Kinetic modelling of kerogen cracking during oil shale process : influence of organic matter source

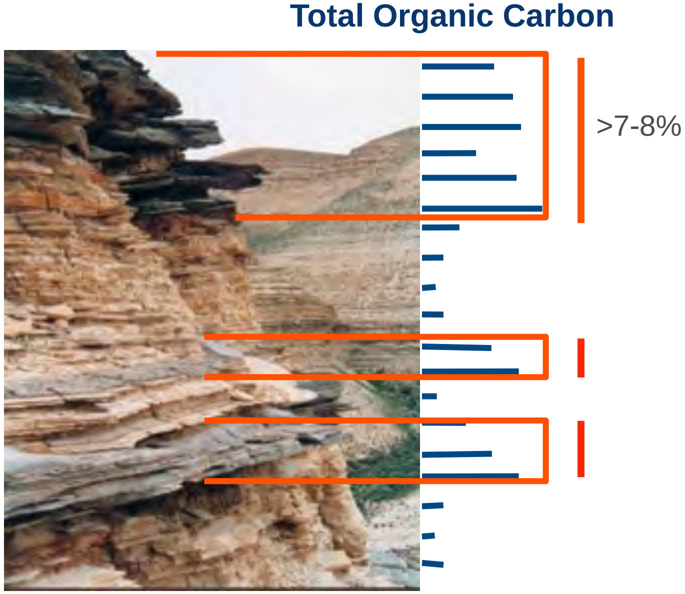
F. Behar and P. Allix

General outline

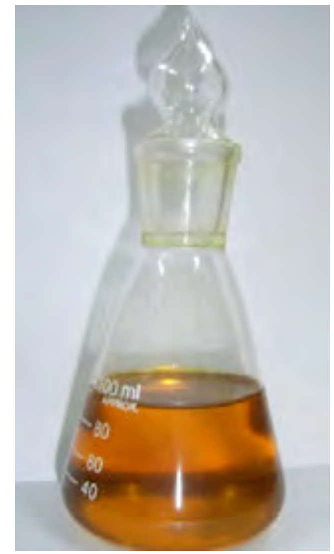
- **I – Introduction**
- **II – Kerogen characterization**
  - Definition of the main organic matter
    - Initial geological deposit
    - Oil shale potential
- **III – Understanding the main reaction of kerogen cracking**
  - Kinetic schema
  - Micro pilot reactor
  - Mass balances
  - Compositional model
- **IV – Impact on oil shale yield and chemical composition**
  - Primary products
  - Secondary reaction
- **V – Conclusions**

Oil shale pyrolysis : new challenges for unconventional resources

Solid organic matter (kerogen)



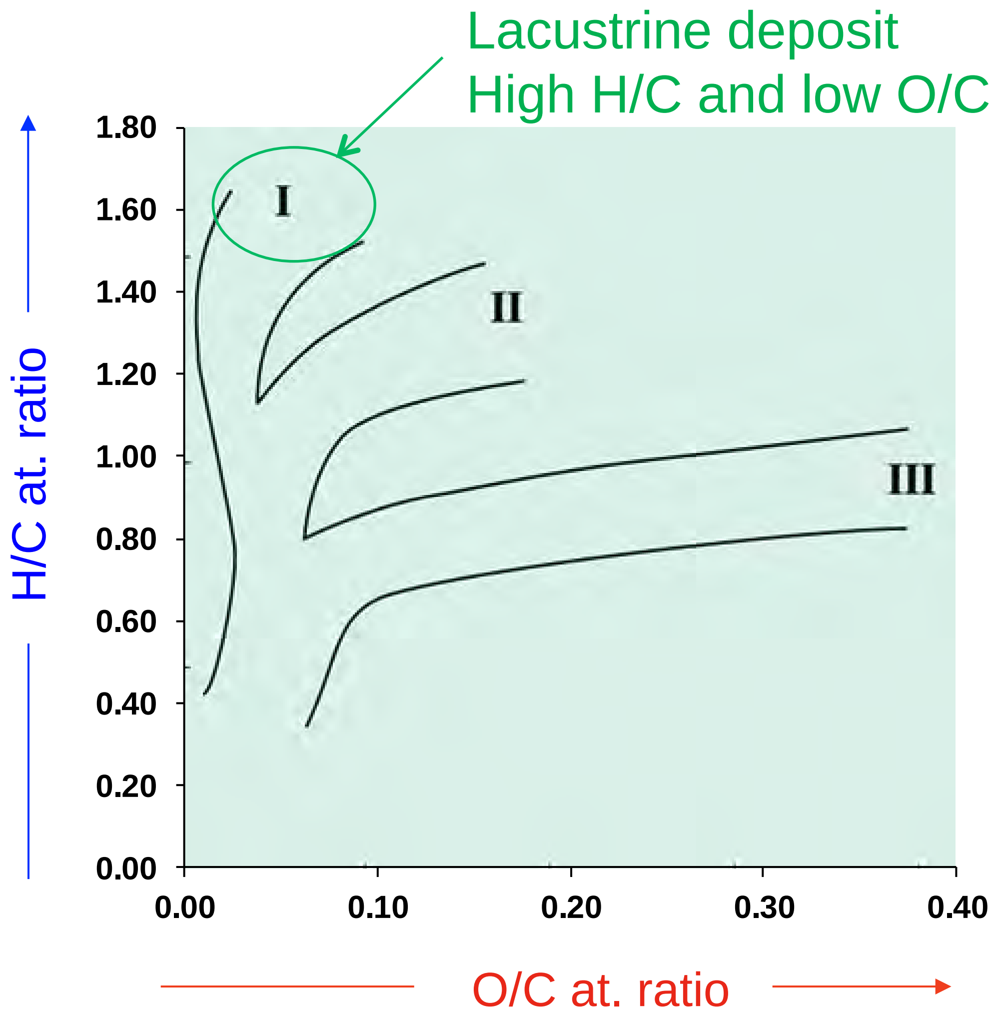
Oil shale process
T : 200 to 400°C
Weeks to months



°API > 30

How does organic matter quality impact yield and chemical composition of the produced oil ?

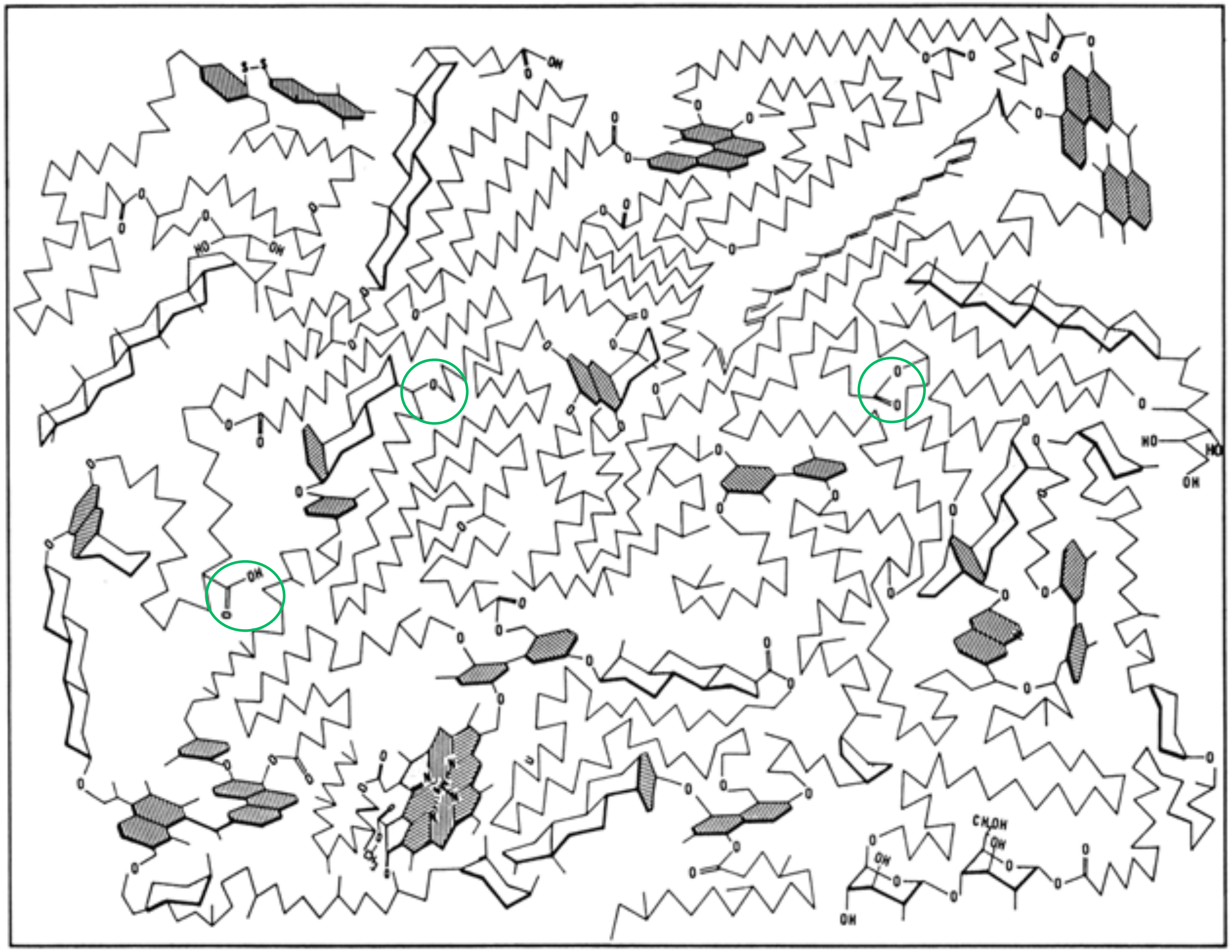
Classification of organic matter in source rocks



Van Krevelen diagram

F.

Classification of organic matter in source rocks



Aliphatic chains
Low aromatic content
Ester – Acids – Ether

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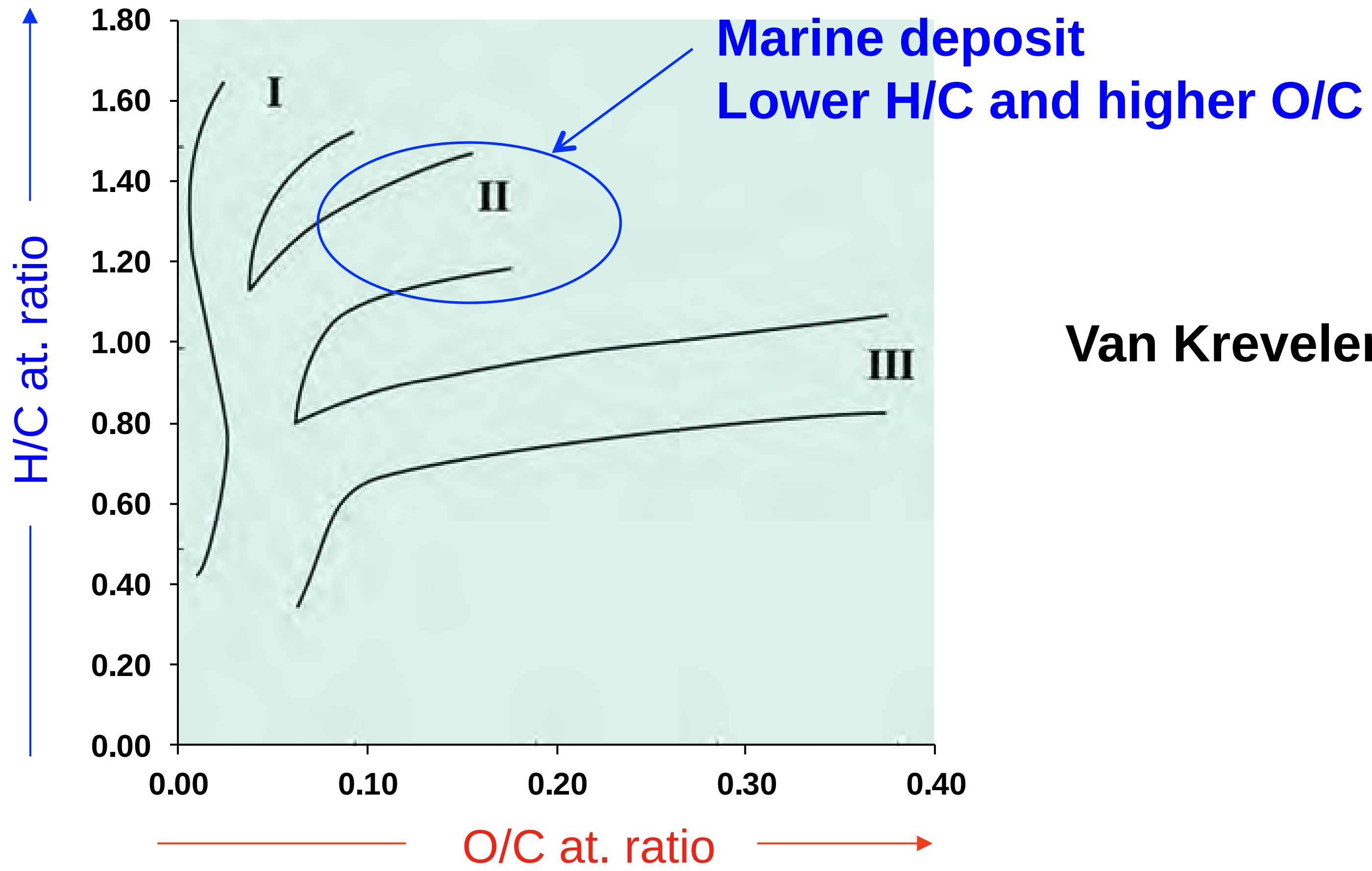
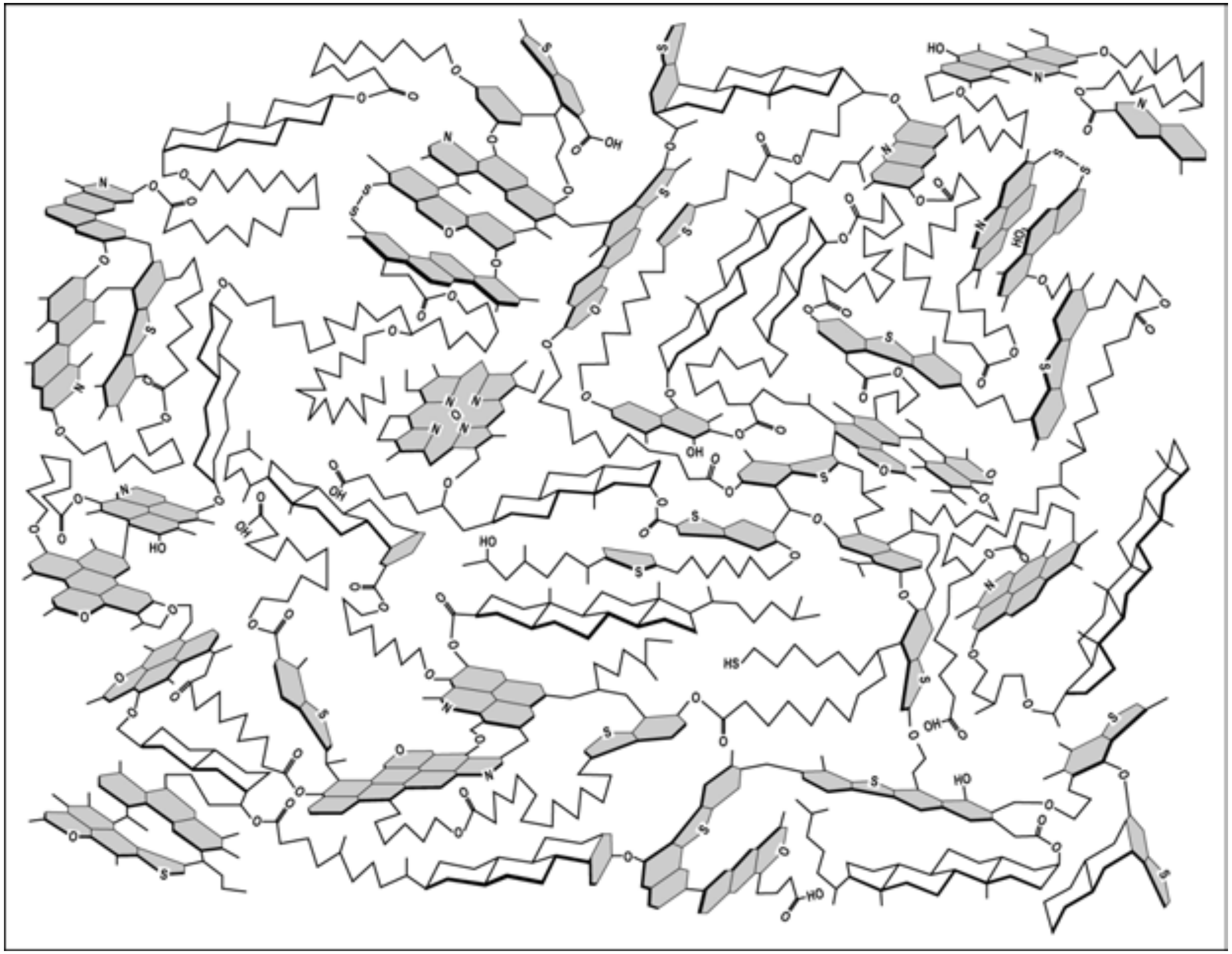
Classification of organic matter in source rocks



Van Krevelen diagram

F. Behar a

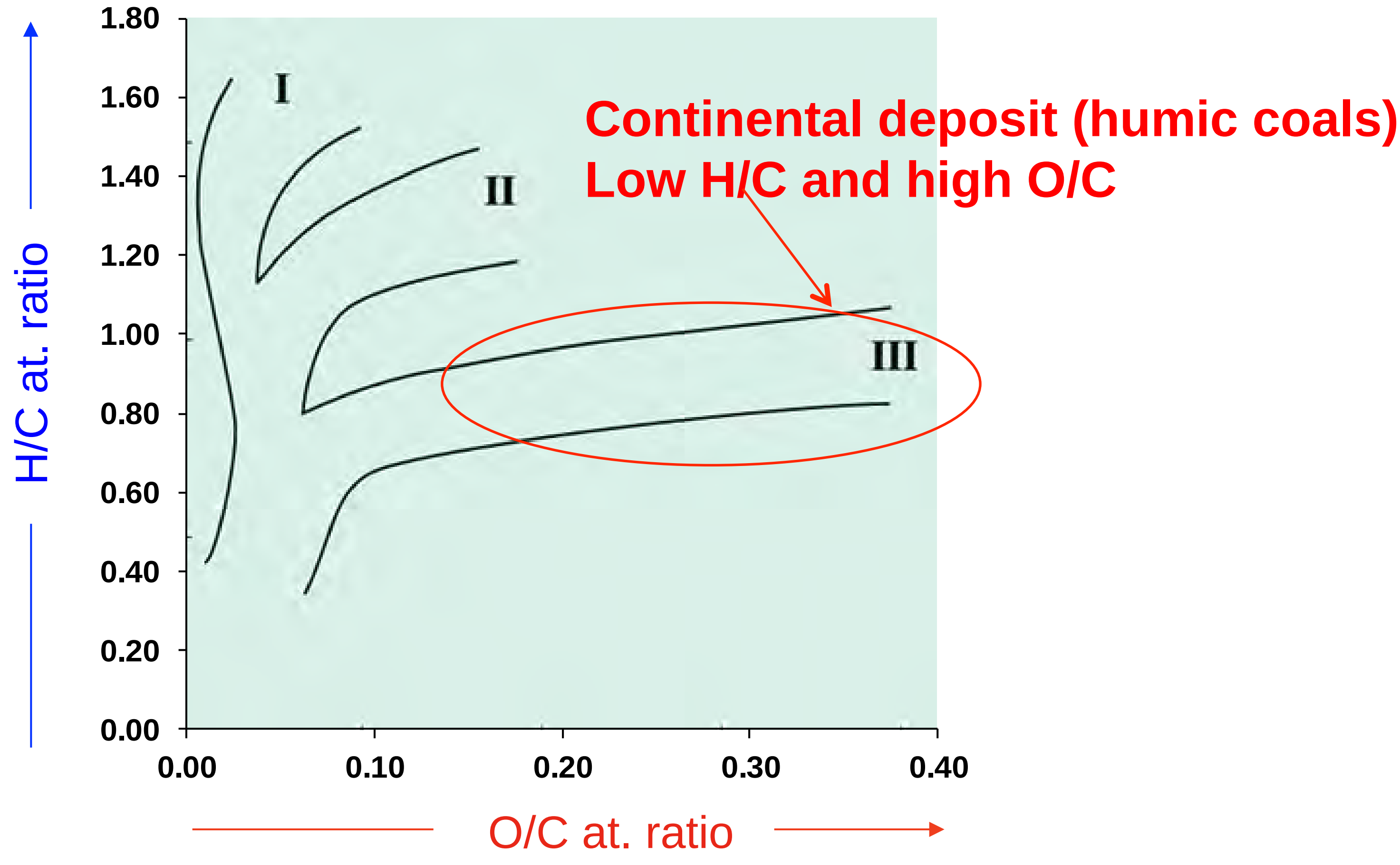
Chemical structure of marine organic matter (Type II)



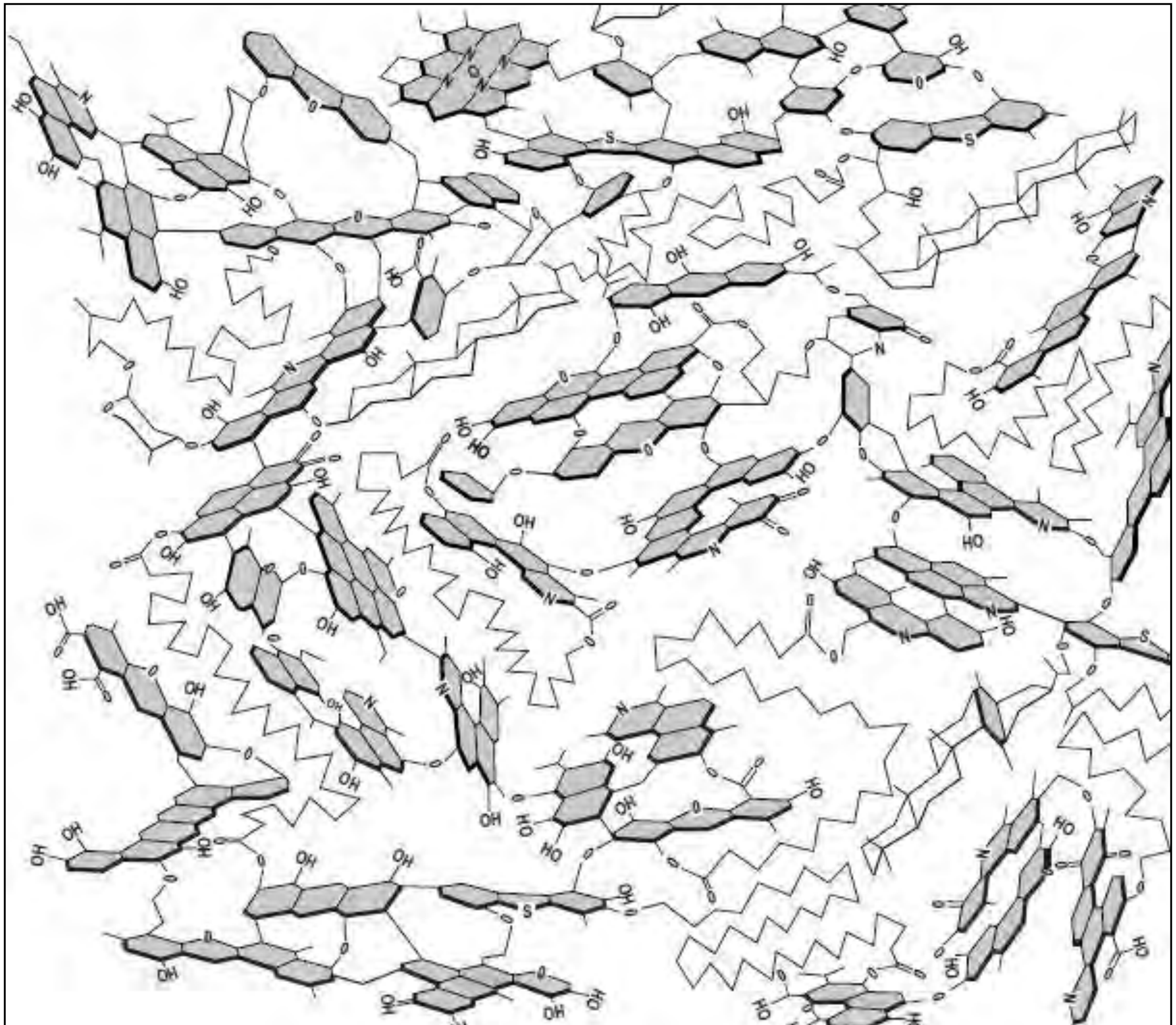
Aliphatic chains and cyclanes
Significant aromatic content
Ester – Acids – Ether

<u>Type II – S</u>
High sulfur content
Confined marine deposit

Classification of organic matter in source rocks



Chemical structure of continental organic matter (Type III)



Aromatics and phenols
Ester – Acids – Ether

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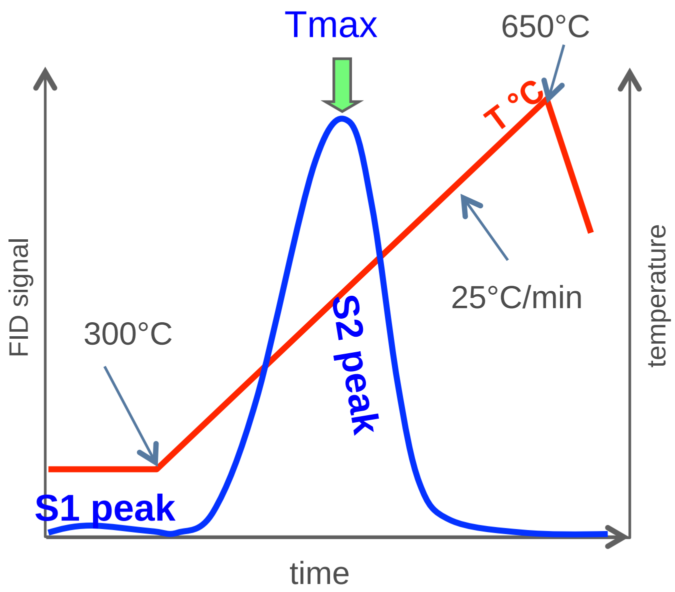
Shale oil potential

Rock Eval pyrolysis

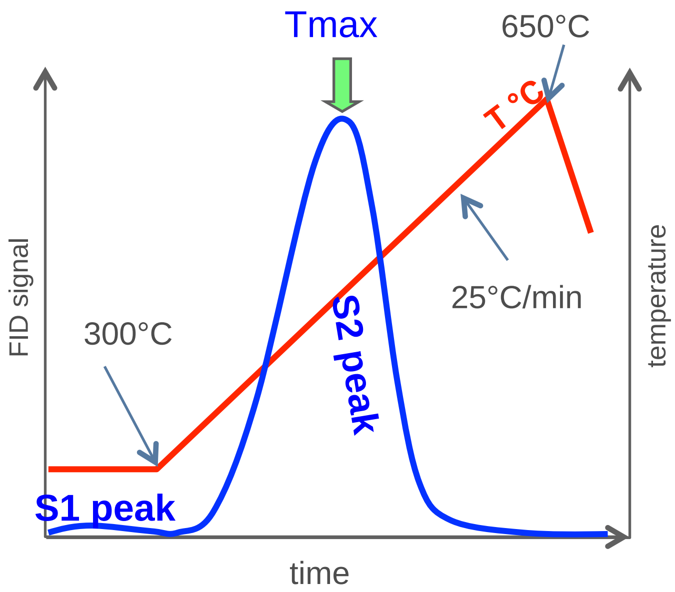


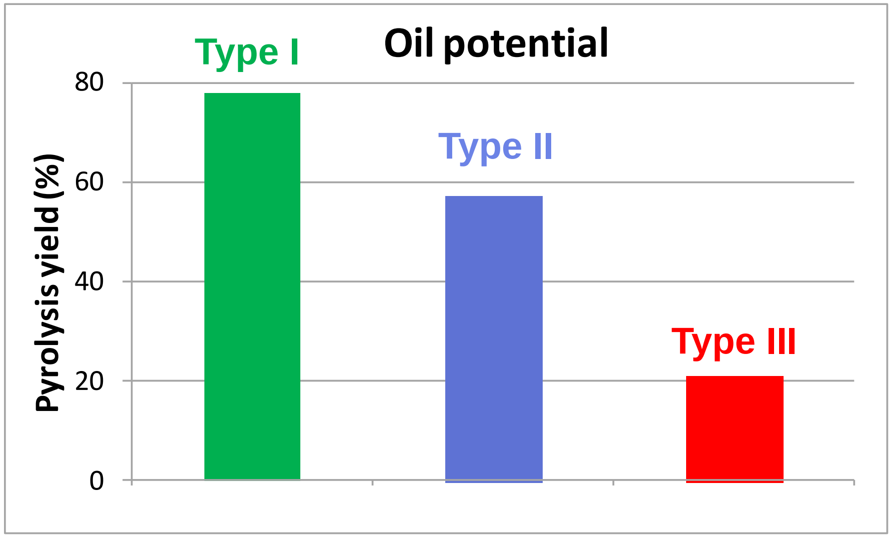
At 650°C : 100% kerogen conversion

➔ S2 = maximum yield

Shale oil potential

Rock Eval pyrolysis





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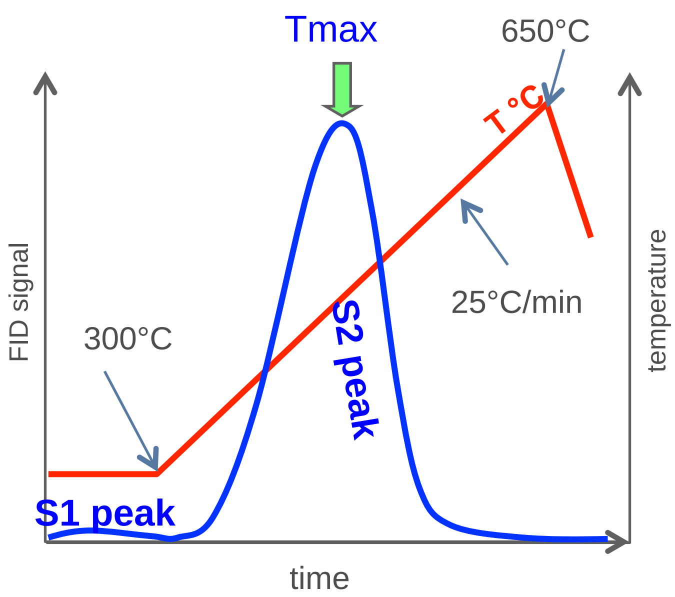
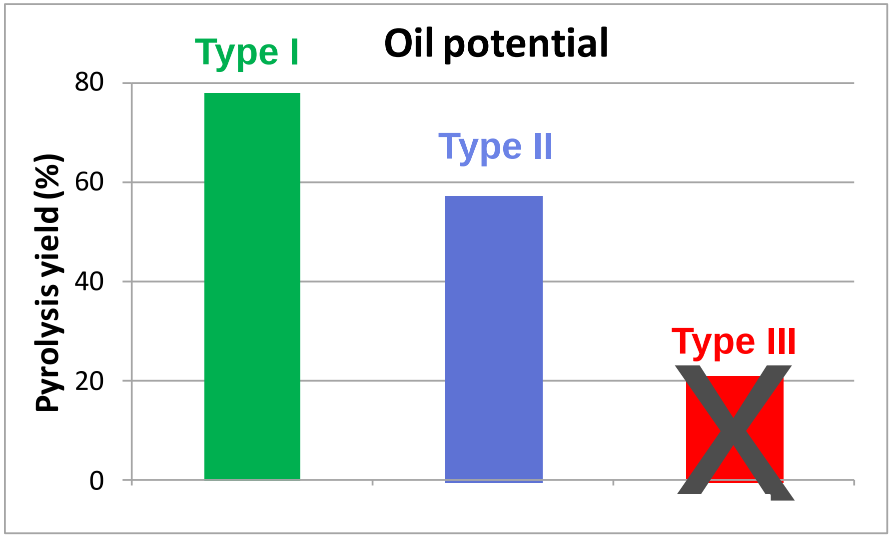
Shale oil potential : f (organic matter type)

Rock Eval pyrolysis





At 650°C : 100% kerogen conversion
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Oil shale pyrolysis :
Type I and II are good candidates

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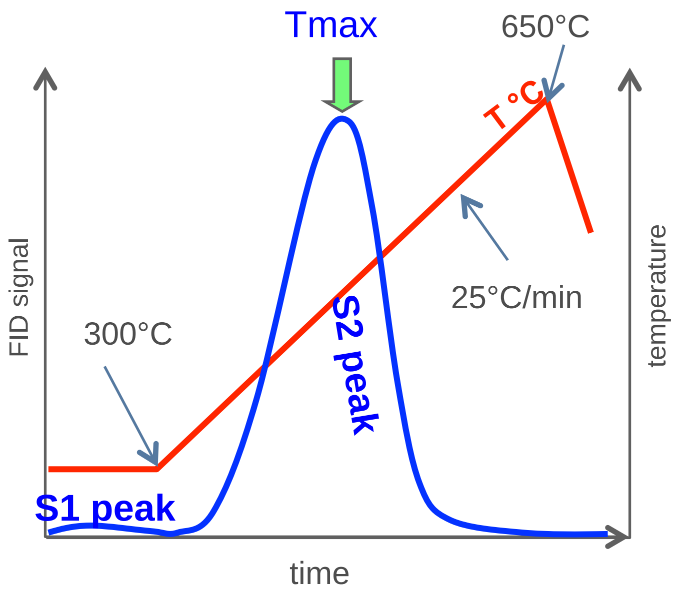
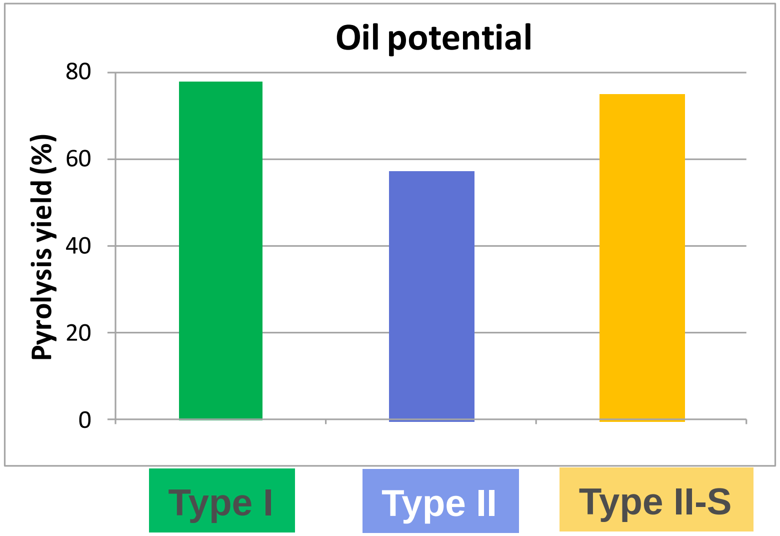
Shale oil potential : f (organic matter type)

Rock Eval pyrolysis





At 650°C : 100% kerogen conversion
➔ S2 = maximum yield

Oil shale pyrolysis :
Type I, II and II – S are good candidates

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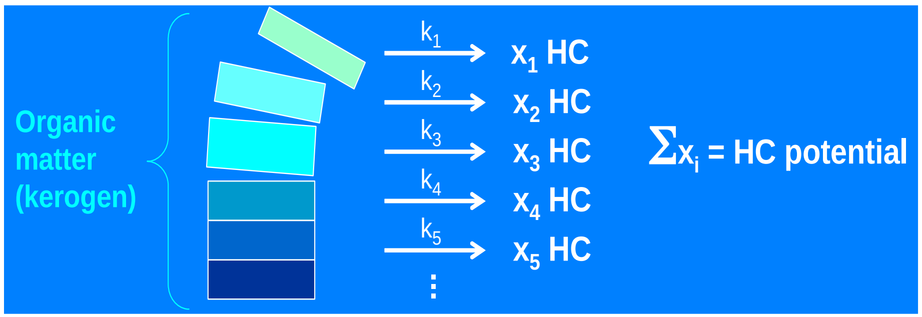
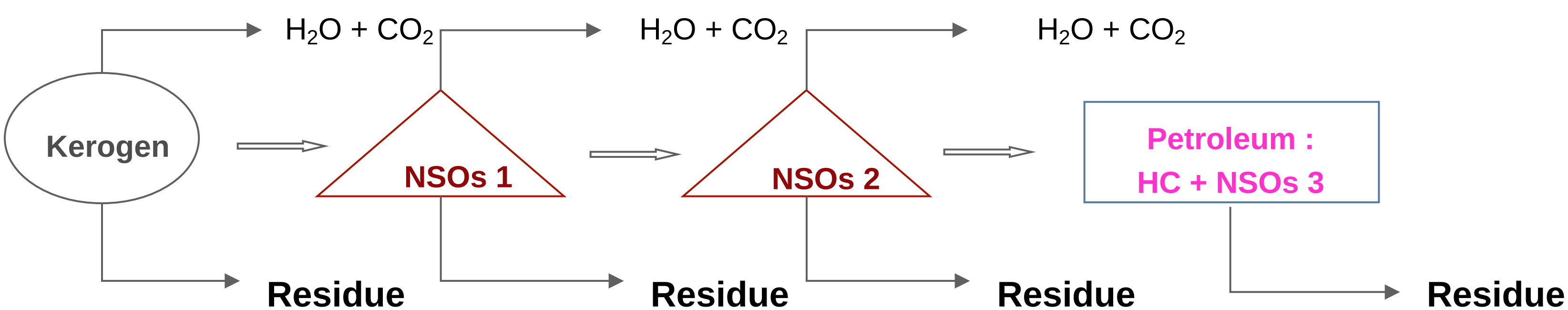
Two types of kinetic schema for kerogen cracking

I – Parallel reactions : hydrocarbons are primary products
(Burnham and Brown 1987; Ungerer, 1991...)



II – Successive reactions : HC are not directly generated from kerogen
(Fitzgerald and van Krevelen, 1959,Tissot, 1969, Lewan 1983, Behar et al., 2008…)



NSOs 1 and 2 = Asp + Resins

Kerogen cracking in laboratory conditions

- **Open system pyrolysis**
  - Generated asphaltenes are cracked and not vaporised
  - HC potential from asphaltenes cannot be quantified
  - ➔ Only apparent kinetic schema : parallel reactions

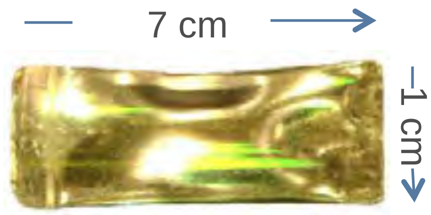
- **Closed pyrolysis system**
  - Generated asphaltenes recovered by solvent extraction

  - ➔ Kinetics of asphaltenes generation and cracking
  - ➔ Discrimate between parallel and successive kinetic schema

TOTAL

Micro reactor : analytical workflow

Pyrolysis experiments:
Sealed gold tubes
300 – 400°C
1 week to 6 months



Kerogen amount : 250 mg – 4 g

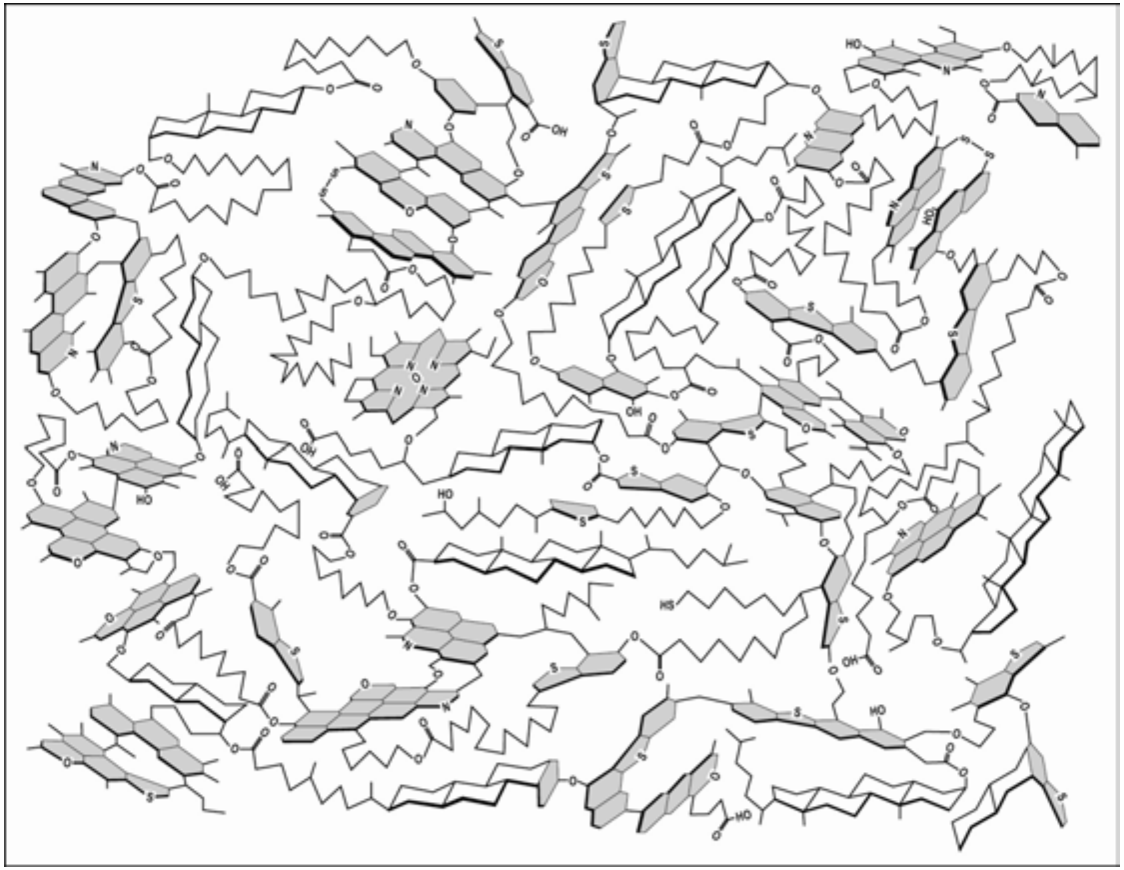
Source rock
↓ HF/HCl
Kerogen

Initial kerogen

- Gas
  - C_1 and C_2-C_5
  - CO_2, H_2S
- C_6-C_{14}
  - Sat
  - Aro
- C_{14+}
  - Sat
  - Aro
  - NSOs
- Residual kerogen and prechar

gas + liquid + solid > 95%

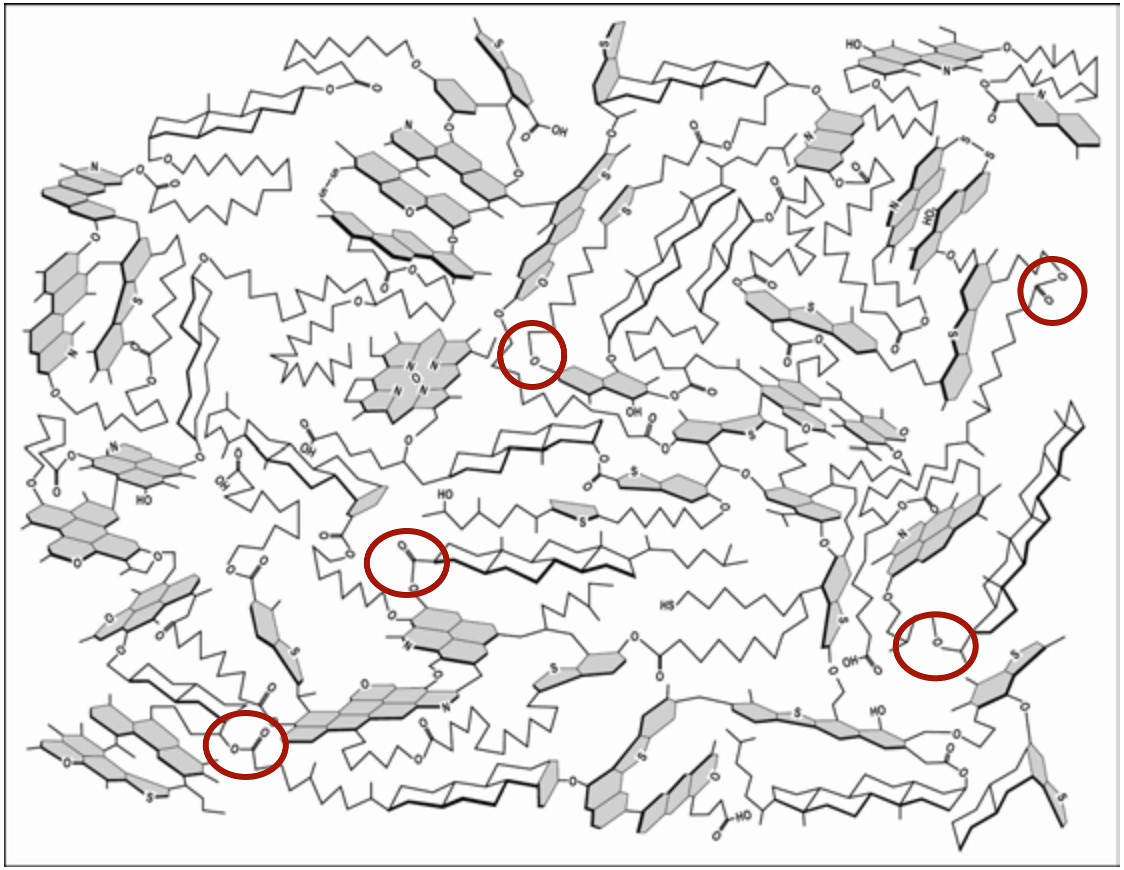
Thermal cracking of kerogen



- Complex molecule of high molecular weight

- Functional groups between kerogen moieties

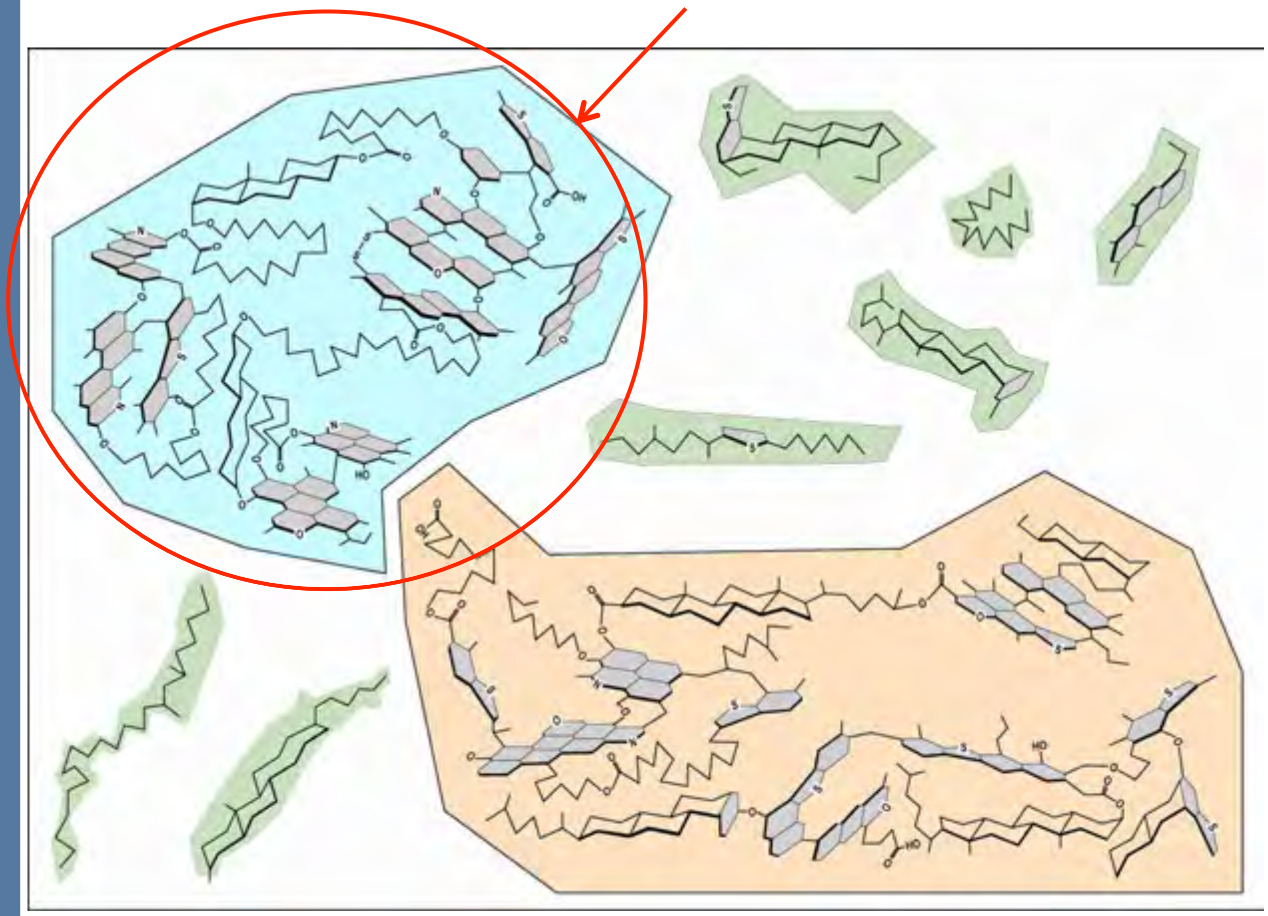
Thermal cracking of kerogen



Thermal cracking of functional groups

Liquid products : asphaltenes and HC

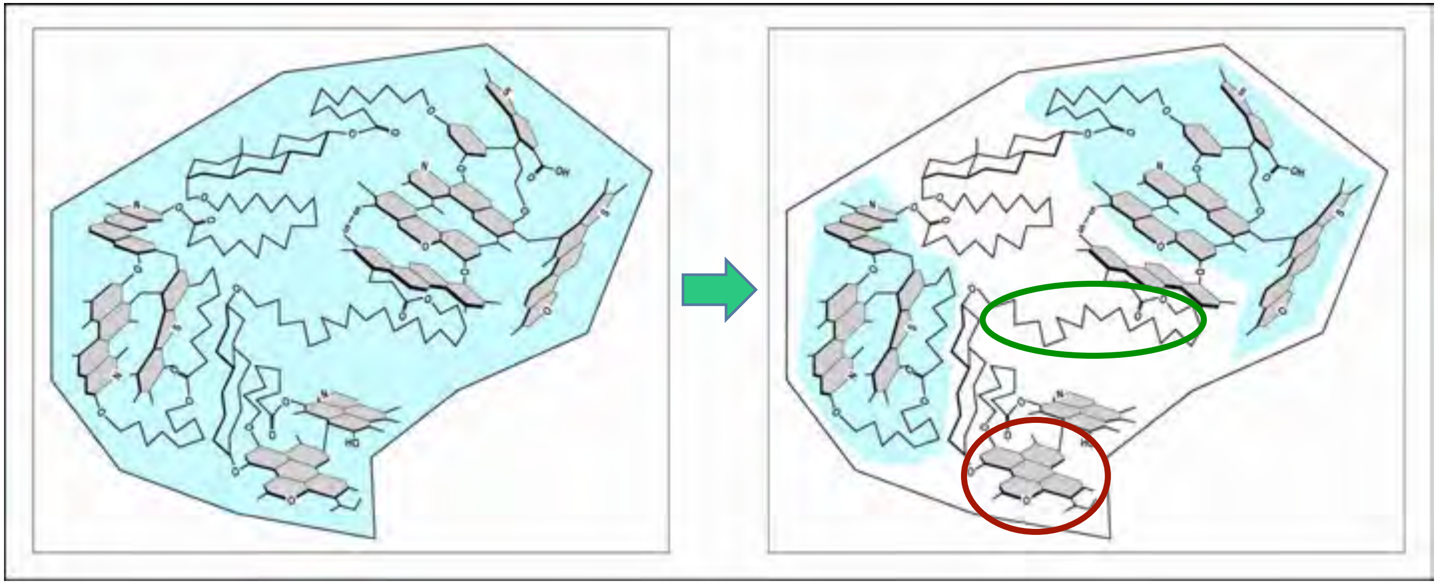
Asphaltenes



kerogen

Asphaltenes
First source of HC (1)

Asphaltenes cracking : resins generation



Asphaltenes → **Resins + HC2**

Asphaltenes → **Char precursor**

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HC generation : 3 main reactions

Kerogen	➔ $(CO_2 + H_2S)_1$ + Asphaltenes + HC1 + residual kerogen
Asphaltenes	➔ $(CO_2 + H_2S)_2$ + Resins + HC2 + prechar
Resins	➔ $(CO_2 + H_2S)_3$ + HC3 + prechar

HC generation : 3 main reactions

Kerogen	**➔ $(CO_2 + H_2S)_1$ + Asphaltenes + HC1 + residual kerogen**
Asphaltenes	**➔ $(CO_2 + H_2S)_2$ + Resins + HC2 + prechar**
Resins	**➔ $(CO_2 + H_2S)_3$ + HC3 + prechar**

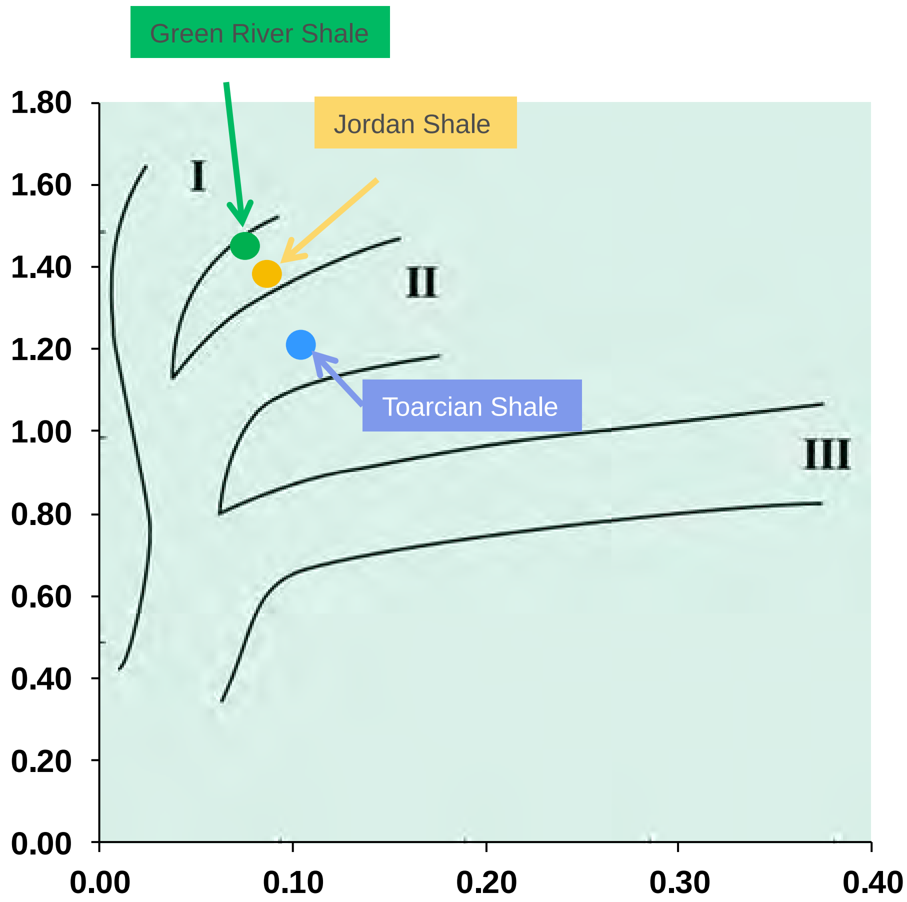
Oil shale pyrolysis

2 main steps for hydrocarbon production
1 – Cracking of non mobile compounds (kero + asp + res.)
2 – Partial cracking of the mobile compounds (*resins* and HC)

Results on 3 selected oil shales

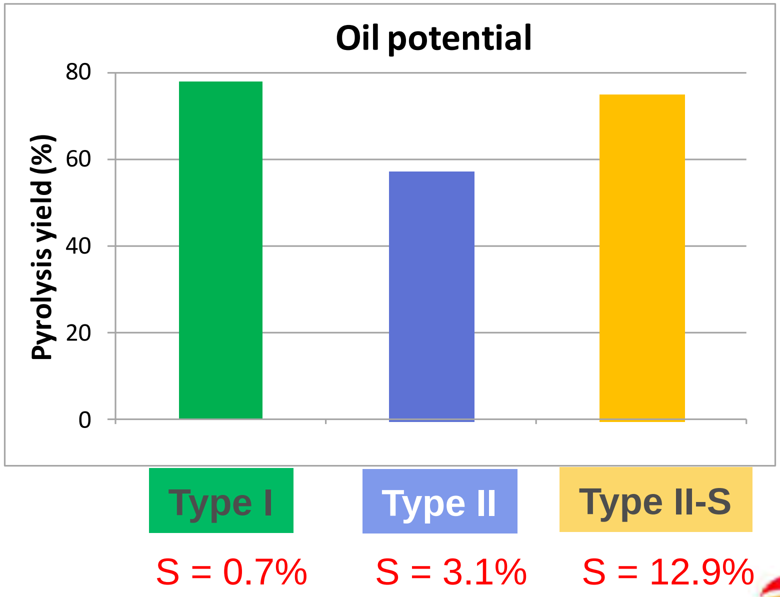
TOTAL

Results on 3 selected oil shales



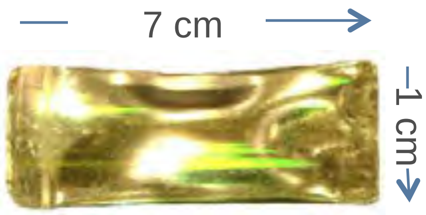
Type I lacustrine : Green River Shale (USA)
Type II marine : Toarcian Shale (France)
Type II-S marine : Jordan Shale (Jordanie)

Oil shale potential : 300-600°C at 25°C/min



Experimental simulation in closed micro reactor

T = 325°C
time from 1 to 216h



Initial amount : 250 mg – 4 g

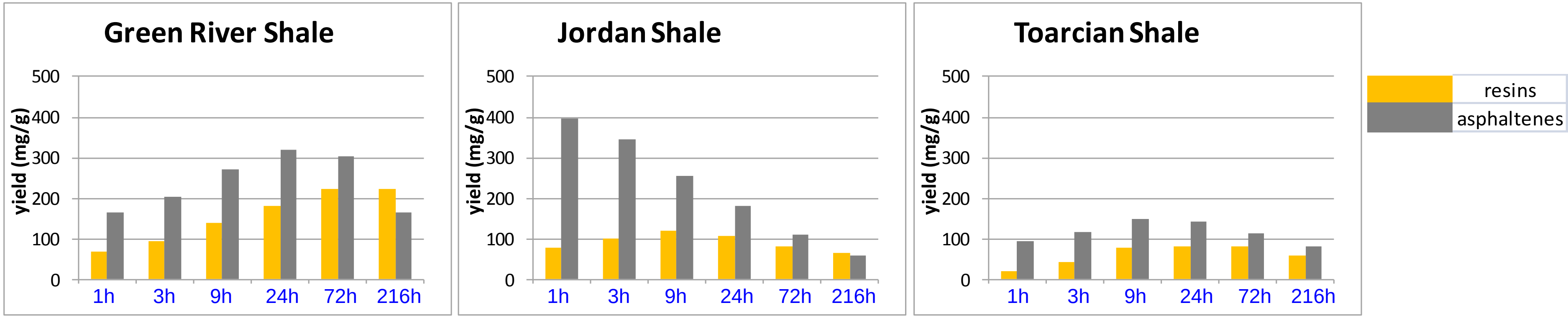
Initial kerogen

- Gas
  - C_1 and C_2-C_5
  - CO_2, H_2S
- C_6-C_{14}
  - Sat
  - Aro
- C_{14+}
  - Sat
  - Aro
  - NSOs
- Residual kerogen and prechar

gas + liquid + solid > 95%

Fluid composition during kerogen conversion

T = 325°C 1 to 216h
Kerogen conversion > 80% at 216h



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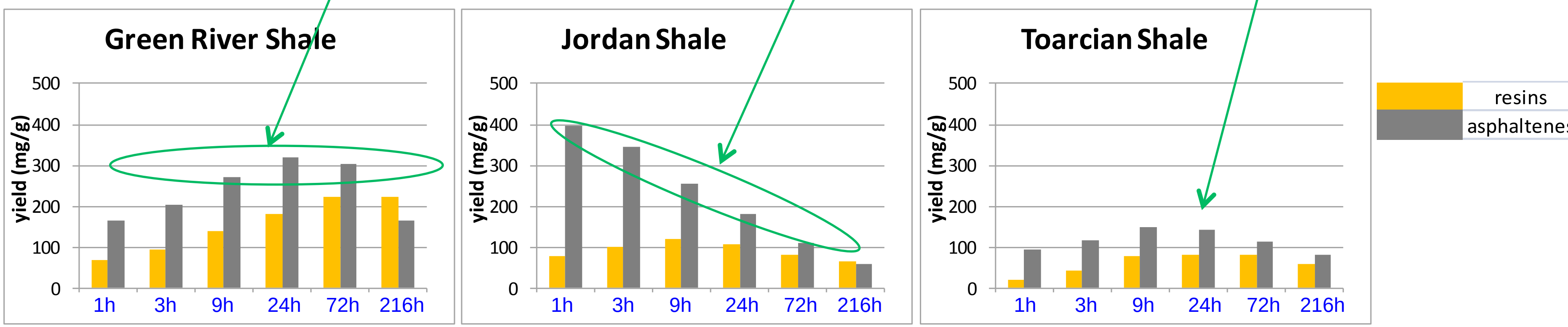
Fluid composition during kerogen conversion

T = 325°C

Asp max : 300 mg/g
Res max : 200 mg/g

Asp max : 400 mg/g
Res max : 100 mg/g

Asp max : 150 mg/g
Res max : 80 mg/g



Total NSOs = 50%

Total NSOs = 50%

Total NSOs = 23%

Asphaltenes : unstable class
Resins : more stable class

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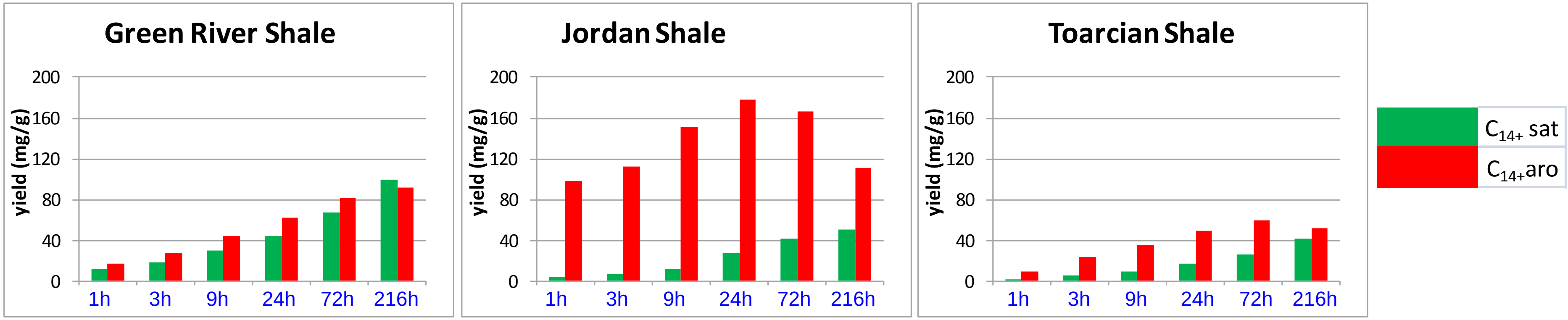
Fluid composition during kerogen conversion

T = 325°C



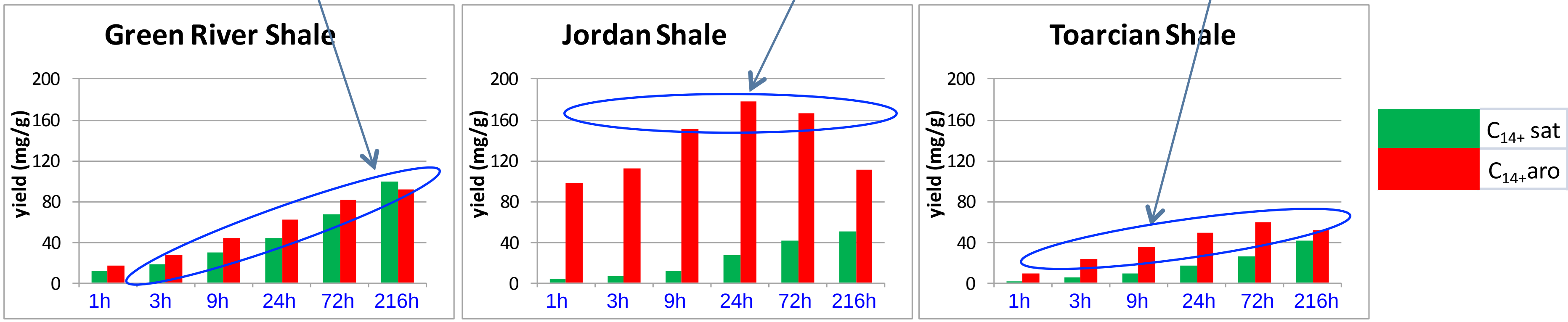
Fluid composition during kerogen conversion

T = 325°C

C_{14+} Sat max = 10%
C_{14+} Aro max = 9%

C_{14+} Sat max = 5%
C_{14+} Aro max = 18%

C_{14+} Sat max = 4%
C_{14+} Aro max = 6%



Total C_{14+} HC = 19%

Total C_{14+} HC = 23%

Total C_{14+} HC = 10%

C_{14+} sat : almost stable
C_{14+} aro : unstable

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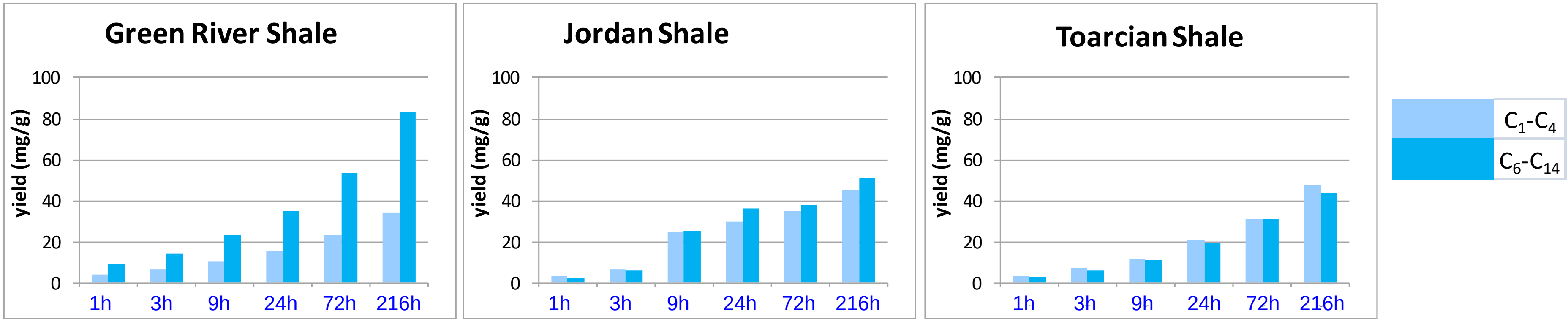
Fluid composition during kerogen conversion

T = 325°C

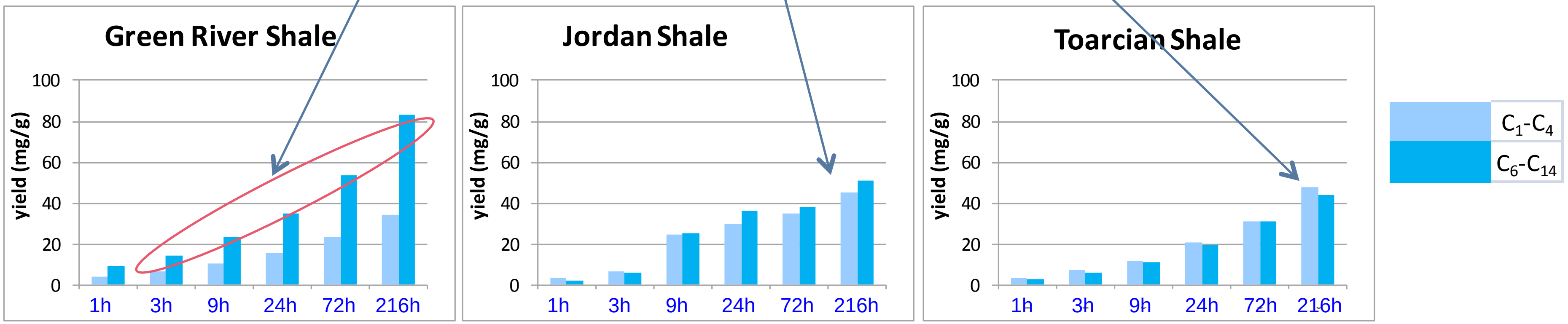


Fluid composition during kerogen conversion

T = 325°C

C_1-C_4 max = 4%
C_6-C_{14} max = 8%

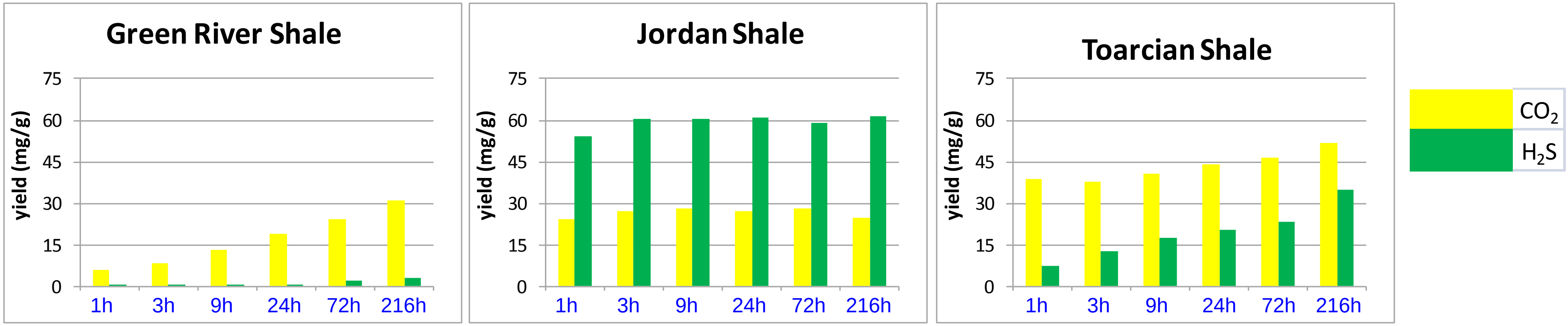
C_1-C_4 max = 4%
C_6-C_{14} max = 5%



Maximum C_6-C_{14} for the Type I kerogen

Fluid composition during kerogen conversion

T = 325°C



TOTAL

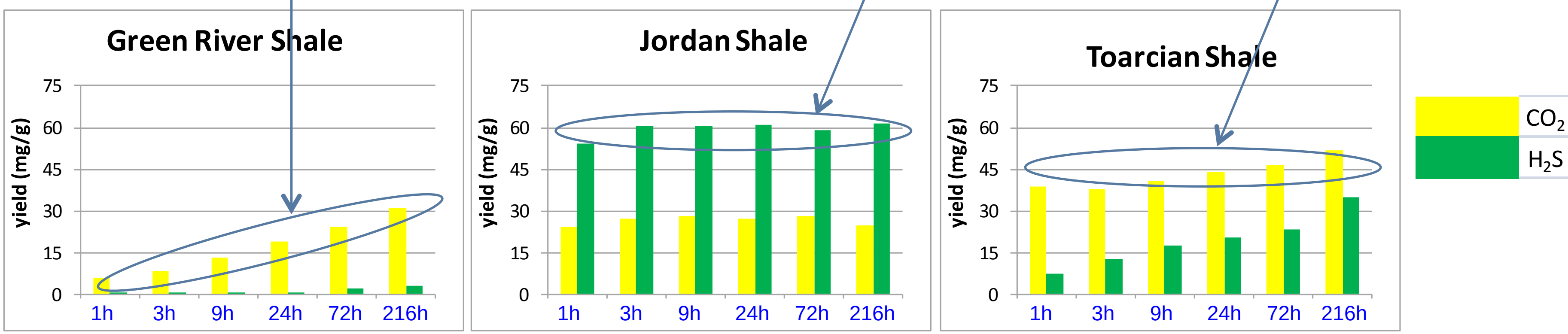
Fluid composition during kerogen conversion

T = 325°C

CO_2 max : 3%
H_2S max : 0.5%

CO_2 max : 3%
H_2S max : 6%

CO_2 max : 5%
H_2S max : 3%



Total Acid gas = 3.5%

Total Acid gas = 9%

Total Acid gas = 8%

Acid gas : very early generation

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Summary

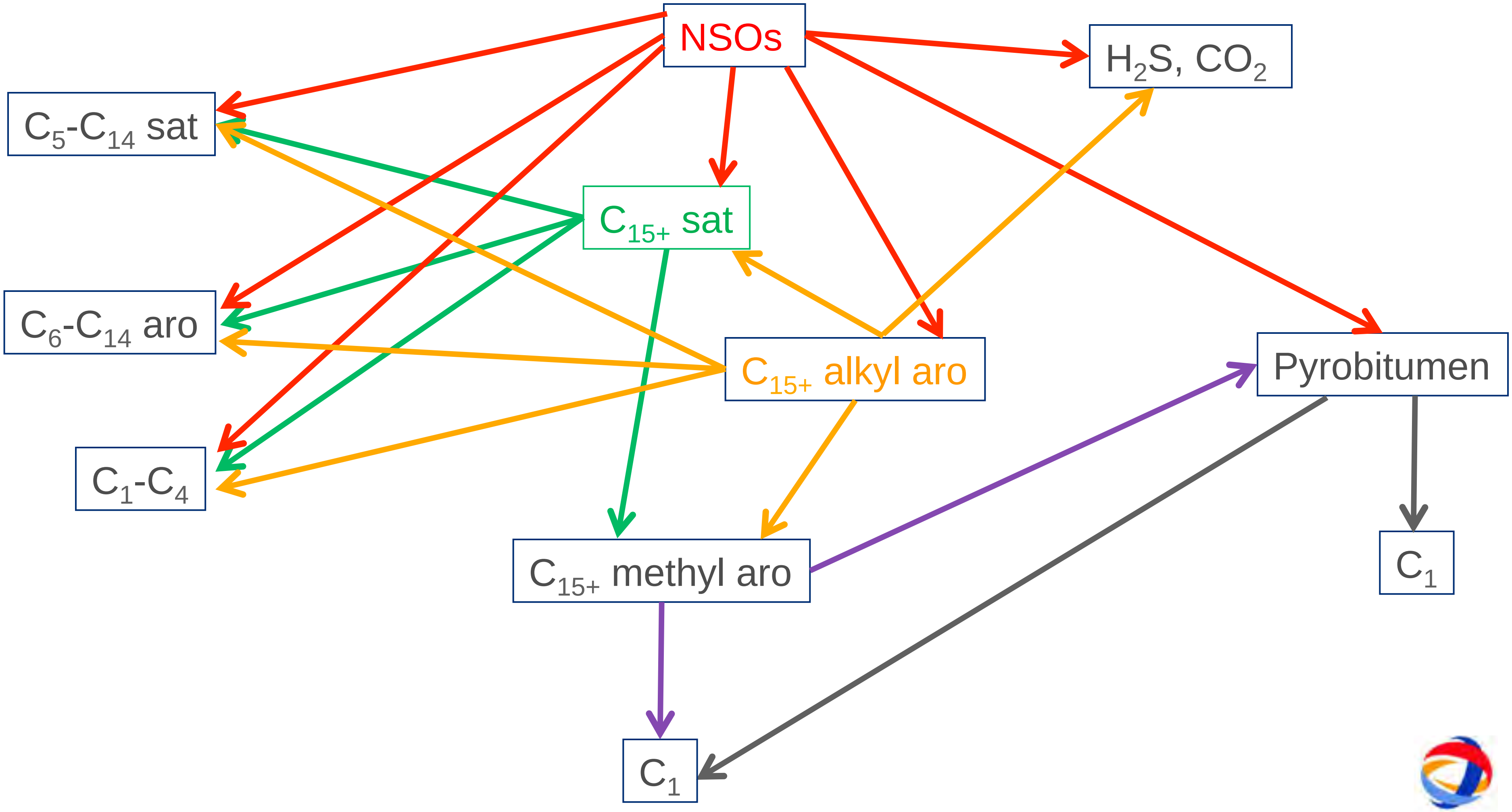
- **First step : kerogen cracking**
  - Most of the asphaltenes are degraded
  - Resins are more stable class
  - C_{14+} aromatics start to be cracked at high kerogen conversion
  - C_{14+} saturates are almost stable

Still high content in NSOs (asp + resins) : production of low °API and low mobility fluid, ➔ significant secondary cracking reaction

- **Second step : influence of the secondary cracking reaction**
  - Available compositional kinetic schema

TOTAL

Compositional kinetic schema for NSOs and HC cracking



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- **Second step : influence of the secondary cracking reaction**
  - Available compositional kinetic schema

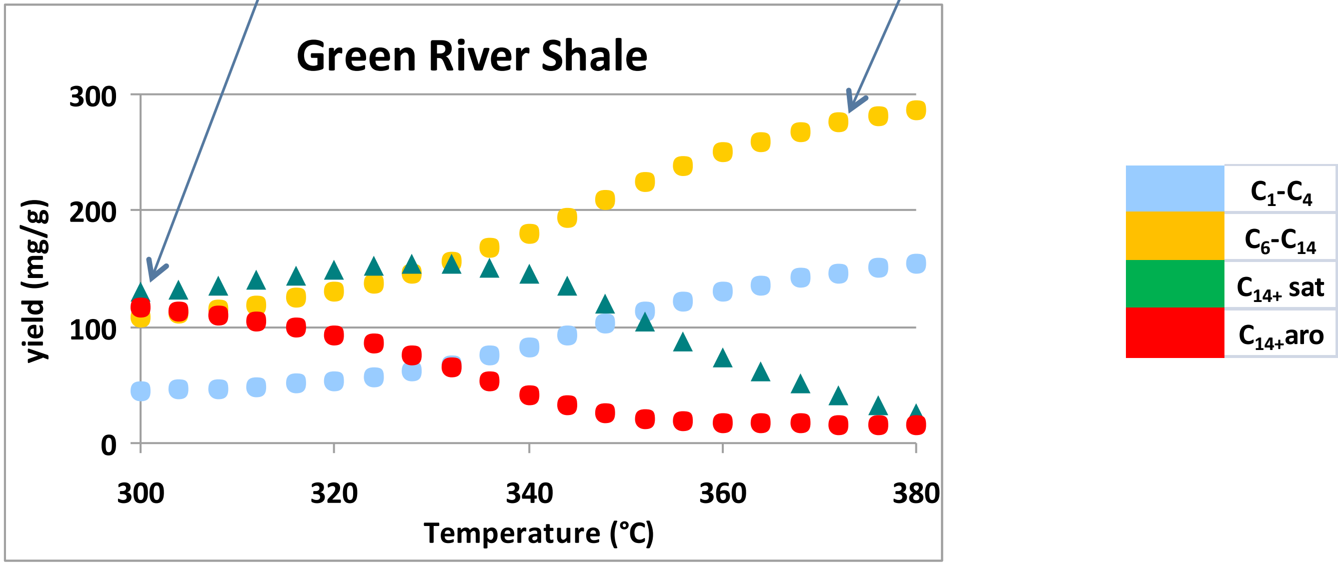
➔ Application to the fluid composition obtained at 325°C/216h

Step 2 : thermal cracking of the generated products
Kerogen conversion > 80%

T : 300 – 380°C at 4°C/day
Total duration : 3 months

C_6-C_{14} max from C_{14+} sat cracking
High ratio C_1-C_4/C_6-C_{14}

C_{14+} HC = 22%
C_{14+} sat = 12%

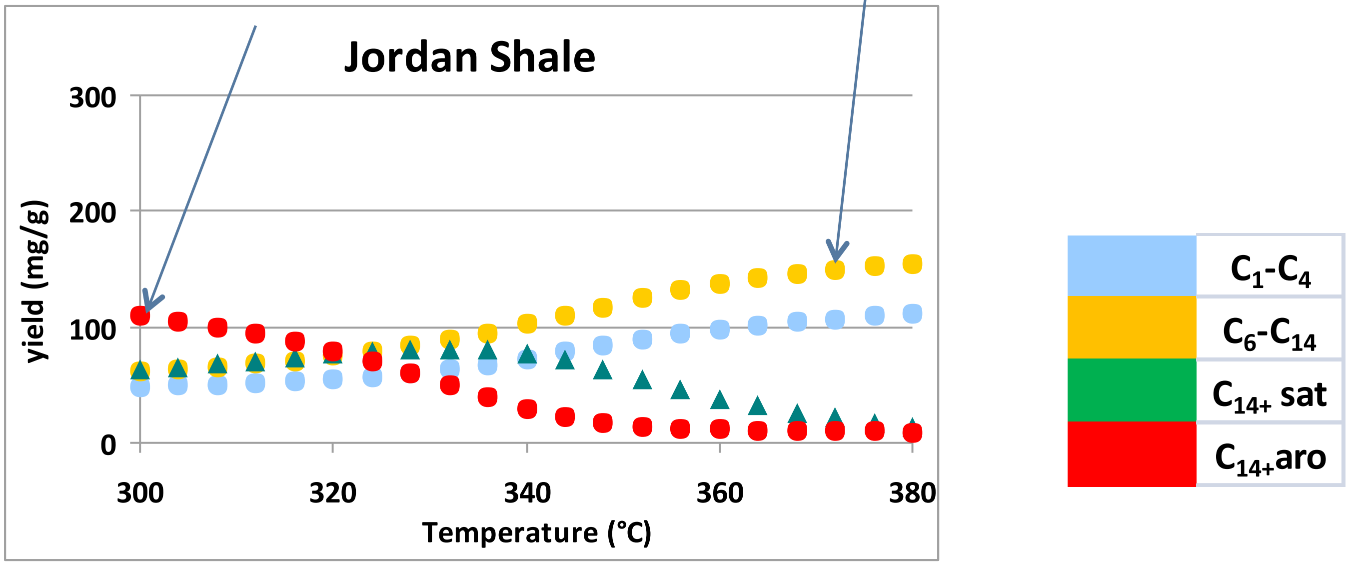


Step 2 : thermal cracking of the generated products
Kerogen conversion > 80%

T : 300 – 380°C at 4°C/day
Total duration : 3 months

C_{14+} HC = 17%
C_{14+} sat = 6%

Lower C_6-C_{14} yield
lower ratio C_1-C_4/C_6-C_{14}



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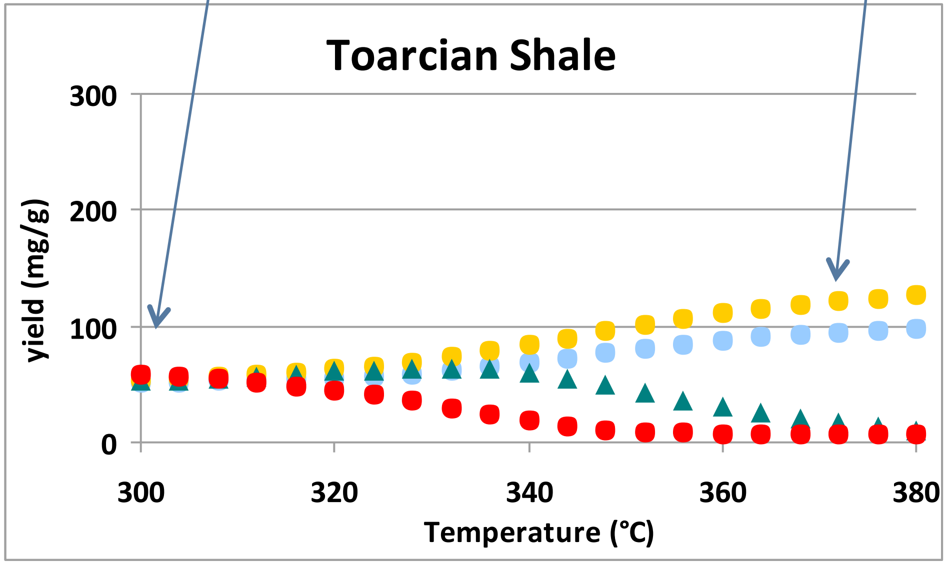
Step 2 : thermal cracking of the generated products
Kerogen conversion > 80%

T : 300 – 380°C at 4°C/day
Total duration : 3 months

C_{14+} HC = 12%
C_{14+} sat = 6%

similar C_6-C_{14} as for the Jordan shale
low ratio C_1-C_4/C_6-C_{14}



(light blue)	C_1-C_4
(yellow)	C_6-C_{14}
(green)	C_{14+} sat
(red)	C_{14+}aro

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Conclusions : key geochemical parameters for optimizing oil shale process

- **I – Organic matter type**
  - Best candidate : Lacustrine organic matter source
- **II – Organic carbon richness**
  - Best candidate : Lacustrine
  - Marine –S soure rock
- **III – Good geochemical parameters**
  - Organic carbon richness : necessary but not sufficient
  - Low organic sulfur content
  - High asphaltenes and resins yield during pyrolysis
  - C_{14+} sat / C_{14+} aro >> 1 in the generated hydrocarbons

TOTAL