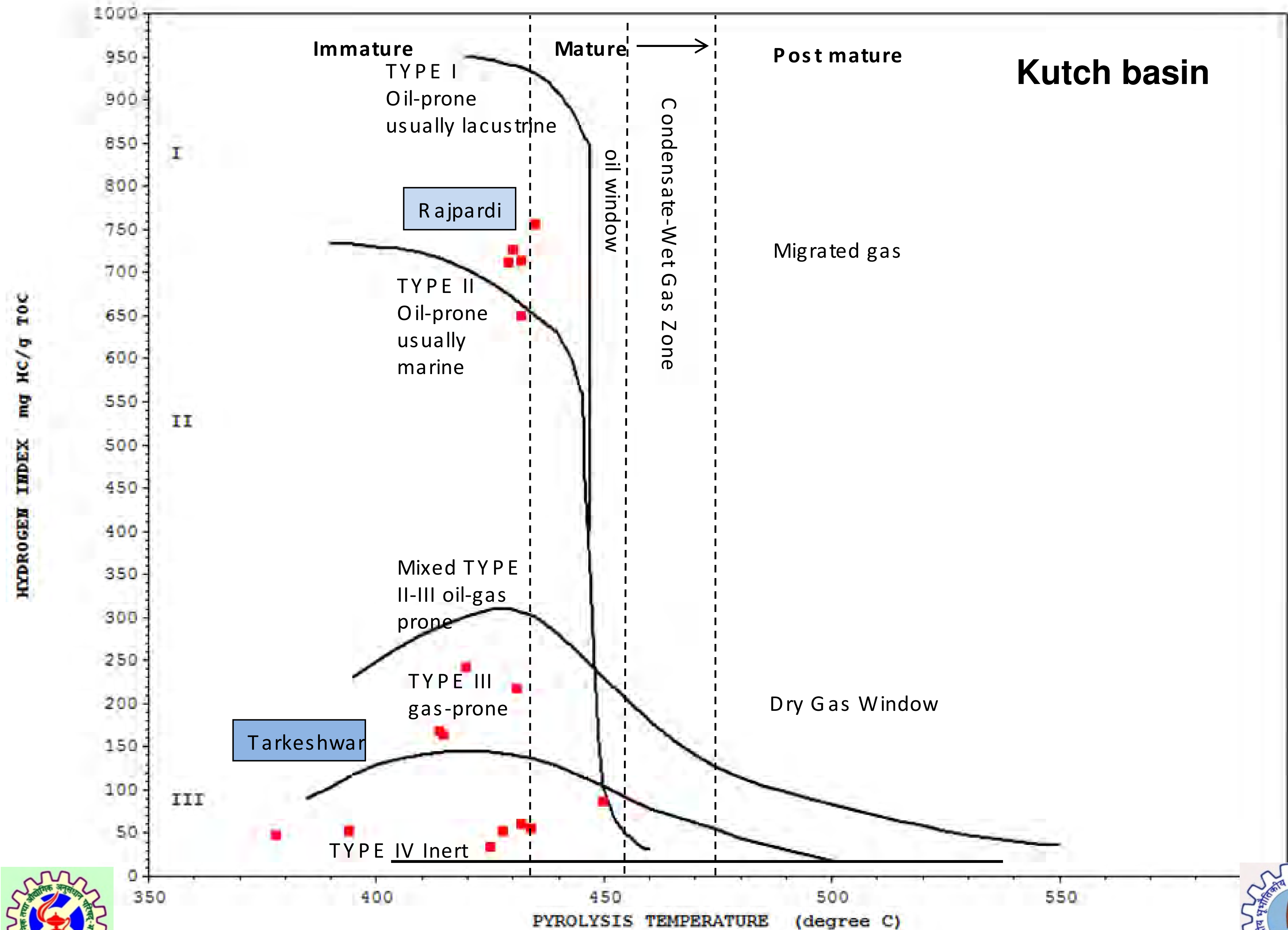


4. Conclusion

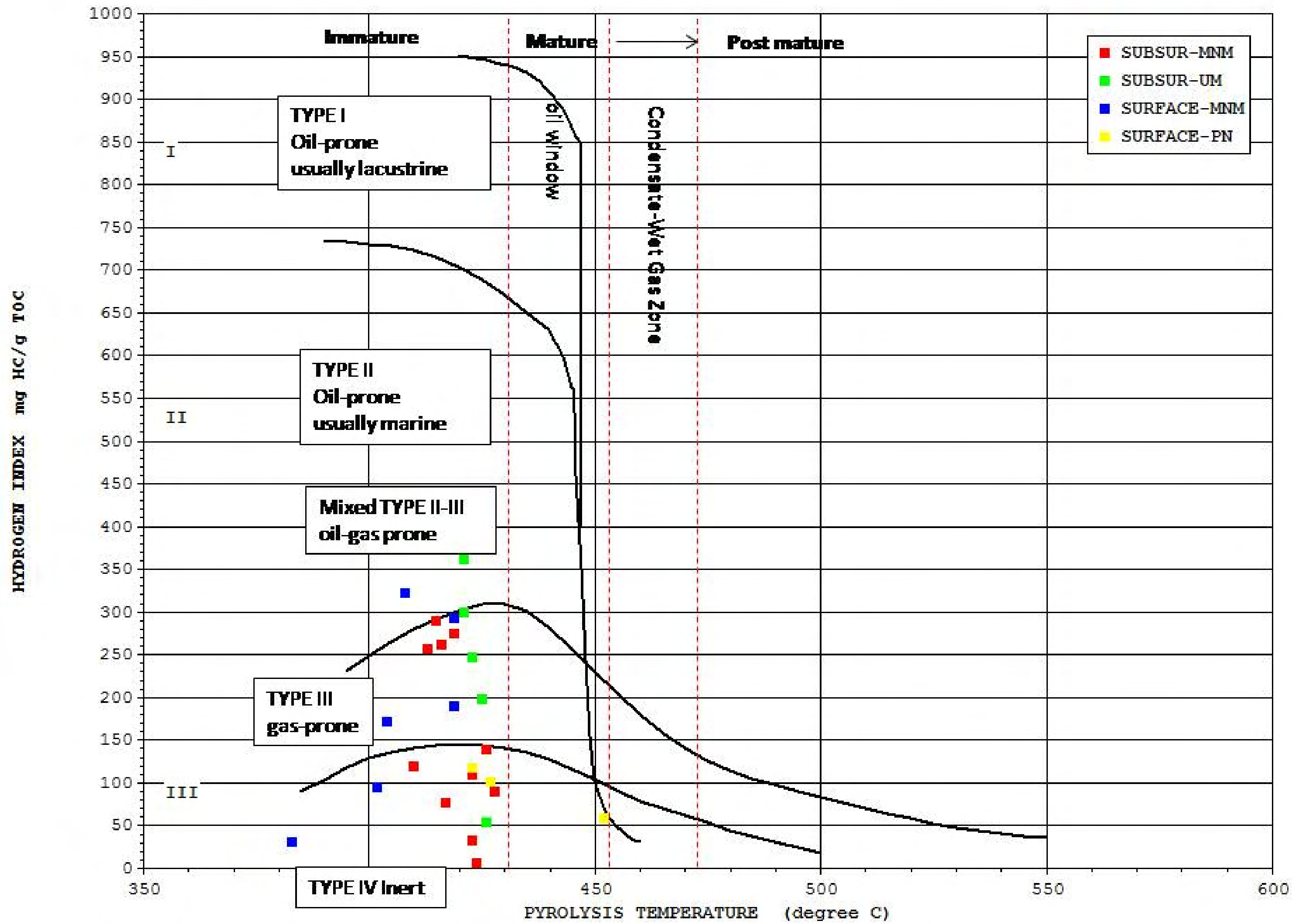
- High TOC, S1 and S2 peaks are characteristic of the 100% of samples.
- The Tmax values suggest an over mature phase for the hydrocarbons.
- The organic matter in majority of samples contains Type III kerogen and has generation potential for the gaseous HC's hydrocarbons. The Subathu Group might act as source for these gaseous hydrocarbons.
- Estimations on expelled and retained gas inferred from the geochemical properties can be made by the taking into account the generation potential, source rock thickness and porosity of the shale formations.
- With a suitable gas generation potential initiatives taken towards detail studies from viewpoint of shale gas prospect in

Acknowledgements

The Oil industry Development Board is acknowledged for the financial support.



Kutch basin
Immature
Mature
Post mature
TYPE I
Oil-prone
usually lacustrine
Rajpardi
TYPE II
Oil-prone
usually
marine
oil window
Condensate-Wet Gas Zone
Migrated gas
Mixed TYPE
II-III oil-gas
prone
TYPE III
gas-prone
Tarkeshwar
Dry Gas Window
TYPE IV Inert
I
II
III
HYDROGEN INDEX mg HC/g TOC
PYROLYSIS TEMPERATURE (degree C)
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
350
400
450
500
550



Cambay basin

THANK YOU!