#### Deconvoluting Mixed Petroleum and the Effect of Oil and Gas-Condensate Mixtures on Identifying Petroleum Systems\*

Kenneth Peters<sup>1,2</sup> and Andrew Murray<sup>3</sup>

Search and Discovery Article #42564 (2020)\*\*
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#### **Abstract**

Geochemical analyses of mixed petroleum commonly underestimate input from the more gas-prone source, e.g., inferred input from coaly Sleipner-Hugin source rock is anomalously low compared to that from the Draupne Formation in mixed fluids from the South Viking Graben (SVG; Patience, 2003; Cornford, 2018). We mathematically mixed various pairs of endmembers, including oil and gas condensate (<3,000 and >3,000 scf/bbl, respectively), which we deconvoluted by alternating least squares regression of compound ratios (ALS-R) and concentrations (ALS-C) in the traditional C<sub>15+</sub> range. Results show that ALS-R underestimates input of gas condensate while ALS-C correctly predicts the relative contributions of both endmembers. Furthermore, hierarchical cluster analysis (HCA) of compound ratios to establish genetic families can be misleading. Mixtures having major proportions of gas condensate can cluster with those dominated by the oil endmember.

This work supports previous conclusions that ALS-C reliably predicts mix composition, while ALS-R does not (Peters et al., 2008). For example, ALS-R for mathematical mixtures of Draupne oil (SVG\_o) and Sleipner-Hugin gas condensate (SVG\_g) underestimates SVG\_g by up to 82%. The 10:90 mix of SVG\_o to SVG\_g deconvolutes by ALS-R to 92:8 (severely underestimated SVG\_g) and by ALS-C to 10:90. In the HCA dendrogram, mixtures with up to 75% SVG\_g (GLR=1,070-9,734 scf/bbl) cluster with others dominated by SVG\_o. A more distal cluster of mixtures contains 80-95% SVG\_g (GLR=10,312-12,044 scf/bbl). The endmember SVG\_g (0:100; GLR=12,622 scf/bbl) clusters as another distinct genetic group. Thus, many fluids assigned to the oil-prone source rock by HCA have strong input from the gas-prone endmember. Unfortunately, many publications use ALS-R to deconvolute mixtures (e.g., Justwan et al., 2006). The large range of GLR for the above mixtures (1,070-12,622 scf/bbl) is unrelated to differential biodegradation or thermal maturation.

In conclusion, compound ratios must cover the entire boiling range of mixed petroleum to avoid bias in HCA for genetic affinity of mixed oil and gas condensate. Deconvolution based on  $C_{15+}$  compound ratios underestimates input of gas condensate to such mixtures and compound concentrations are required.

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# Deconvoluting Mixed Petroleum and the Effect of Oil and Gas-Condensate Mixtures on Identifying Petroleum Systems



#### Kenneth Peters<sup>1,2</sup> and Andrew Murray<sup>3</sup>

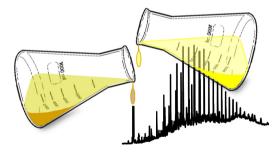
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#### **Purpose and Methods**

- What is the impact of mixed light and heavy petroleum on fluid-source assignment and predicted gas-liquid ratio (GLR)?
- Biomarker concentrations for four pairs of petroleum fluids having endmember GLRs from ~100 to ~50,000 scf/bbl were mathematically mixed in 5% increments.
- Each series of mixtures was evaluated for genetic affinity by hierarchical cluster analysis (HCA) and for source allocation by alternating least squares regression of compound ratios (ALS-R) and concentrations (ALS-C).

 $\frac{17 \text{ independent source-related variables}}{\text{Pr/Ph, C}_{19}/\text{C}_{23}, \text{ C}_{22}/\text{C}_{21}, \text{ C}_{24}/\text{C}_{23}, \text{ C}_{26}/\text{C}_{25},}\\ \text{Tet/C}_{23}, \text{ C}_{27}\text{T/C}_{27}, \text{ C}_{28}/\text{H, C}_{29}/\text{H, X/H, C}_{31}/\text{R,}\\ \text{St/H, \%C}_{27}, \text{\%C}_{28}, \text{\%C}_{29}, \text{S1/S6, OI/H} \\ \end{aligned}$ 





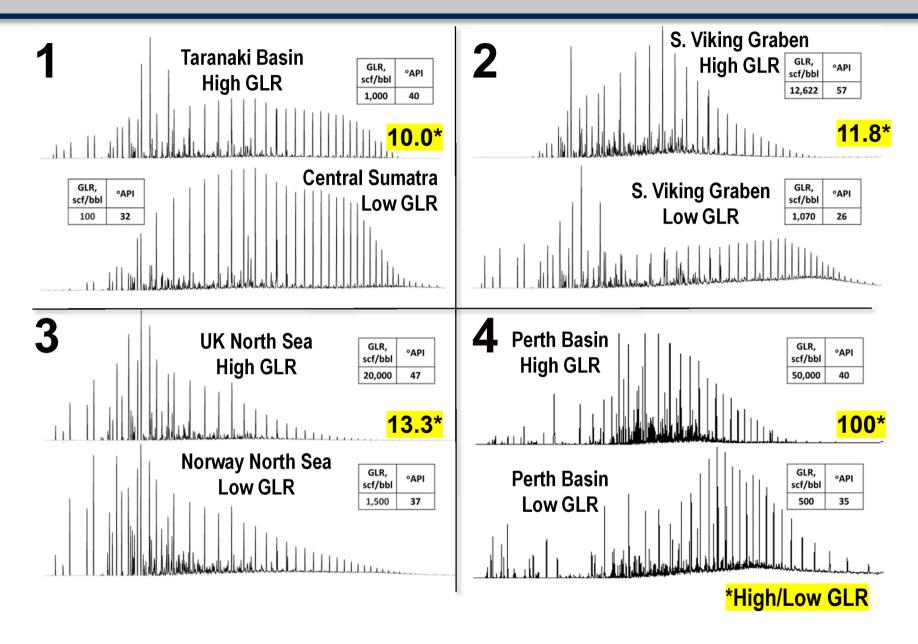
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#### Presenter's notes:

black oil volatile oil gas condensate
GLR <2000 2000-3000 >3000 scf/bbl
API <40 40-45 45-50

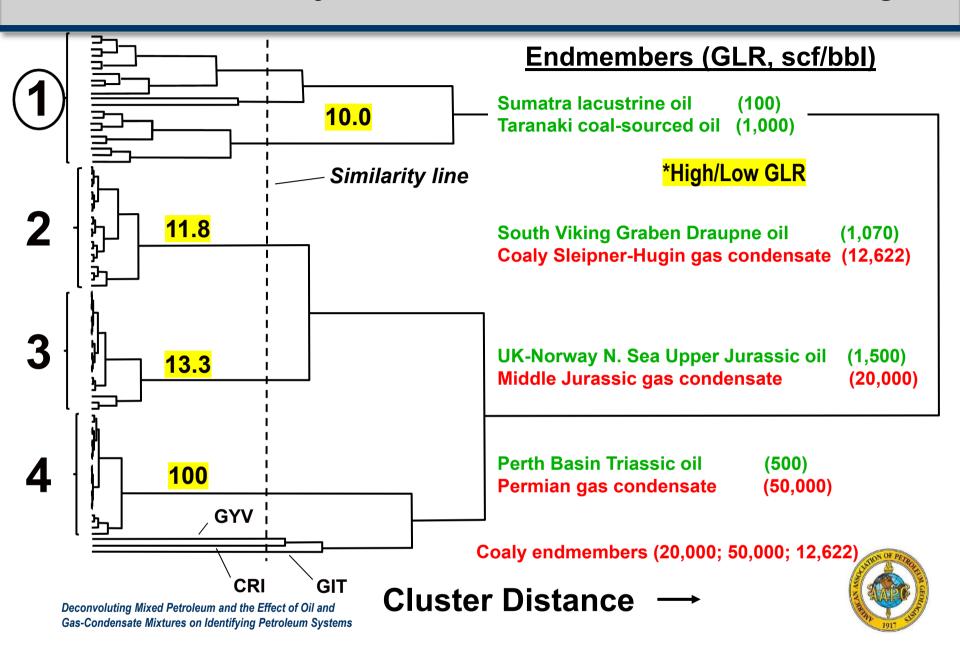
ALS refers to an algorithm to estimate the contributions from mixed sources, projecting that estimate onto the original data to produce an estimate of the chromatographic pattern in each of the component oils. Users modify the projected chromatogram to add constraints that are not possible (e.g., no negative peaks) to form a revised estimate of a logical set of chromatographic patterns, then reverse the process to estimate a new set of concentrations across all oils, then add a constraint (i.e., no negative concentrations and add up to 100%) and repeat: therefore "alternating".

# GCs and Gas-Liquid Ratios Differ for the Endmembers



Presenter's notes:  $GOR = gas-oil\ ratio$ ;  $<3,000 = oil\ (<45\ API)$ ,  $3,000-100,000 = gas\ condensate$  Therefore we will use GLR to include gas condensates.

## **HCA of Four Binary Petroleum Mixtures is Misleading**



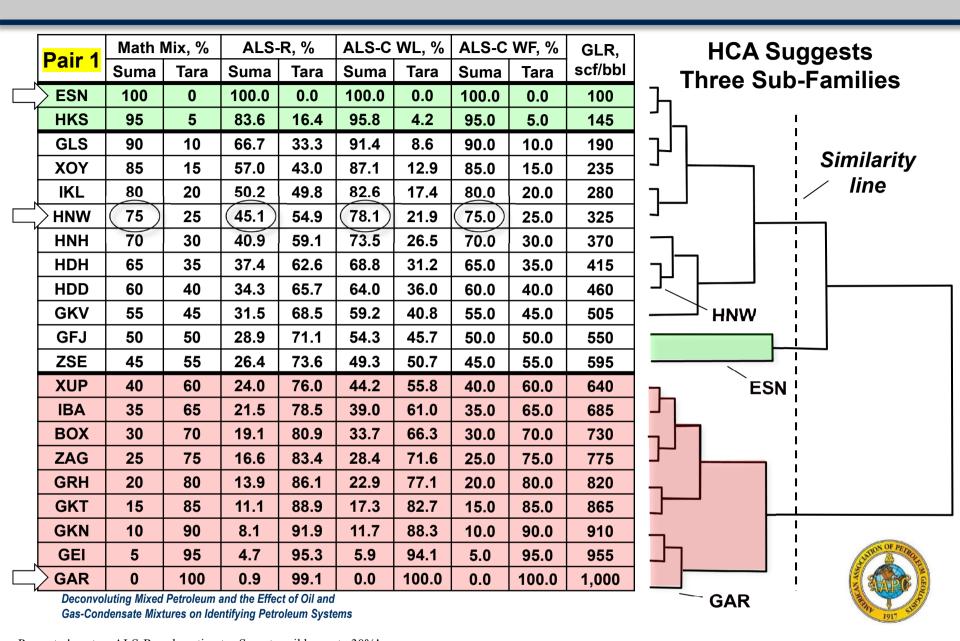
Presenter's notes: Four sets of binary mixtures were obtained by mathematically mixing whole fluid concentrations of compounds for the two endmembers. Seventeen biomarker ratios calculated for each mixture were used to construct the HCA dendrogram, traditionally used to identify genetic affinities. The cluster analysis suggests at least four genetic oil families and three outliers based on the vertical similarity line.

Note that the cluster distances between samples in each binary mix decrease as the difference in GLR between endmembers increases. This occurs because with higher GLR of the gas condensate, the relative influence of the oil on cluster distance increases.

For HCA: autoscale preprocessing, Euclidean distance, incremental linkage GOR = gas-oil ratio; <3,000 = oil (<45o API), 3,000-100,000 = gas condensate Therefore we will use GLR to include gas condensates.

Families with and without noise are identical, although cluster distances are slightly greater between families without added noise.

#### **ALS-C** Reliably Deconvolutes Mixtures; ALS-R Does Not



Presenter's notes: ALS-R underestimates Sumatra oil by up to 30%!

Mass balance (WL and WF): To calculate whole-liquids concentrations, ppm values from Geomark RFDbase were corrected to the saturates concentration using the P/N ratio, then corrected to the concentration in the  $C_{15+}$  fraction using %saturates (relative to total saturates, aromatics, resins, and asphaltenes), and finally corrected to the  $C_{6+}$  concentration using the %loss upon topping (i.e.,  $C_6-C_{15}$ ). The whole-fluid concentration ( $C_{1+}$ ) can then be calculated by using the GLR (m/m).

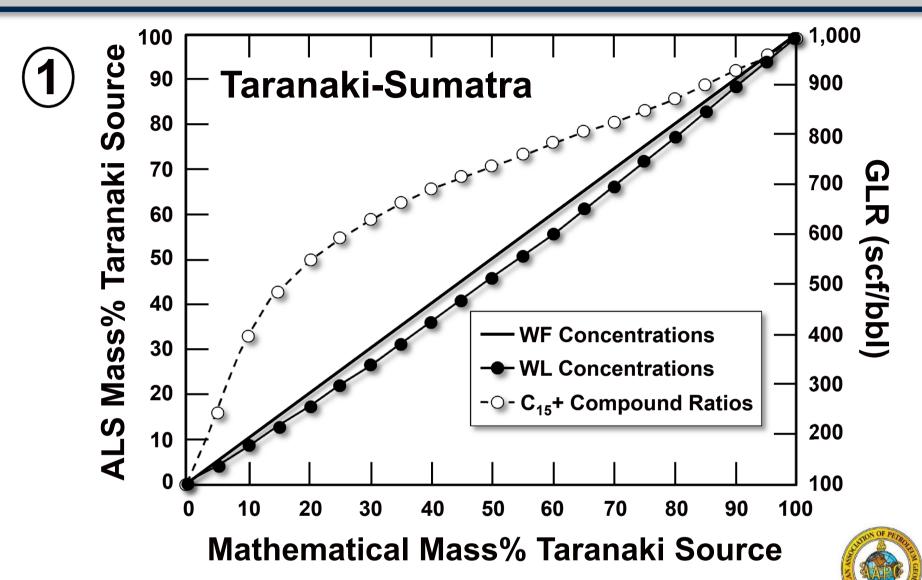
These results confirm Peters et al. (2008), where ALS-C gives reliable predictions of mix composition, while ALS-R does not.

Note that the vertical order of individual samples or sub-families on a dendrogram can change by rotation around the horizontal tie line that connects them. Only cluster distance is important. For example, the sub-family that includes ESN could rotate to the top of the dendrogram over the sub-family that contains HNW around the horizontal tie between them.

For ALS: Variance scale preprocessing, 21 samples, 25 independent variables:

Pr, Ph, C<sub>19</sub> Tri, C<sub>23</sub> Tri, C<sub>22</sub> Tri, C<sub>21</sub> Tri, C<sub>24</sub> Tri, C<sub>26</sub> Tri, C<sub>25</sub> Tri, Tet, C<sub>27</sub> Tri, C<sub>27</sub>H(Tm), C<sub>28</sub>H, 29H, C<sub>30</sub>H, X, C<sub>31</sub>R, Steranes, Hopanes, C<sub>27</sub> Ster, C<sub>28</sub> Ster, C<sub>29</sub> Ster, S1, S6,

#### **ALS-R Overestimates Taranaki Coaly Input and GLR**

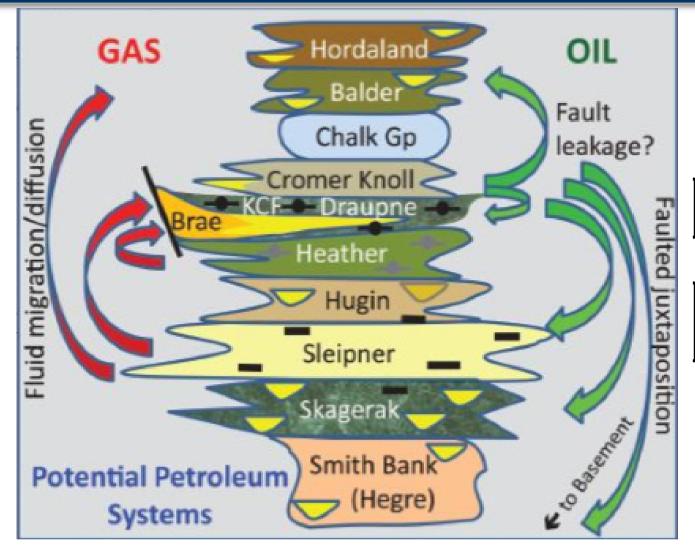


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Presenter's notes: ALS-R underestimates Sumatra oil by up to 30%! At 30% math mass% Taranaki, ALS-R predicts GLR of ~600 scf/bbl, but it should be ~300 scf/bbl. Oil-oil mixtures: Biomarkers are more abundant in the Taranaki than the Sumatra oil, which results in the unusual case where Taranaki input and GLR are overestimated by ALS-R. Normally, coaly input and GLR for an oil-gas condensate mixture are underestimated by ALS-R.

Mass balance (WL and WF): To calculate whole-liquids concentrations, ppm values from Geomark RFDbase were corrected to the saturates concentration using the P/N ratio, then corrected to the concentration in the  $C_{15+}$  fraction using %saturates (relative to total saturates, aromatics, resins, and asphaltenes), and finally corrected to the  $C_{6+}$  concentration using the %loss upon topping (i.e.,  $C_6-C_{15}$ ). The whole-fluid concentration ( $C_{1+}$ ) can then be calculated by using the GLR (m/m).

#### South Viking Graben: Where Did All the Coal Gas Go?



**SVG** oil

**SVG** gas

From Cornford (2018)

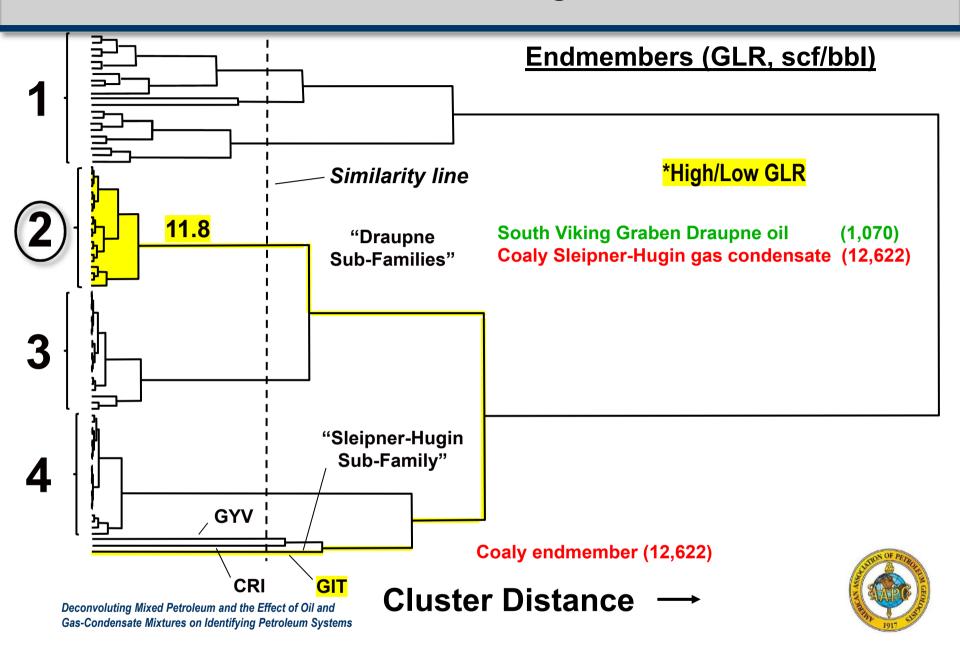
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Presenter's notes: South Viking Graben: Draupne (low GLR), coaly Sleipner-Hugin (high GLR) North and Central Graben: Kimmeridge Clay (low GLR), coaly Pentland (high GLR)

Mid-Norway: Spekk (low GLR), coaly Åre (high GLR)



## HCA is Biased for the Low vs. High GLR Endmember



Presenter's notes: Only the endmember Sleipner-Hugin gas condensate plots separately. All other mixtures (up to 95% Sleipner-Hugin) plot in the HCA near the Draupne endmember, i.e., the 'Draupne Sub-Families' contain up to 95% Sleipner-Hugin input.

Note that the cluster distances between samples in each binary mix decrease as the difference in GLR between endmembers increases. This occurs because with higher GLR of the gas condensate, the relative influence of the oil on cluster distance increases.

HCA is biased for the low GLR endmember because biomarker concentrations are generally higher than the high GLR endmember. However, this does not apply to the Taranaki-Sumatra mixed series because the low GLR endmember (Taranaki) has higher biomarker concentrations than the high GLR endmember.

GOR = gas-oil ratio; <3,000 = oil (<45o API), 3,000-100,000 = gas condensateTherefore we will use GLR to include gas condensates.

#### **ALS-R Underestimates Sleipner-Hugin Coaly Endmember**

		Math Mix, %		ALS-R, %		ALS-C WL, %		ALS-C WF, %		GLR.	South Viking Graben			
	Pair 2	SVG	SVG	SVG	SVG	SVG	SVG	SVG	SVG	scf/bbl	Sub-Families			
Ν		oil	gas	oil	gas	oil	gas	oil	gas	00000	1			
	GQB	100	0	99.8	0.2	100.0	0.0	100.0	0.0	1,070	GQB   GQB			
	ZMC	95	5	99.7	0.3	98.3	1.7	95.0	5.0	1,648	1   85-700%			
	XEO	90	10	99.6	0.4	96.5	3.5	90.0	10.0	2,225	SVG oil			
ĺ	XER	85	15	99.5	0.5	94.6	5.4	85.0	15.0	2,803	] <b>- i</b> i			
ĺ	GLX	80	20	99.3	0.7	92.5	7.5	80.0	20.0	3,380	] ]			
	GNF	75	25	99.2	0.8	90.2	9.8	75.0	25.0	3,958				
	GNH	70	30	99.0	1.0	87.8	12.2	70.0	30.0	4,536	SVG oil			
	GNK	65	35	98.9	1.1	85.1	14.9	65.0	35.0	5,113				
	GPJ	60	40	98.7	1.3	82.2	17.8	60.0	40.0	5691	GZI			
ĺ	GPK	55	45	98.4	1.6	79.0	21.0	55.0	45.0	6,268	│			
	GPL	50	50	98.2	1.8	75.4	24.6	50.0	50.0	6,846	SVG oil			
	GZI	45	55	97.9	2.1	71.5	28.5	45.0	55.0	7,424	]			
	BUZ	40	60	97.6	2.4	67.2	32.8	40.0	60.0	8,001	] ¬ [:]			
	ATW	35	65	97.2	2.8	62.3	37.7	35.0	65.0	8,579	]			
	CKM	30	70	96.7	3.3	56.8	43.2	30.0	70.0	9,156	│			
	GKQ	25	75	96.1	3.9	50.6	49.4	25.0	75.0	9,734				
	HDT	20	80	95.2	4.8	43.4	56.6	20.0	80.0	10,312	PXM : To			
	NYM	15	85	93.9	6.1	35.1	64.9	15.0	85.0	10,889	GIT			
	PXM	10	(90)	91.7	(8.3)	25.4	(74.6)	10.0	(90.0)	11,467				
Ń	GIR	5	95	86.2	13.8	13.9	86.1	5.0	95.0	12,044	SVG gas			
	GIT	0	100	0.0	100.0	0.0	100.0	0.0	100.0	12,622				
•	Deconvoluting Mixed Petroleum and the Effect of Oil and													

Presenter's notes: Only the endmember Sleipner-Hugin gas condensate plots separately. All other mixtures (up to 95% Sleipner-Hugin) plot in an area of the HCA dendrogram near the Draupne endmember. ALS-R underestimates SVG gas by as much as 82% (PXM), whereas ALS-C correctly deconvolutes all artificial mixtures.

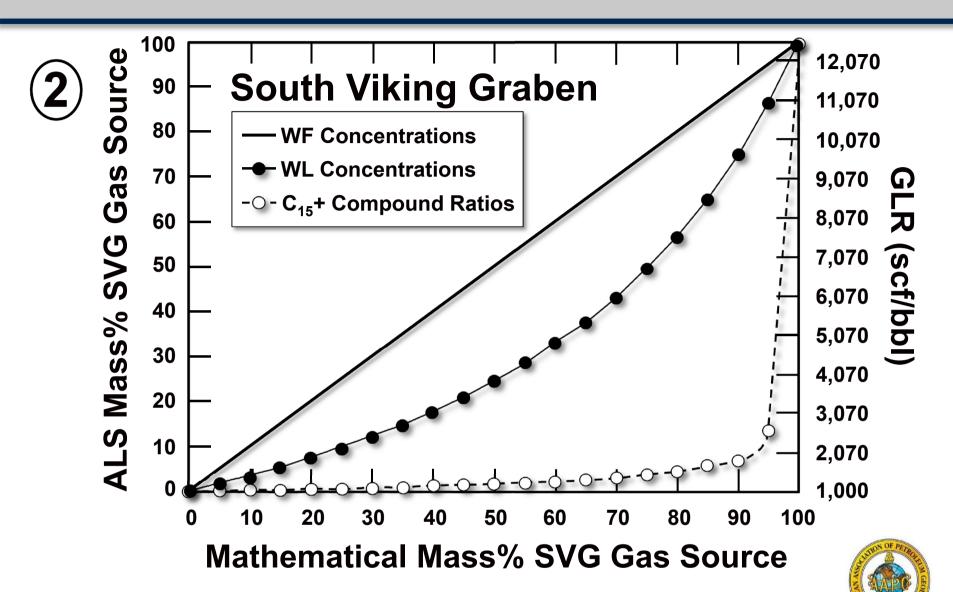
GLR increases from pure Upper Jurassic Draupne oil to pure Middle-Upper Jurassic coaly Sleipner-Hugin gas condensate in the South Viking Graben. GLR oil <3000 sf/bbl; GLR gas condensate = 3000-15,000 scf/bbl.

As shown on the HCA, mixtures with up to 75% SVG gas might be considered to cluster with mixtures dominated by SVG oil.

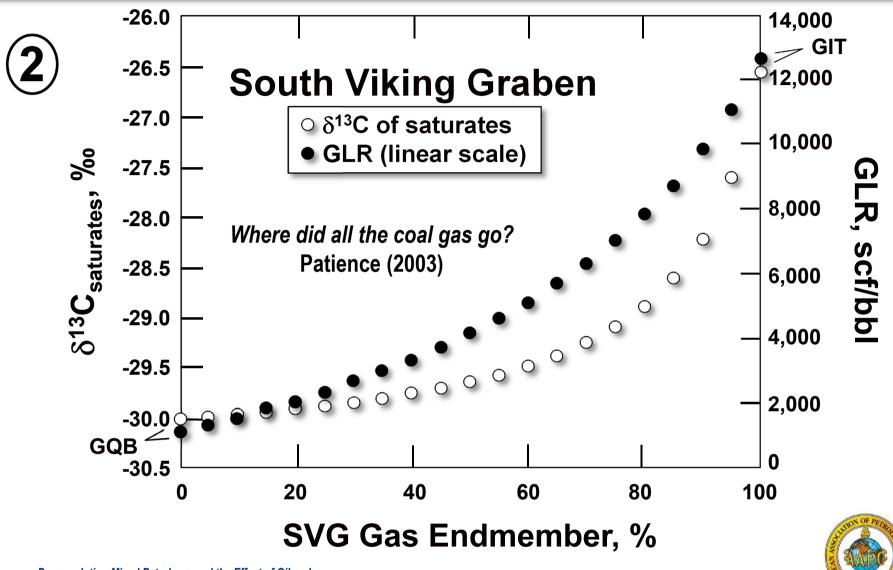
Gas-Condensate Mixtures on Identifying Petroleum Systems

The coaly source rock of the Middle Jurassic petroleum system in the greater North Sea is included in the Bryne/Lulu Formations in Denmark, the Pentland Formation in the UK, and the Sleipner and Hugin formations in Norway.

#### **ALS-R Underestimates Sleipner-Hugin Coaly Input, GLR**



#### Isotopes are Also Biased for the Low GLR Endmember



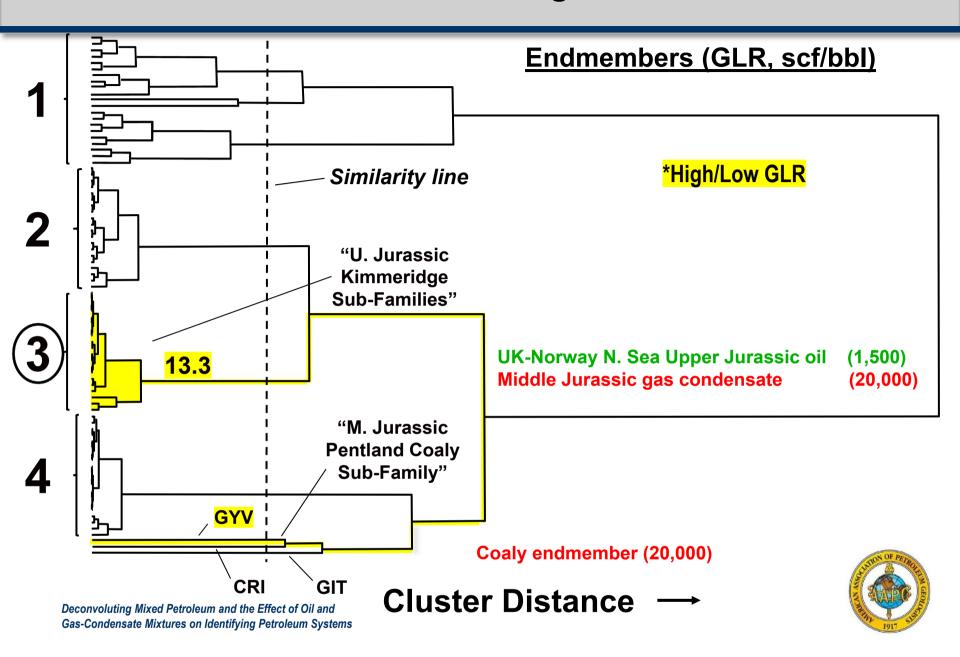
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Presenter's notes: Calculated d<sup>13</sup>C for the mixtures closely resemble the SVG oil endmember (Draupne; -30.02‰) until the SVG gas endmember (Sleipner-Hugin) contributes more than ~80% by mass to the mixture. This provides an explanation for the question "Where did all the coal gas go?". Note that GLR increases more rapidly than d<sup>13</sup>C, so that mixtures thought to be primarily SVG oil will show unexpectedly high GLR.

The GLR curve (black dots) plots ALS-C WL vs. GLR predicted assuming a linear relationship between mathematical SVG-gas vs. GLR (see Excel). Our results differ substantially from Justwan et al. (2006) who based their interpretations on biomarker and isotope analyses of the  $C_{15+}$  fraction for crude oils *and condensates* from the South Viking Graben.

Justwan H. et al., 2006. Geochemical characterization and genetic origin of oils and condensates in the South Viking Graben, Norway. Marine and Petroleum Geology 23, 213-239.

## HCA is Biased for the Low vs. High GLR Endmember



Presenter's notes: HCA is biased for the low GLR endmember because biomarker concentrations are generally higher than the high GLR endmember. However, this does not apply to the Taranaki-Sumatra mixed series because the low GLR endmember (Taranaki) has higher biomarker concentrations than the high GLR endmember.

Note that the cluster distances between samples in each binary mix decrease as the difference in GLR between endmembers increases. This occurs because with higher GLR of the gas condensate, the relative influence of the oil on cluster distance increases.

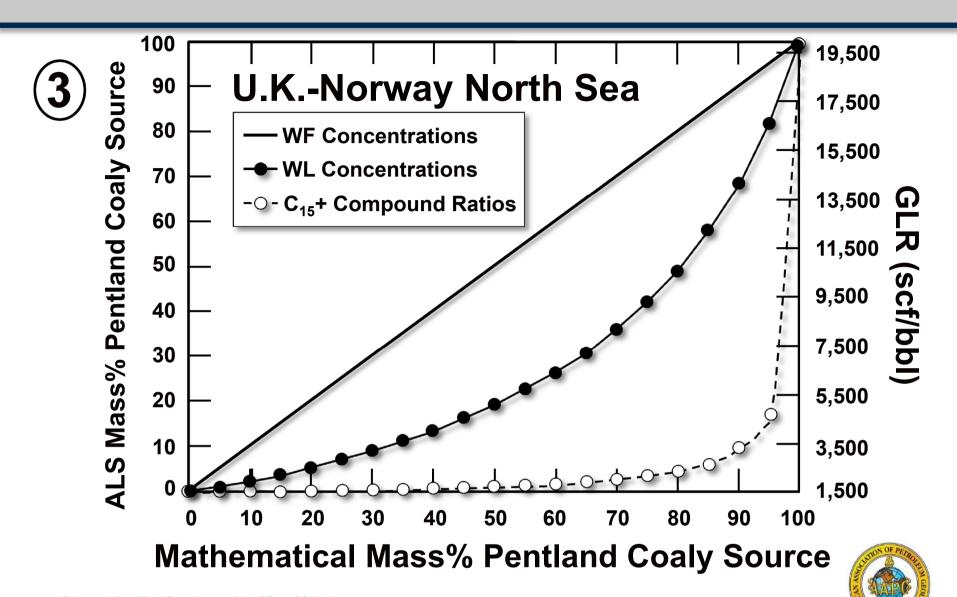
Families with and without noise are identical, although cluster distances are slightly greater between families without added noise.

## **ALS-R Underestimates M. Jurassic Pentland Endmember**

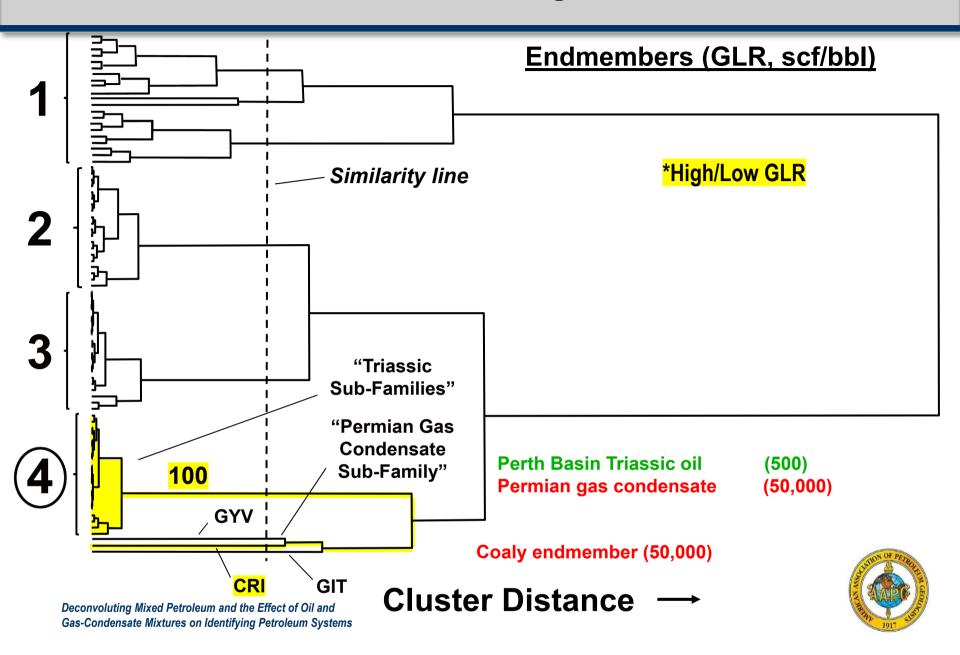
		Math Mix, %		ALS-R, %		ALS-C WL, %		ALS-C WF, %		GLR,	U.KNorway North				
	Pair 3	UJ oil	MJ gas	UJ oil	MJ gas	UJ oil	MJ gas	UJ oil	MJ gas	scf/bbl	Sea Sub-Families				
	HDF	100	0	100.0	0.0	100.0	0.0	100.0	0.0	1,500	1 1				
•	WUT	95	5	99.9	0.1	98.7	1.3	95.0	5.0	2,425	<b>h</b> :				
	XJM	90	10	99.9	0.1	97.4	2.6	90.0	10.0	3,350	HDF				
	GHA	85	15	99.8	0.2	95.9	4.1	85.0	15.0	4,275	65-100%				
	FQU	80	20	99.7	0.3	94.3	5.7	80.0	20.0	5,200	լ				
	FXU	75	25	99.6	0.4	92.5	7.5	75.0	25.0	6,125	<b>"                                     </b>				
	GJI	70	30	99.4	0.6	90.6	9.4	70.0	30.0	7,050					
	GLU	65	35	99.3	0.7	88.4	11.6	65.0	35.0	7,975	[ <del>                                    </del>				
	GNR	60	40	99.1	0.9	86.1	13.9	60.0	40.0	8,900	1 !   1				
	GQM	55	45	98.9	1.1	83.4	16.6	55.0	45.0	9,825	35-60%				
	GQV	50	50	98.7	1.3	80.4	19.6	50.0	50.0	10,750					
	GUR	45	55	98.4	1.6	77.1	22.9	45.0	55.0	11,675	η : [ · · · · · · · · · · · · · · · · · ·				
	HNR	40	60	98.0	2.0	73.3	26.7	40.0	60.0	12,600	,P ;				
	HNV	35	65	97.6	2.4	68.9	31.1	35.0	65.0	13,525	ال				
	VIUW	30	70	97.0	3.0	63.8	36.2	30.0	70.0	14,450	ZIUW Pentland gas				
ĺ	GBC	25	75	96.2	3.8	57.8	42.2	25.0	75.0	15,375	85-95%				
	GDN	20	80	95.0	5.0	50.7	49.3	20.0	80.0	16,300	Pentland gas To				
	GDP	15	85	93.2	6.8	42.1	57.9	15.0	85.0	17,225	GYV				
	GHK	10	90	89.9	(10.1)	31.4	(68.6)	10.0	(90.0)	18,150	· ·				
	GPR	5	95	81.9	18.1	17.8	82.2	5.0	95.0	19,075	July OF PERROP				
	GYV	0	100	0.0	100.0	0.0	100.0	0.0	100.0	20,000					
		•	l Petroleum a tures on Iden	GHK											

Presenter's notes: ALS-R underestimates Middle Jurassic Pentland gas condensate by up to 80%, i.e., ALS-R is biased for the low GLR endmember Kimmeridge oil.

#### **ALS-R Underestimates Pentland Coaly Input and GLR**



## HCA is Biased for the Low vs. High GLR Endmember



Presenter's notes: The fourth binary mixture from the Perth basin includes endmembers showing the greatest difference in GLR (500 vs. 50,000 scf/bbl). This results in a very tight cluster for all mixtures near the Triassic oil endmember on the HCA dendrogram, except for the Permian (coaly) endmember (CRI).

For HCA: autoscale preprocessing, Euclidean distance, incremental linkage GOR = gas-oil ratio; <3,000 = oil (<45o API), 3,000-100,000 = gas condensate Therefore we will use GLR to include gas condensates.

Note that the cluster distances between samples in each binary mix decrease as the difference in GLR between endmembers increases. This occurs because with higher GLR of the gas condensate, the relative influence of the oil on cluster distance increases.

Families with and without noise are identical, although cluster distances are slightly greater between families without added noise.

#### **ALS-R Severely Underestimates Permian Gas Condensate**

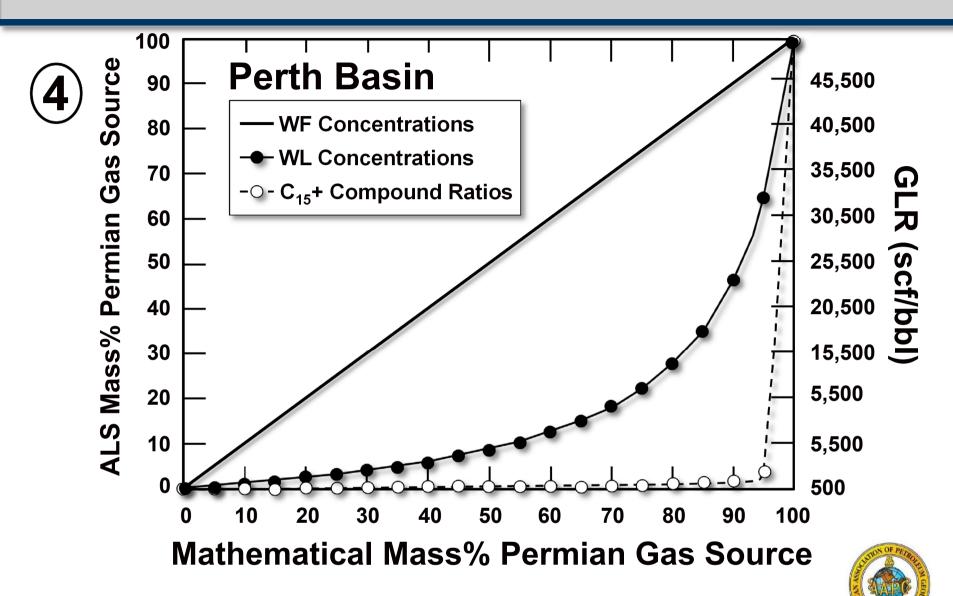
		Math	Mix, %	ALS	-R, %	ALS-C	WL, %	ALS-C WF, %		GLR,	
	Pair 4	Tri oil	Per gas	Tri oil	Per gas	Tri oil	Per gas	Tri oil	Per gas		S
	> IFC	100	0	100.0	0.0	100.0	0.0	100.0	0.0	500	
V	JAS	95	5	100.0	0.0	99.5	0.5	95.0	5.0	2,975	
	MED	90	10	100.0	0.0	99.0	1.0	90.0	10.0	5,450	L
	GDX	85	15	99.9	0.1	98.3	1.7	85.0	15.0	7,925	ا ا
	GFE	80	20	99.9	0.1	97.7	2.3	80.0	20.0	10,400	ιŀ
	GHO	75	25	99.9	0.1	96.9	3.1	75.0	25.0	12,875	ıЛ
	GHU	70	30	99.9	0.1	96.1	3.9	70.0	30.0	15,350	1
	GHV	65	35	99.8	0.2	95.1	4.9	65.0	35.0	17,825	Г
	GHZ	60	40	99.8	0.2	94.0	6.0	60.0	40.0	20,400	1
	GNI	55	45	99.8	0.2	92.8	7.2	55.0	45.0	22,775	
	GPW	50	50	99.7	0.3	91.3	8.7	50.0	50.0	25,250	h
	GXK	45	55	99.7	0.3	89.6	10.4	45.0	55.0	27,725	1
	IZZ	40	60	99.6	0.4	87.5	12.5	40.0	60.0	30,200	
	KYI	35	65	99.5	0.5	85.0	15.0	35.0	65.0	32,675	J)
	UIX	30	70	99.4	0.6	81.8	18.2	30.0	70.0	35,150	ľ
	HQF	25	75	99.2	0.8	77.8	22.2	25.0	75.0	37,625	ľ
	HNJ	20	80	99.0	1.0	72.4	27.6	20.0	80.0	40,100	ĺ
	GNJ	15	85	98.7	1.3	64.9	35.1	15.0	85.0	42,575	
	GNY	10	90	98.0	( 2.0 )	53.8	(46.2)	10.0	(90.0)	45,050	
	BUU	5	95	96.5	3.5	35.6	64.4	5.0	95.0	47,525	
	CRI	0	100	0.0	100.0	0.0	100.0	0.0	100.0	50,000	\

**Perth Basin Sub-Families HQF** 25-60% Triassic oil **IFC** 65-100% Triassic oil 80-95% Permian gas **HNJ** To **BUU GNY** 

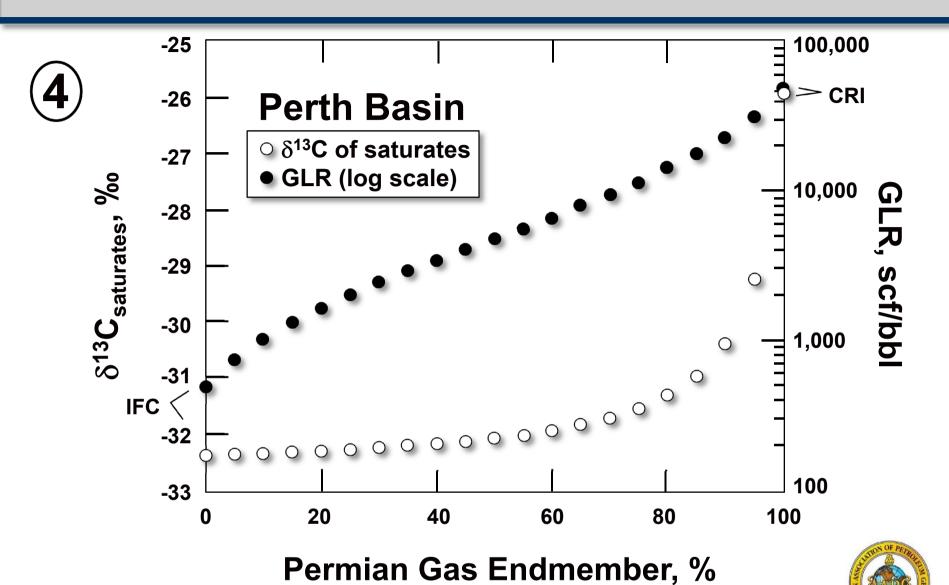
Deconvoluting Mixed Petroleum and the Effect of Oil and Gas-Condensate Mixtures on Identifying Petroleum Systems

Presenter's notes: ALS-R underestimates the contribution of Permian gas condensate to the binary mixtures by up to 88% (GNY).

#### **ALS-R Underestimates Coaly Permian Input and GLR**

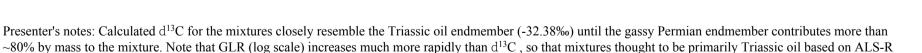


#### Isotopes are Also Biased for the Low GLR Endmember



Deconvoluting Mixed Petroleum and the Effect of Oil and Gas-Condensate Mixtures on Identifying Petroleum Systems

(ratios) will show unexpectedly high GLR.



#### **Conclusions for Binary Mixtures of Petroleum**

- HCA of compound ratios identifies genetic fluid families through a range of molecular weight but can be misleading for mixtures of endmembers with distinct compound concentrations or GLRs.
- ALS-R can deconvolute oil-oil mixtures having similar GLRs, but mixtures having different GLRs, compound ratios, and concentrations mix in non-linear fashion.
- ALS-R fails to deconvolute mixtures of oil and gas condensate;
   underestimates GLR and the contribution from gas-condensate.
- ALS-C deconvolutes mixtures (two or more endmembers), but GCMS quantification requires internal standards. ALS-C whole fluid ( $C_1$ +) is more accurate than ALS-C whole liquid ( $C_6$ +).
- Many interpreters use ALS-R to deconvolute mixtures, thus yielding inaccurate results.

Deconvoluting Mixed Petroleum and the Effect of Oil and Gas-Condensate Mixtures on Identifying Petroleum Systems



Presenter's notes: Precision (repeatability) vs. accuracy

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## Different Basins, Same Rift and Bias Against Coal Gas

