Comparison of the Structure and Reactivity of an Australian Algal Coal with Jordanian and Colorado Oil Shales

W. Roy. Jackson[1,2*] , Mohammad W. Amer[1,2], Yi Fei[1,2], Marc Marshall[1,2], and Alan L. Chaffee[1,2]

1 School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

2 Centre for Green Chemistry, Monash University, Victoria 3800, Australia

Introduction

- There is extensive background knowledge of coal liquefaction including liquefaction of the algal coal torbanite
- Currently, there is strong interest in improving methods of extracting oil from oil shale, which is derived from algae
- Aim: to establish what relationships exist between the reactivity of torbanite and typical oil shales

What are oil shale & Torbanite?

Oil Shale

- Minerals
- Bitumen
  - Organic solvent soluble at room temp.
- Kerogen

Torbanite

- Kerogen

Materials

- The torbanite studied is derived from freshwater algae living in the Permian period (250-300 million years ago)

- It comes from the Greta seam, New South Wales, Australia

- Ash yield 4.3 wt% db

Torbanite

- Elemental Analysis C, 82.6%, H, 10.6%, N, 0.8%, S, 0.1% O, 5.8% dmmf basis

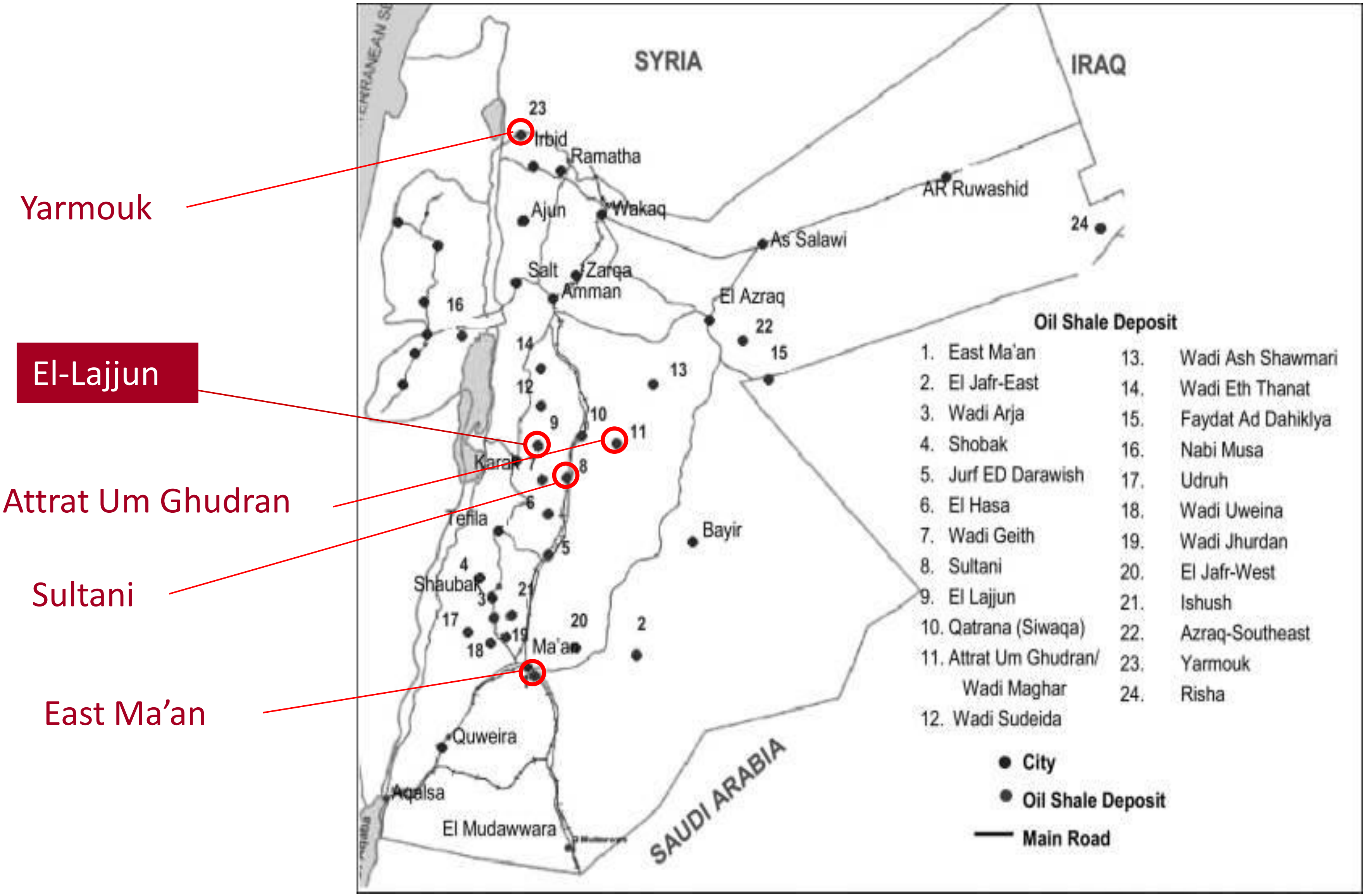
- Atomic H/C ratio 1.53

- Mainly derived from long chain alkadienes

  $CH_2{=}CH{-}(CH_2)_n{-}CH{=}CH{-}(CH_2)_7{-}CH_3$ n= 15,17,19

Jordanian oil shale

- The Jordanian oil shales studied are derived from marine algae living in the Maastrichtian age (65-70 million years ago)
- They come from El-Lajjun and Sultani (see map)
- Ash yield 75.8 wt% db (El-Lajjun), 72.3 wt% db (Sultani)
- Elemental Analysis C, 71.6%, H, 8.7%, N, 1.7%, Org. S, 9.8% O, 8.2% dmmf basis (El-Lajjun)
- Atomic H/C ratio 1.45 (El-Lajjun)
- Fe, 1.9 wt% db (El-Lajjun)

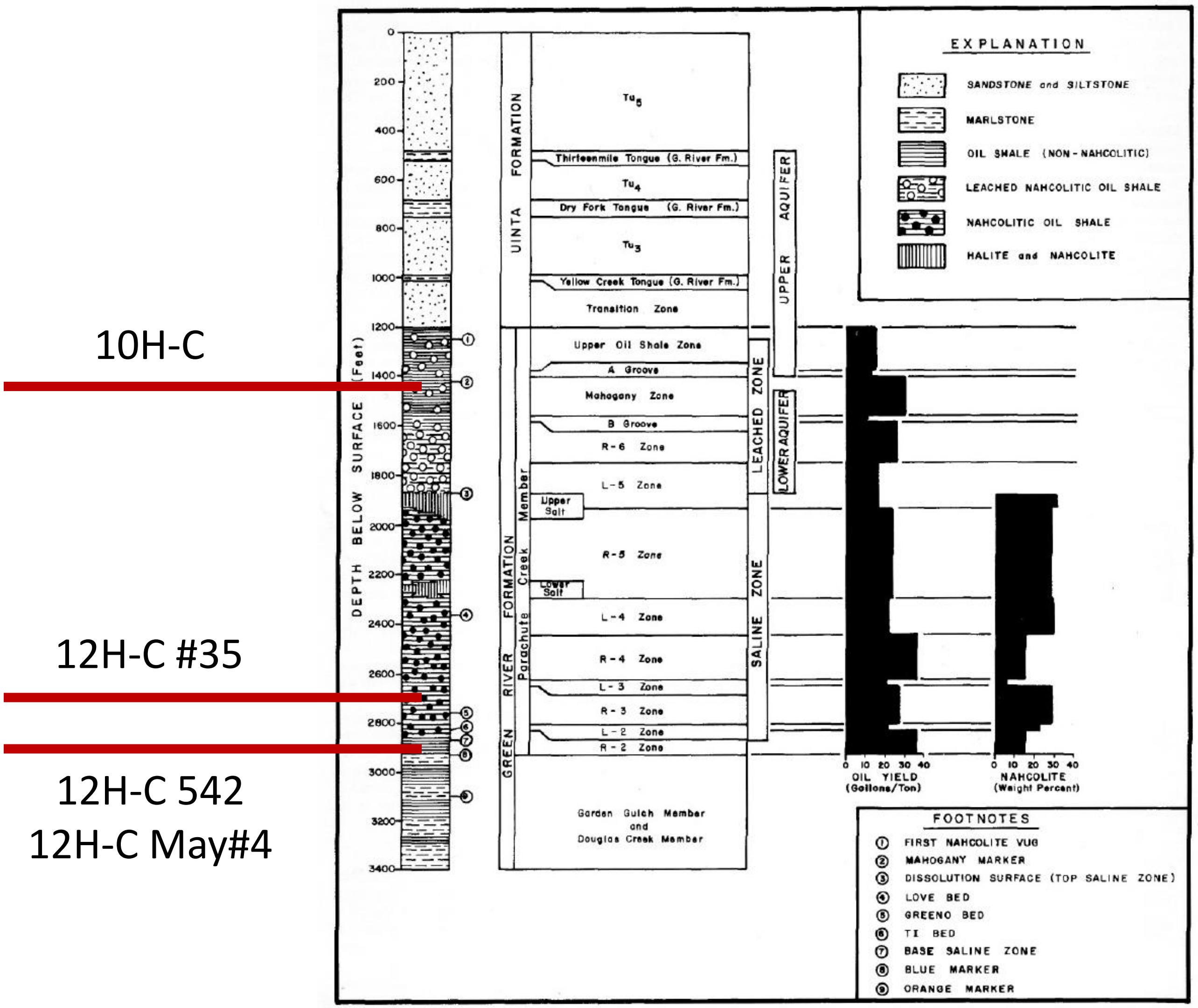


Yarmouk
El-Lajjun
Attrat Um Ghudran
Sultani
East Ma'an
SYRIA
IRAQ
SAUDI ARABIA
Irbid
Ramatha
Ajun
Wakaq
Salt
Zarqa
Amman
AR Ruwashid
As Salawi
El Azraq
Karak
Tefila
Shaubak
Ma'an
Bayir
Quweira
Aqaba
El Mudawwara
Oil Shale Deposit
1. East Ma'an
2. El Jafr-East
3. Wadi Arja
4. Shobak
5. Jurf ED Darawish
6. El Hasa
7. Wadi Geith
8. Sultani
9. El Lajjun
10. Qatrana (Siwaqa)
11. Attrat Um Ghudran/ Wadi Maghar
12. Wadi Sudeida
13. Wadi Ash Shawmari
14. Wadi Eth Thanat
15. Faydat Ad Dahiklya
16. Nabi Musa
17. Udruh
18. Wadi Uweina
19. Wadi Jhurdan
20. El Jafr-West
21. Ishush
22. Azraq-Southeast
23. Yarmouk
24. Risha
City
Oil Shale Deposit
Main Road

Colorado oil shale

- The Colorado oil shale is derived from lacustrine algae living in the Paleocene Epoch (55-65 million years ago)
- It comes from the Mahogany Layer, Green River formation, Colorado, above the water table (see diagram)
- Ash yield 73.2 wt% db

Rich and Lean Oil Shale Zones (Green River Formation)

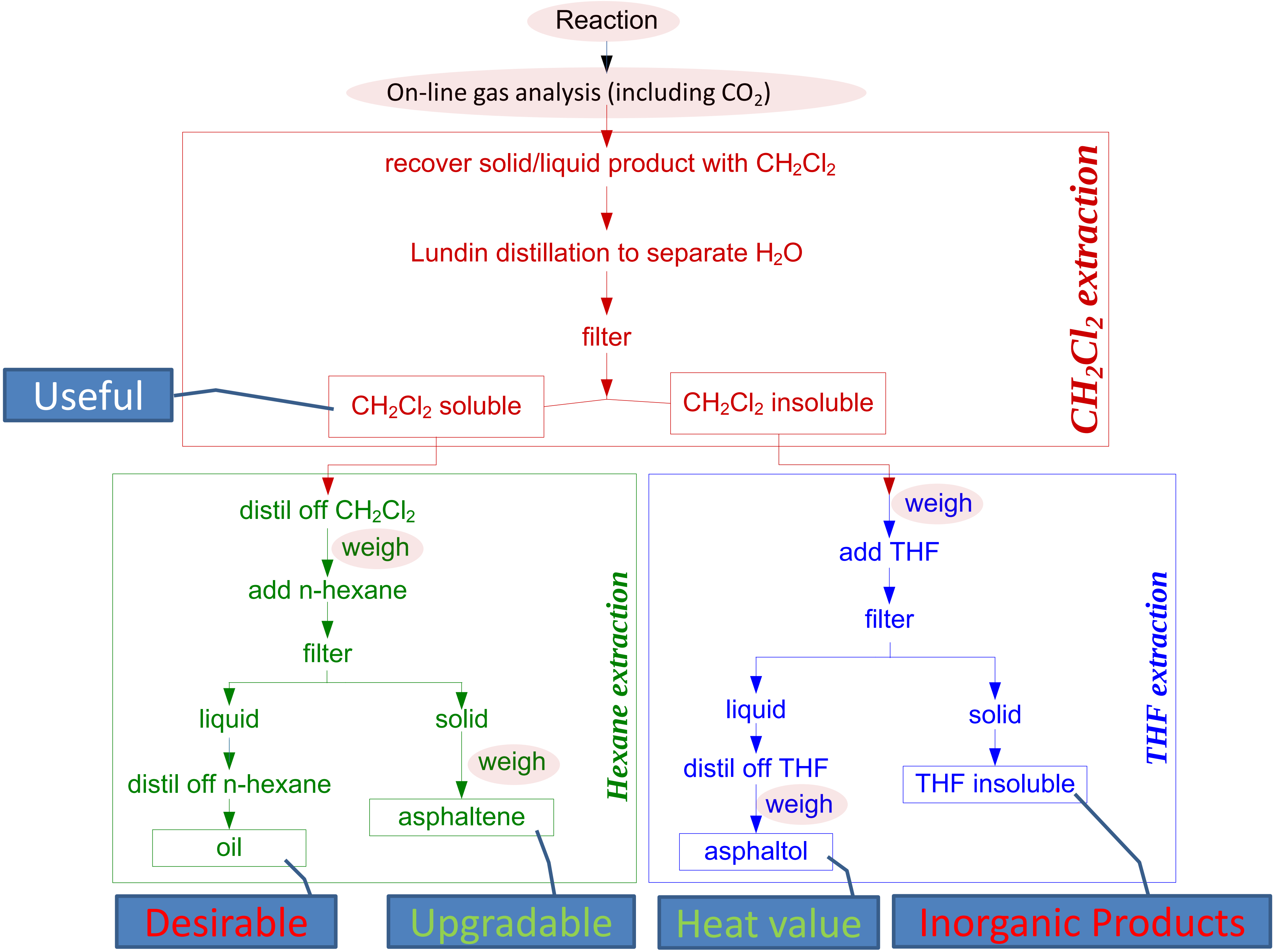


From Cole, R. D.; Daub, G. J.; Weston, L. K.., The Green River Formation in Piceance Creek and Eastern Uinta Basins Field Trip, 1995

Experimental
Autoclave reactions

- Temperature 355-425°C
- Gas N_2, H_2, CO (3 MPa cold)
- Time 1-5 hours
- Charge 2.1, 4.2 g
- 27 ml Autoclave
- Heat up time 2-4 min
- Analysis- ^1H NMR & GC-MS

for CH_2Cl_2 solubles



Reaction
On-line gas analysis (including CO_2)
recover solid/liquid product with CH_2Cl_2
Lundin distillation to separate H_2O
filter
CH_2Cl_2 soluble
CH_2Cl_2 insoluble
CH_2Cl_2 extraction
Useful
distil off CH_2Cl_2
weigh
add n-hexane
filter
liquid
solid
distil off n-hexane
weigh
oil
asphaltene
Hexane extraction
weigh
add THF
filter
liquid
solid
distil off THF
weigh
THF insoluble
asphaltol
THF extraction
Desirable
Upgradable
Heat value
Inorganic Products

Results

Reactions of Torbanite

T (^oC)	Gas	Asphaltene	Oil+H2O
355	N_2	0.4	5.9
	H_2	0.3	3.2
390	N_2	1.1	13.5
	H_2	1.3	12.7
425	N_2	12.6	72.4
	H_2	13.8	70.3

Reaction for 1 hour, HC gases + CO_2 < 5%

Homogeneous structure leads to dramatic changes in reactivity with temperature

Reactions of Jordanian oil shales

T (°C)	Reactant	Gas	Asphaltene	Oil+H2O
355	El-Lajjun	N_2	26.8	33.8
		H_2	30.0	38.3
	Sultani	N_2	19.9	47.1
		H_2	2.3	46.6
390	El-Lajjun	N_2	18.4	57.9
		H_2	9.2	74.7
	Sultani	N_2	10.1	64.3
		H_2	7.8	59.7
425	El-Lajjun	N_2	4.9	62.8
		H_2	6.1	72.2
	Sultani	N_2	2.8	74.0
		H_2	4.3	79.0

Reaction for 1 hour, $CO_2 < 2\%$, little inorganic carbonate decomposition

- H_2 results usually better; maybe due to Fe catalysis
- Asphaltene to oil ratio drops significantly between 355 & 390°C

Extraction and reactions of El-Lajjun shale kerogen

- Kerogen isolated by successive extraction with 50% NaOH at 160^{o}C followed by 5M HCl and then H_2O at room temperature
- Reaction at 390^{o}C

Gas	Asphaltene	Oil+H2O
N_2	15.4	50.4
H_2	14.2	46.7

- Conversion for N_2 reaction similar to shale but for H_2 reaction less than for shale
- Is this due to removal of Fe during kerogen extraction?

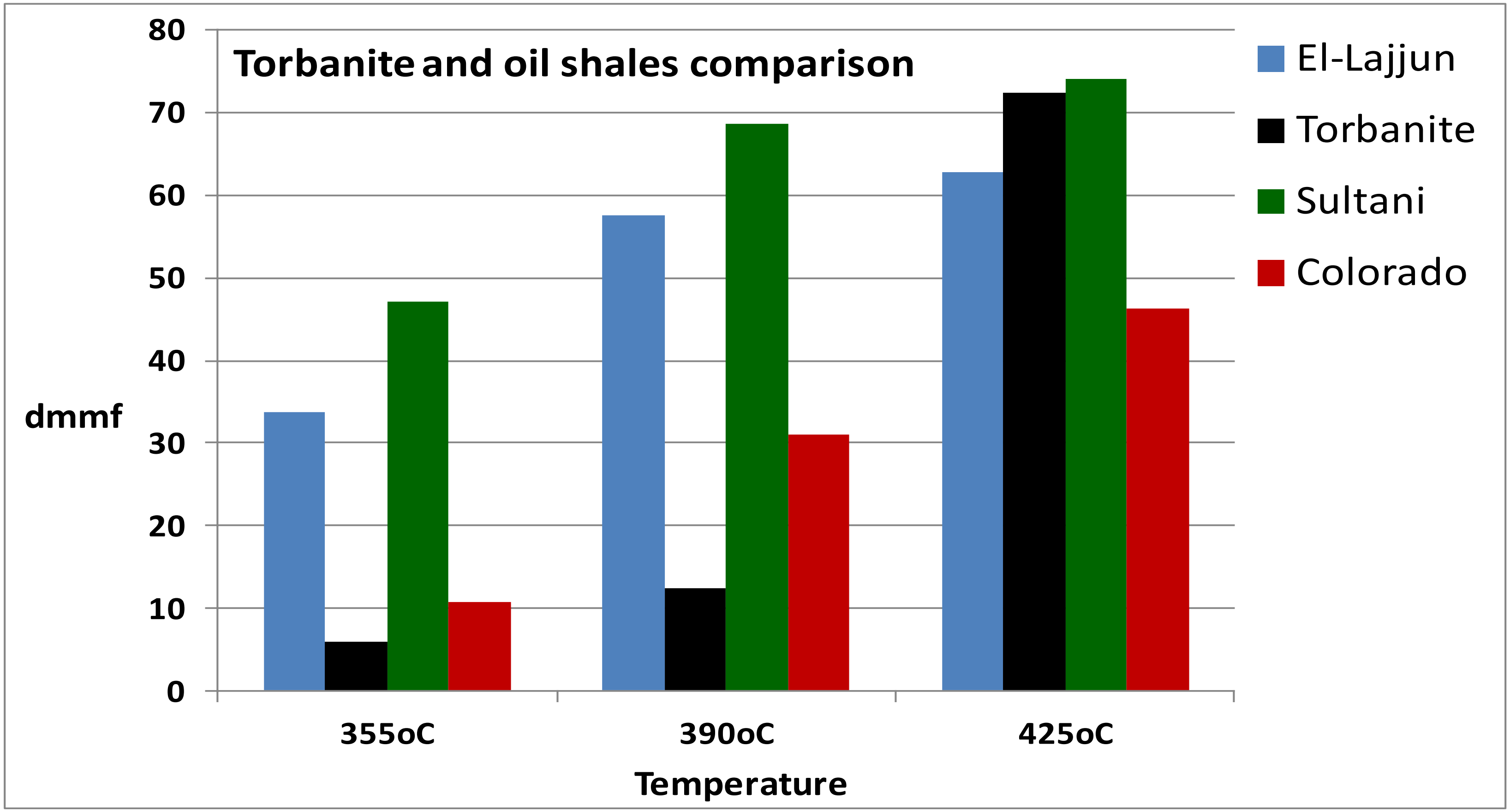
Reactions of Colorado oil shale

T (°C)	Gas	Asphaltene	Oil+H2O
355	N_2	2.3	10.8
	H_2	0.6	12.7
390	N_2	18.5	31.1
	H_2	-	-
425	N_2	11.9	46.3
	H_2	13.8	55.4

Reaction for 1 hour, CO_2 yields 2-4%

- H_2 results usually better
- Significantly less reactive than Jordanian shales

Comparison of Reactivity



Reaction for 1 hour, gas N_2, hexane soluble

- Sultani>El-Lajjun>Colorado

Elemental analysis of CH_2Cl_2 soluble material

Shale	gas Charge	C	H	N	S	O (by diff.)	at H/C ratio
		wt%					
El-Lajjun	H_2	79.3	9.3	1.4	6.5	3.5	1.40
Sultani	H_2	81.0	10.5	1.3	3.7	3.5	1.54
Colorado 10H-C, 1440-5'	CO	82.4	10.3	2.6	<0.3	4.6	1.50
Colorado 12H-C, 2896.1-.5'	CO	83.4	10.5	3.0	<0.3	3.1	1.50

Reaction for 1 hour, CH_2Cl_2 solubles. The O by diff. for Sultani is uncertain

- S content high for El-Lajjun
- The products from the two Colorado oil shale are similar

^{1}H NMR of CH_2Cl_2 soluble material

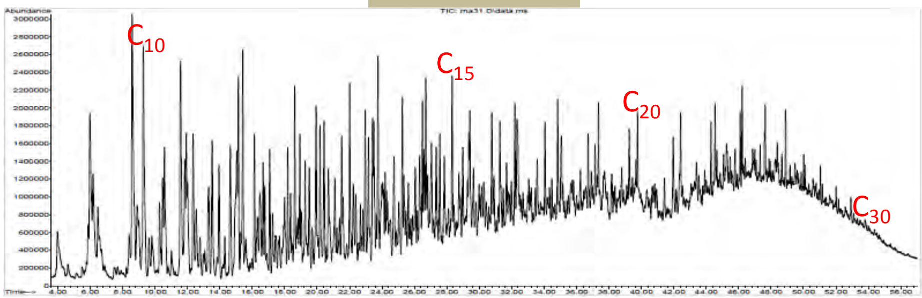
Reractant	T °C	H_{ar}	H_{α}	H_{β}	H_{γ}
El-Lajjun	390	0.09	0.07	0.53	0.31
Sultani	390	0.06	0.15	0.54	0.25
Colorado 10H-C, 1440-5'	425	0.06	0.16	0.62	0.16
Torbanite	425	0.07	0.12	0.68	0.12

Reaction for 1 hour, under N_2, CH_2Cl_2 solubles
H_{ar}, 6-9 ppm; H_{α}, 1.95-4.5 ppm; H_{β}, 1-1.95 ppm; H_{γ}, 0.5-1 ppm

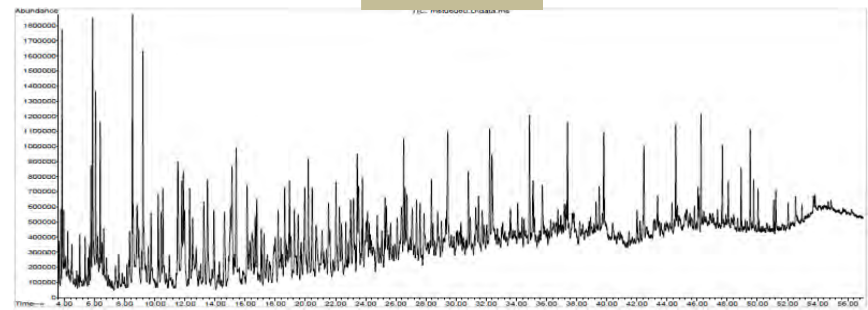
- Low aromatic content
- High H_{β} signifying long aliphatic chains

GC-MS of CH_2Cl_2 soluble material

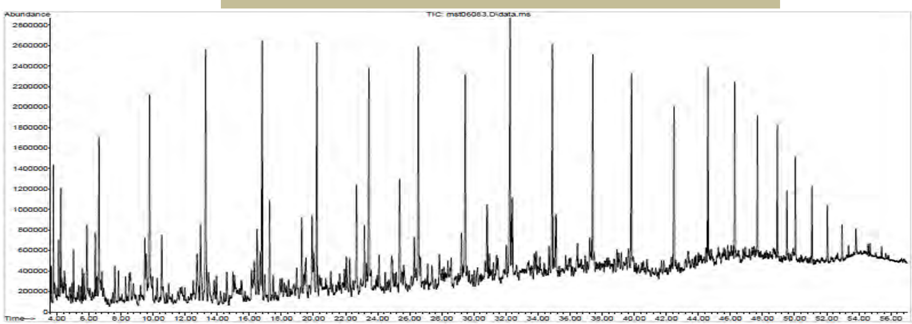
El-Lajjun



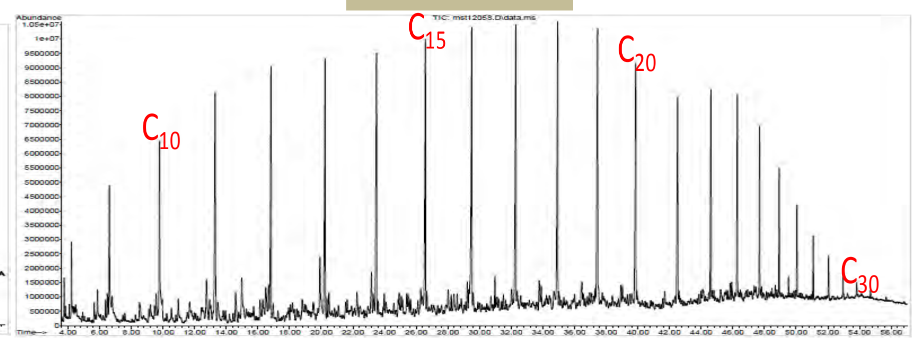
Sultani



Col 12H-C May #4 chunks



Torbanite



Reaction for 1 hour, under N_2, CH_2Cl_2 solubles

- Note close similarity between Colorado and torbanite
- Jordanian oil shales similar to each other despite difference in S content but very different to Colorado & Torbanite

Extended reaction time at 390^{o}C

Shale	Conversion wt% dmmf	
	1h	5h
El-Lajjun	78.5	-
El-Lajjun (355^{o}C)	61.2	65.3
Colorado 10H-C, 1440-5'	51.1	72.0
Torbanite	14.8	89.3

Reaction under N_2, CH_2Cl_2 solubles

- Torbanite and Colorado conversion increase markedly from 390-425^{o}C and with reaction time
- El-Lajjun conversion does not increase with reaction time

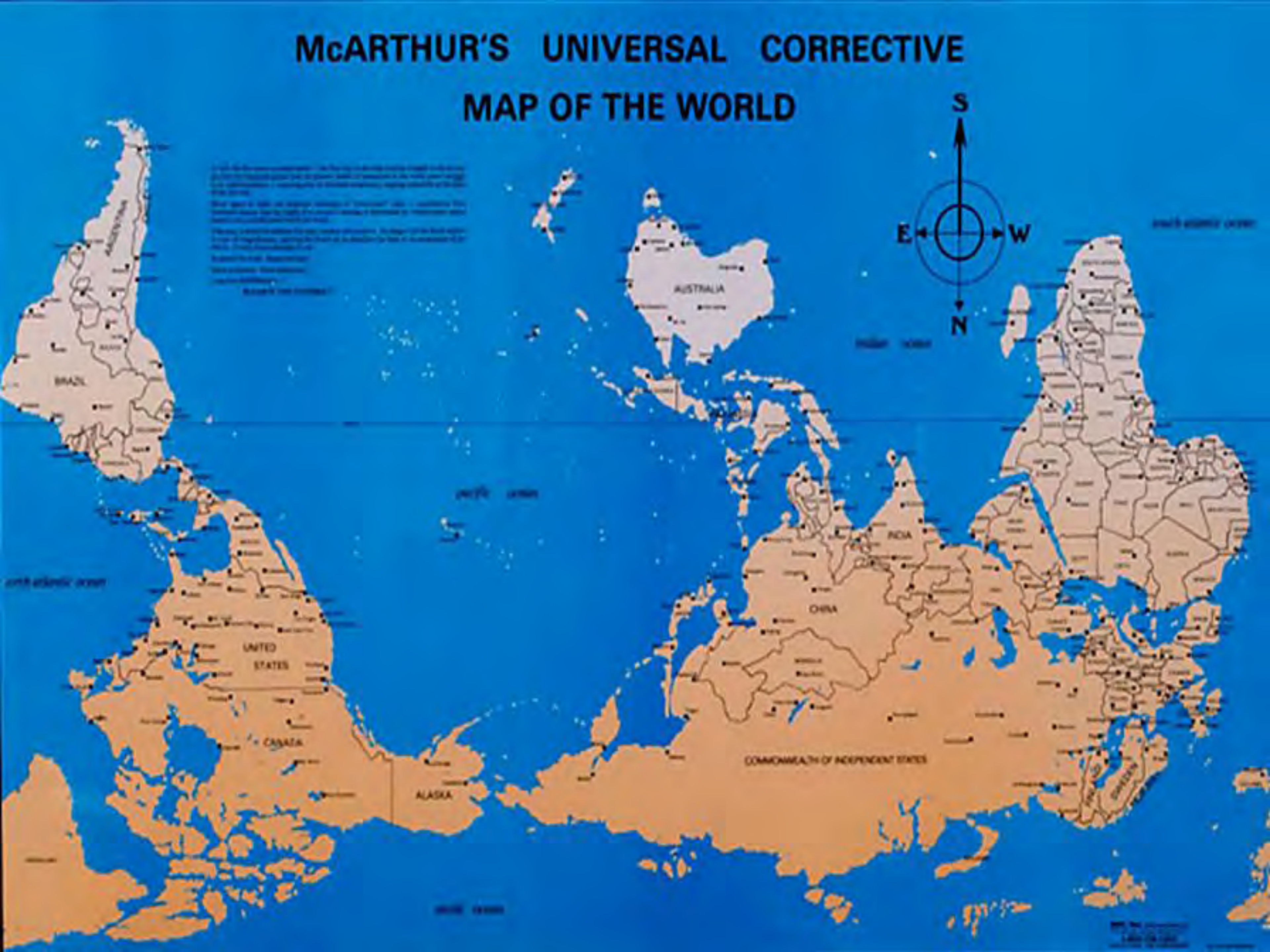
Summary

- The freshwater algal coal Torbanite and lacustrine Colorado oil shale react more slowly than the marine Jordanian oil shales (El-Lajjun and Sultani)

- Products from materials of non-marine algal origin are remarkably similar even though there is a 200 million year difference in age

- The products from the Jordanian shales are more complex due in part to the large number of S compounds

- No direct correlation between organic S content of the shales and the reactivity, Sultani, with significantly less S, reacting more readily than El-Lajjun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