

## Colin Snape

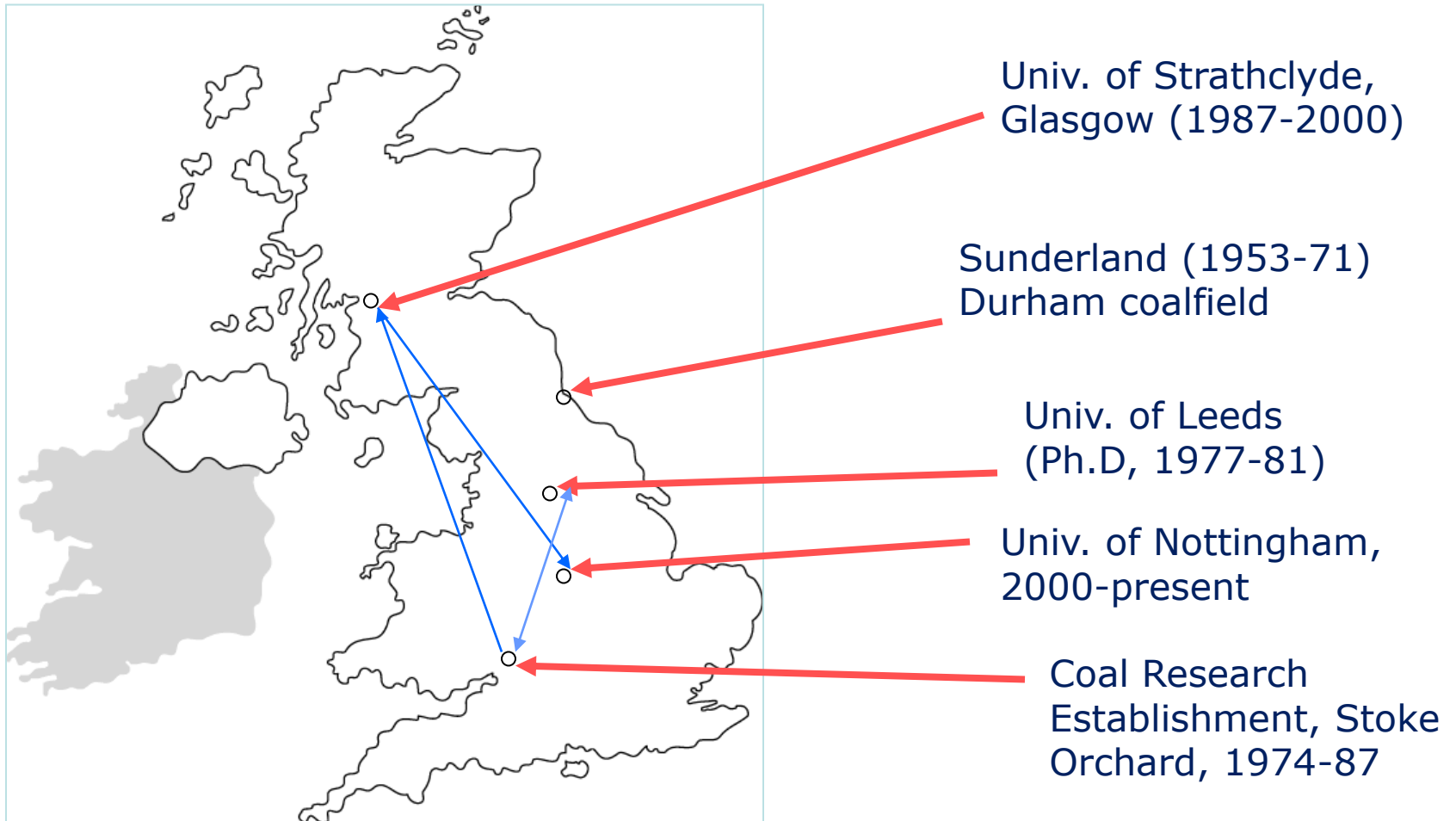
### How the Advanced Structural Characterisation of Coal has Benefitted Utilisation

***The challenge of unraveling the highly heterogeneous structure of coal and its impact on utilisation has meant that coal science has been at the forefront for understanding complex organic matter***

Acknowledge Biomass & Fossil Fuel Research Alliance (BF2RA) for organising event with sponsorship from:

- the British Coal Utilisation Research Association (BCURA)
- Coal Research Forum (CRF),
- IEA Clean Coal Centre
- Royal Society of Chemistry (RSC)
- Energy Sector and the Energy Generation and Supply Knowledge Transfer Network

# My career in coal science



# ***"How the Advanced Structural Characterisation of Coal has Benefitted Utilisation"***

## **Lecture Outline**

- The Early years (Coal Research Establishment)
  - **structure of coal** – understand pyrolysis and liquefaction.
- The Middle Years (University of Strathclyde)
  - applying knowledge on coal to other fields – biomass & polymers, oil exploration.
  - **carbonisation**, understanding fluidity development from a fundamental standpoint, impact on coke properties
  - **Pollutants** – Polycyclic aromatic hydrocarbons (PAHs), source apportionment, Hg control
- The Later years (University of Nottingham)
  - **Combustion** – oxyfuel, catalysis
  - **Biomass co-firing**, utilisation
  - CCS
- Does the UK have a future for coal?
  - – technology and the best available young talent.

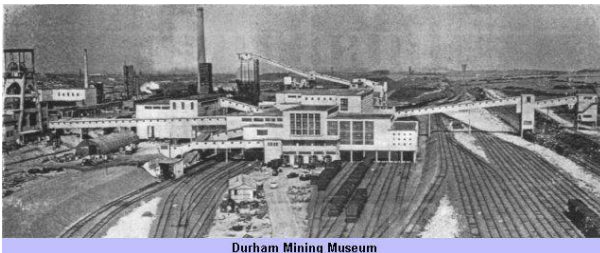
# The North East Coalfield in the 1960s and 70s



Eppleton Colliery

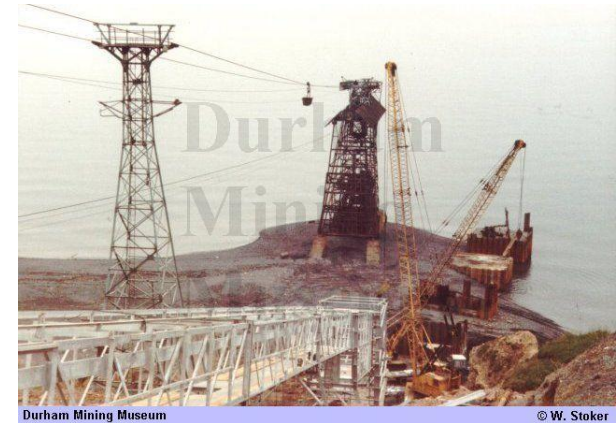


Easington Colliery



Durham Mining Museum

Hawthorn Mine  
and Coking Plant



© W. Stoker

- Fathers side of the family, Easington
- Grandfather moved to NE from South Yorkshire in 1880s.
- Great, great grandfather (born 1788) traced to Eckington, North Derbyshire.



*“Get Carter” 1972, Horden “Beach”*

# **“You wont get me I’m part if the Union” (Strawbs 1973)**

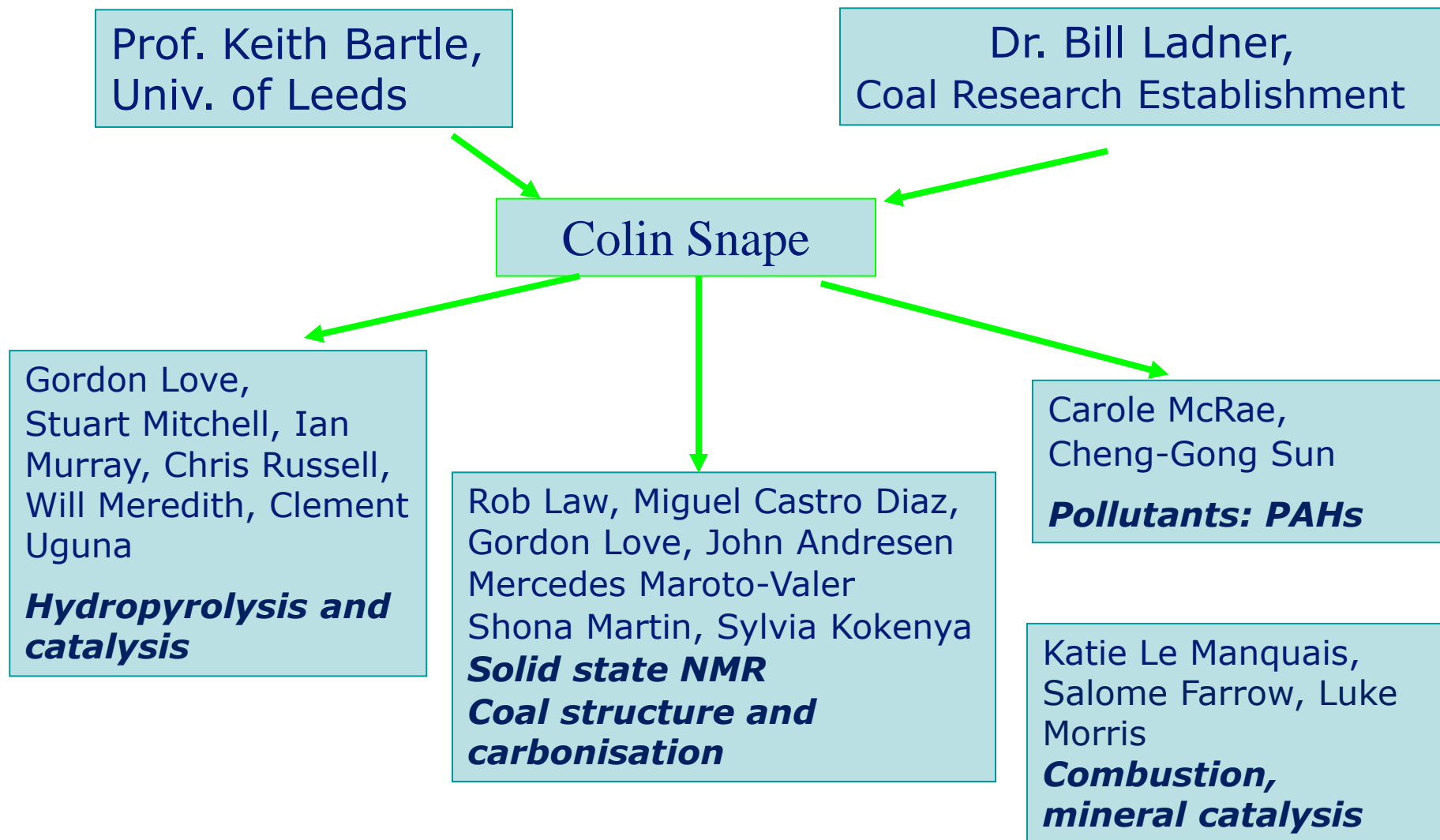
**“You’ve got me because my dad is leading militant in the Durham NUM”**



- My father was not in part of the Durham Winderman’s Association, a separate entity within the NUM and somewhat less militant.
- Oil price rise – coal liquefaction would meet future needs.
- Chemistry/ Analysis and Basic Studies Sections.
- Bill Ladner, Derek Williams, Geoff Kimber, Terry Martin, Dick James.



# My “Scientific Family Tree”



# Low-severity coal liquefaction products provide detailed insights into coal structure

*NCB developed supercritical gas extraction and two-stage hydrogen-donor solvent liquefaction processes, the latter operated at 2 t/d at Point of Ayr.*

- Fuel, 1979, 58, 413-422 (150 citations) and Ph.D thesis
- Key technique is  $^{13}\text{C}$  NMR spectroscopy
- Optimise conditions for quantification



## Structural analysis of supercritical-gas extracts of coals

Keith D. Bartle\*, William R. Ladner†, Terence G. Martin†, Colin E. Snape† and Derek F. Williams†

\*Department of Physical Chemistry, University of Leeds, Leeds LS2 9JT, UK

†National Coal Board, Coal Research Establishment, Stoke Orchard, Cheltenham, Glos. GL52 4RZ, UK

(Received 16 September 1978)

The chemical structure of two extracts prepared by supercritical extraction of low-rank coals with toluene, with and without hydrogen, have been determined using solvent and chromatographic fractionation followed by ultimate analysis,  $^1\text{H}$  nuclear magnetic resonance (n.m.r.) spectroscopy, molecular weight and OH measurements.  $^{13}\text{C}$  n.m.r. and i.r. spectroscopy have been used to obtain confirmatory evidence. The extract obtained in the absence of hydrogen, which amounted to 27% of the coal, was found to contain aromatic structures linked by ring-joining methylene or heterocyclic groups. The hydrogen-assisted extract (47.5 wt % coal) was more condensed and contained more smaller molecules, apparently as a result of the cleavage of heterocyclic groups in the coal. It also incorporated more hydroaromatic substituents.  $^{13}\text{C}$  n.m.r. showed that virtually all the non-phenolic oxygen was present as aromatic ether.

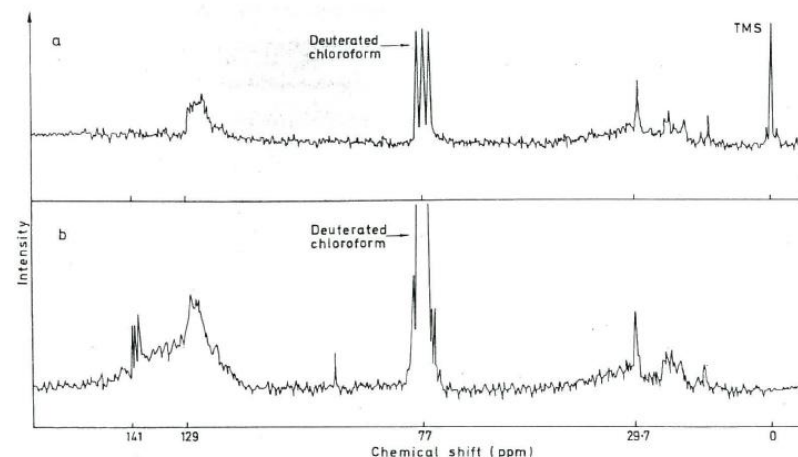


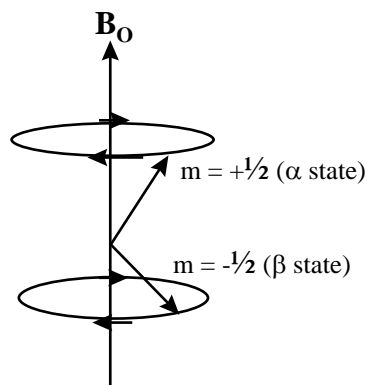
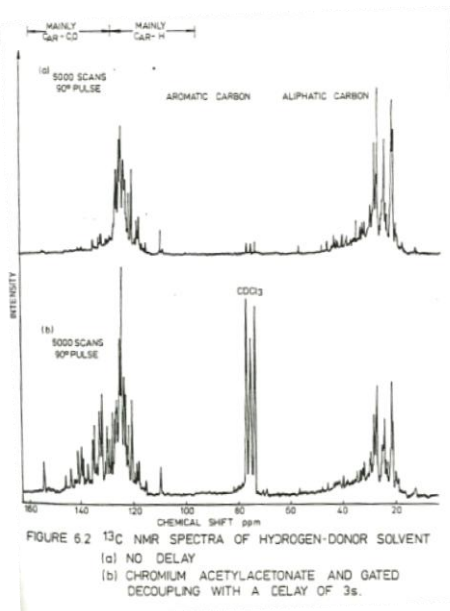
Figure 2  $^{13}\text{C}$  decoupled spectra of coal extract.

(a) No gated decoupling or chromium acetylacetonate.

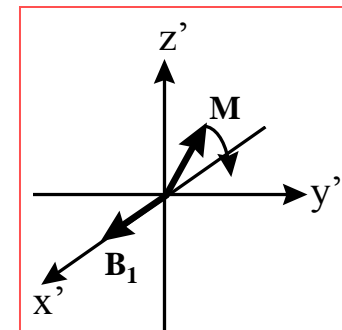
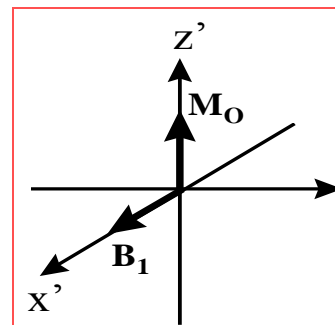
(b) Gated decoupling with 4 s delay and 100 mg of chromium acetylacetonate

# The NMR Phenomenon

- slow relaxation of  $^{13}\text{C}$  aromatic nuclei, accelerate with a paramagnetic reagent



Behaviour of nuclei with magnetic moments



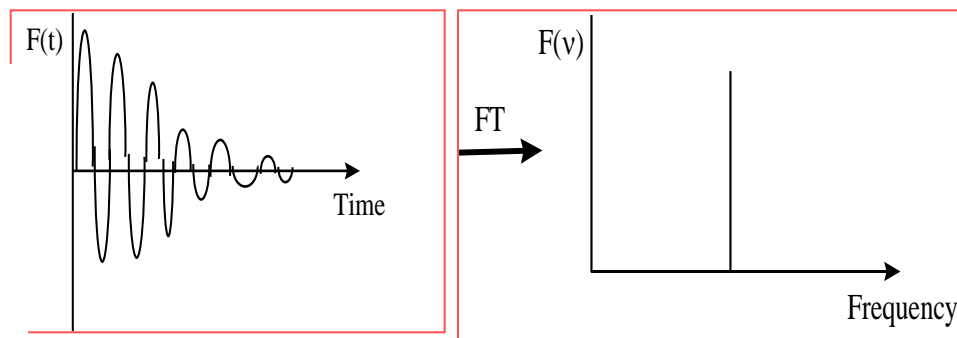
Manipulate magnetism by applying radiofrequency pulses

## Application of quantitative $^{13}\text{C}$ nuclear magnetic resonance spectroscopy to coal-derived materials

William R. Ladner and Colin E. Snape  
National Coal Board, Coal Research Establishment, Stock Orchard, Cheltenham, Glos. GL52 4RZ, UK  
(Received 16 March 1978)

The difficulties associated with obtaining quantitative results from  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy are discussed. By careful choice of the experimental conditions quantitative results have been obtained for a mixture of model compounds, containing most of the types of carbon linkages present in coal-derived materials, and for an aromatic fraction of a coal extract.

W.R. Ladner and C.E. Snape, Application of quantitative  $^{13}\text{C}$  NMR spectroscopy to coal-derived materials, *Fuel*, 1978, **57**, 658-662.



Detection of magnetisation in time domain and transformation to frequency domain

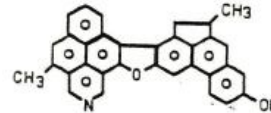
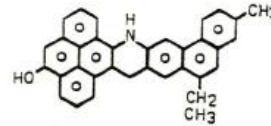


# High yield coal extract structures

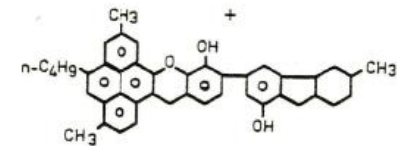
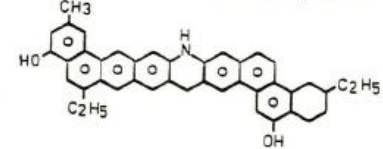
High volatile bituminous and low-rank coals contain:

- Small aromatic nuclei.
- Little naphthenic/hydroaromatic aliphatic structure.
- Short alkyl chains.

ANTHRACENE OIL EXTRACT  
(BITUMINOUS COAL, ANNESLEY)

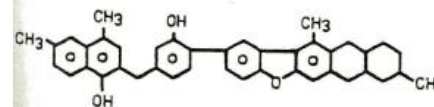
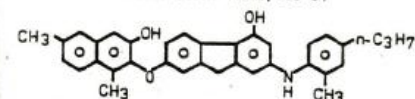


HDS EXTRACT  
(BITUMINOUS COAL, ANNESLEY, 400°C)

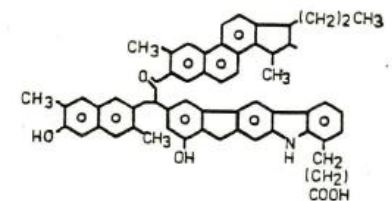


SCG EXTRACTS

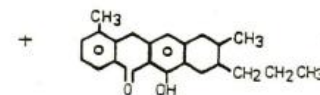
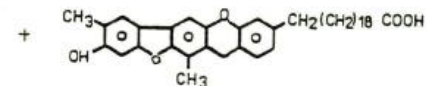
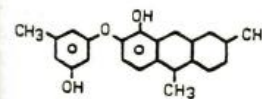
BITUMINOUS COAL (DAW MILL, 420°C)



PERHYDROUS COAL



LIGNITE (USA)



# But, results not entirely consistent with coal models proposed

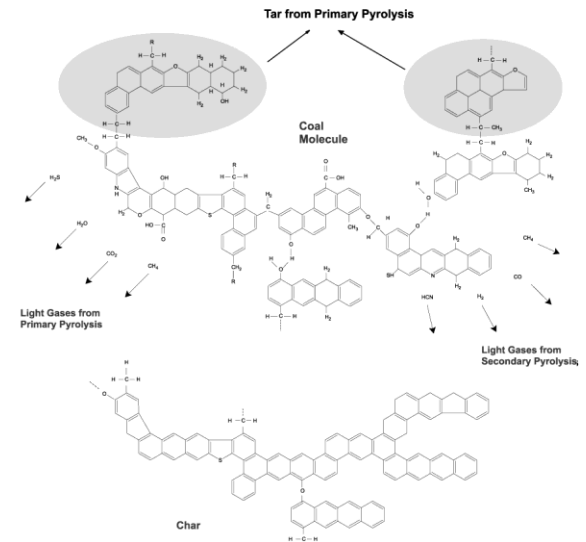
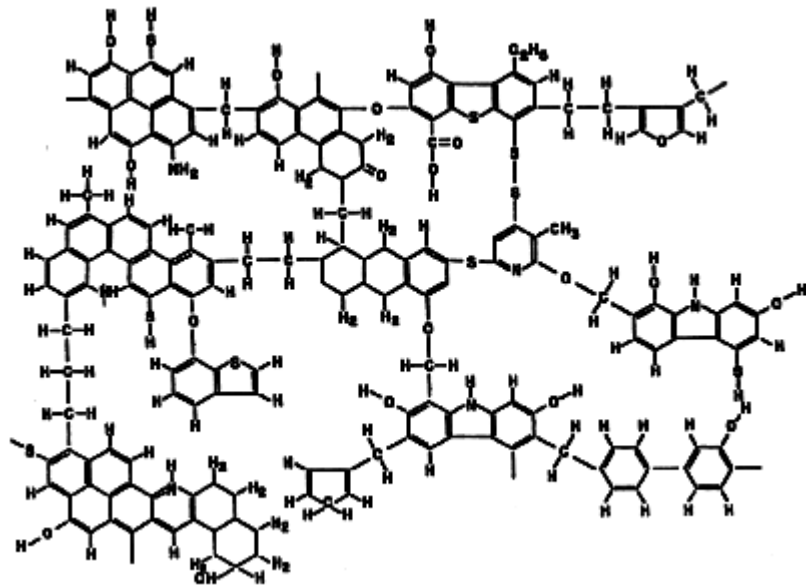


Figure 1. Coal molecular structure and devolatilization (adapted from Solomon et al.<sup>1</sup>)

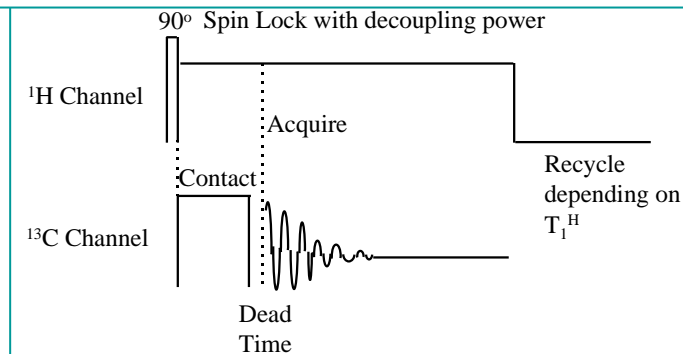
- These models generally displayed low aromaticities and to compensate for this, high proportions of naphthenic (cyclic) aliphatic structures.
- Only answer was to move from solution state measurements on extracts to solid state  $^{13}\text{C}$  measurements on coals and individual macerals.

# Quantitative solid state $^{13}\text{C}$ NMR

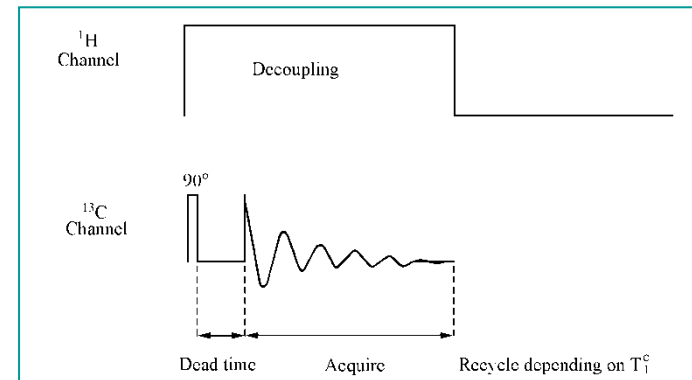
## – carbon skeletal parameters to define coal structure model thermal conversion

### ■ *Easy to do badly, but painstaking to do well!*

Cross-polarisation. Fast, but inevitably non-quantitative – not all C observed, discriminates against aromatic C.



Single pulse excitation, slow and less sensitive, but quantitative – all the C observed.



- Proven for coal then applied to all insoluble organic matter
  - polymers, petroleum source rocks, catalytic cokes (FCC), semi-cokes.
- SPE - higher aromaticities and more non-protonated aromatic C.

K.J. Packer, R.K. Harris, A.M. Kenwright and C.E. Snape, *Fuel*, 1983, 62, 999-1002.

C.E. Snape, D.E. Axelson, R.E. Botto, J.J. Delpuech, P. Tekely, B.C. Gerstein, M. Pruski, G.E. Maciel and M.A. Wilson, *Fuel*, 1989, 68, 547-560.

J. Franz, R. Garcia, G.D. Love, J. Linehan and C.E. Snape, *Energy & Fuels*, 1992, 6, 598-602.



# SPE $^{13}\text{C}$ NMR gives accurate aromaticities for coals

*Energy & Fuels* 1992, 6, 598–602

## Single-Pulse Excitation $^{13}\text{C}$ NMR Measurements on the Argonne Premium Coal Samples

J. A. Franz,<sup>\*,†</sup> R. Garcia,<sup>†</sup> J. C. Linehan,<sup>†</sup> G. D. Love,<sup>‡</sup> and C. E. Snape<sup>\*,‡</sup>

*Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham  
Building, 295 Cathedral St., Glasgow G1 1XL, UK, and Pacific Northwest Laboratory of the  
U.S. Department of Energy P.O. Box 999, Richland, Washington 99352*

*Received February 19, 1992. Revised Manuscript Received May 27, 1992*

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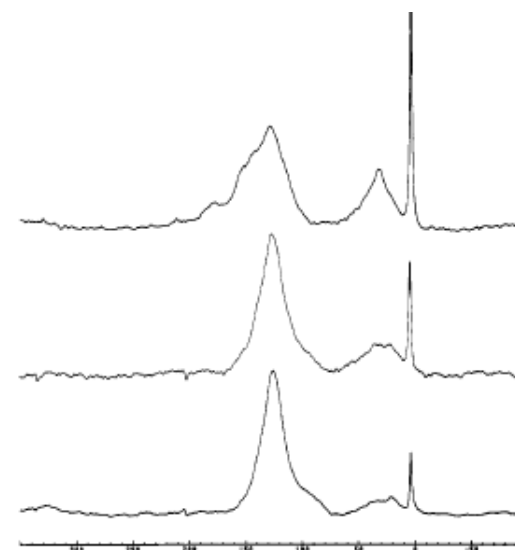
In view of the results of this study and the well-documented inherent problems with cross-polarization (CP)  $^{13}\text{C}$  NMR concerning quantification for coals, it is now clear that the more time-consuming single-pulse excitation (SPE) or Bloch decay measurements are essential for obtaining aromaticities and other carbon skeletal parameters for coals. SPE  $^{13}\text{C}$  NMR has been carried out on the Argonne Premium Coal Samples at both a low and a high field strength (25 and 75 MHz, respectively), high-speed magic angle spinning (13 kHz) being used to suppress spinning sidebands at the higher field. Aromaticity values measured by SPE at low and high field were generally in excellent agreement and were consistently higher than those from CP, the greatest differences being found for the two low-rank coals in the Argonne suite. The use of tetrakis(trimethylsilyl)silane as an internal standard in the low-field measurements indicated that, in general, over 75% of the carbon in the coals is typically observed by SPE.

# Two groups, different field strengths – nearly perfect agreement

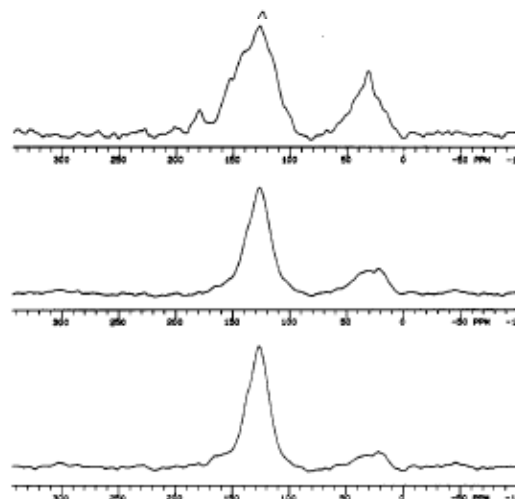
**Table II. Aromaticity Values Derived from SPE Spectra of the Argonne Coals**

sample	% dmmf C	aromaticity (all $sp^2$ carbon)			
		75 MHz	25 MHz		% of C obsd at 25 MHz <sup>d</sup>
			this study	ref 8 <sup>a</sup>	
North Dakota lignite	73	0.77	0.76	0.74	95
Wyodak subbit.	75	0.76	0.75	0.66	95
Illinois No. 6	80	0.72	0.75	0.72	85
			0.75 <sup>b,c</sup>		100 <sup>b</sup>
Pittsburgh No. 8	83	0.75	0.75	0.75	90
Blind Canyon	81	0.67	0.67	0.68	75
Lewis-Stockton	84	0.77	0.78	0.71	75
Upper Freeport	88	0.80	0.81	0.83	75
			0.84 <sup>c</sup>		90 <sup>c</sup>
Pocahontas	91	0.89	0.90	0.89	90

<sup>a</sup> Initial samples. <sup>b</sup> = 100 s delay. <sup>c</sup> After demineralization. <sup>d</sup> This study;  $\pm 5\%$ .



**Figure 1.** 25-MHz SPE spectra of (top to bottom) (a) Wyodak, (b) Upper Freeport, and (c) Pocahontas coals.

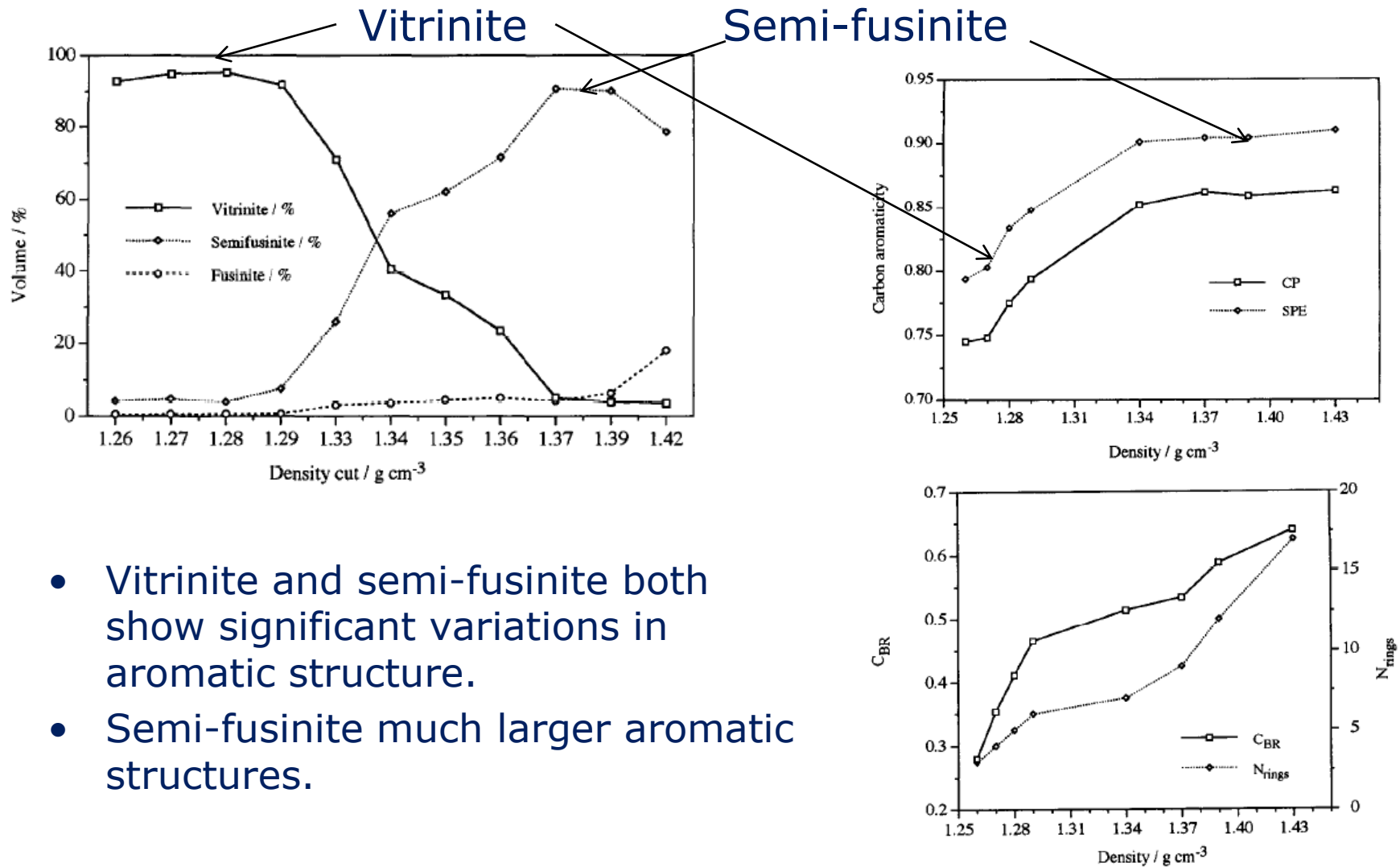


**Figure 2.** 75-MHz SPE spectra of (a, top) Wyodak, (b, middle) Upper Freeport, and (c, bottom) Pocahontas coals.



# Accurate structural parameters and variations about the mean

## – medium volatile bituminous coal



# Hydropyrolysis – historical perspective

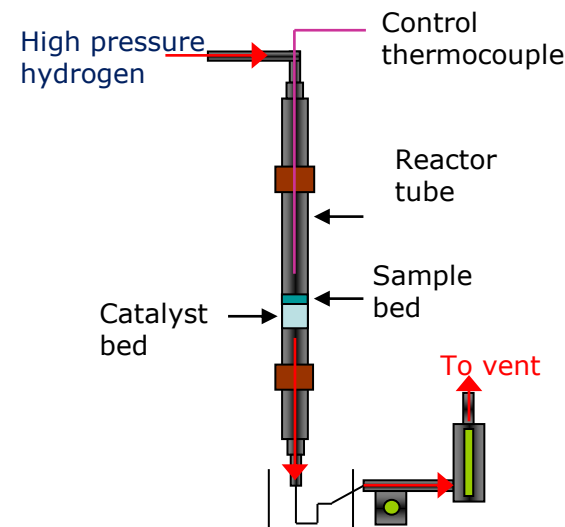
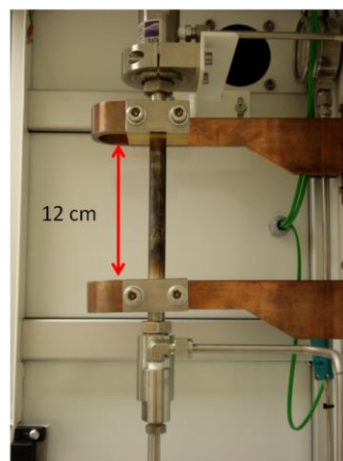
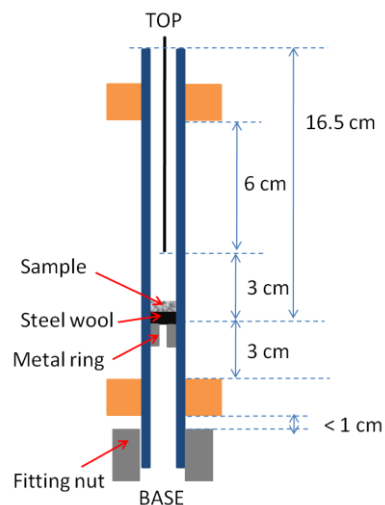
## “from sledgehammer to controlled bond scission”



The University of  
Nottingham

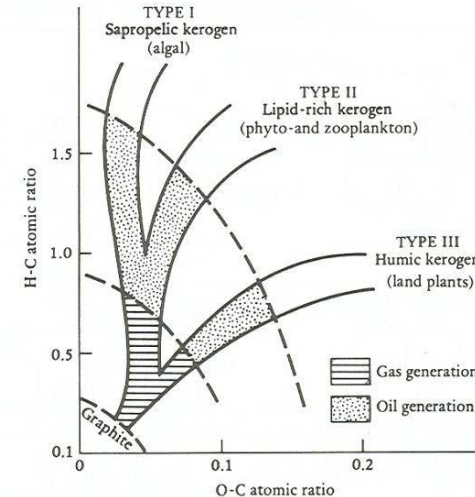
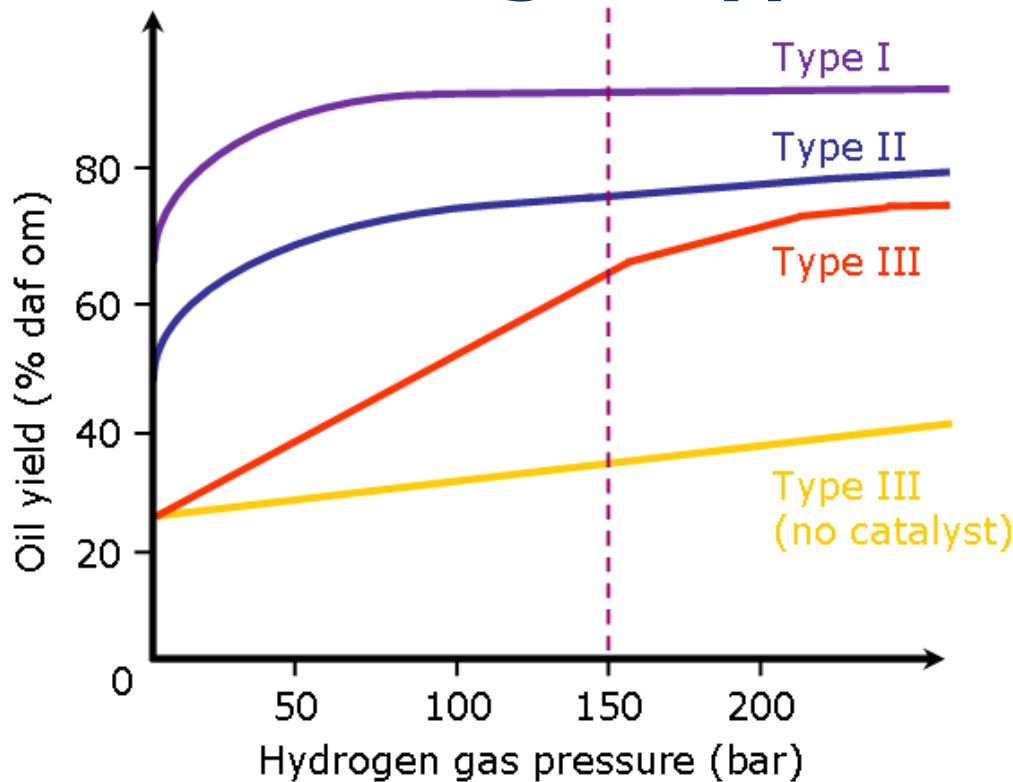
UNITED KINGDOM • CHINA • MALAYSIA

- 1950-70s Direct coal hydrogenation to BTX and SNG  
**- 800°C and 300 bar pressure, ultra high-severity.**
- Late 1980s Lower pressures with catalysts, higher liquid yields with lower gas yields<sup>1</sup>
- 1990s Gordon Love<sup>2</sup>, Stuart Mitchell<sup>3</sup>, first analytical hyppy PhDs  
Organic S groups, quantification from H<sub>2</sub>S release profiles<sup>3</sup>



1. C.E. Snape, C. Bolton, R.G. Dosch and H.P. Stephens, High liquid yields from bituminous coal via hydropyrolysis with dispersed catalysts, *Energy & Fuels*, 1989, **3**, 421-425.
2. G.D. Love, C.E. Snape, A.D. Carr and R.C. Houghton, The release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis, *Organic Geochem.*, 1995, **23(10)**, 981-986.
3. S.C. Mitchell, C.E. Snape, K. Ismail, R. Garcia and K.D. Bartle, Determination of organic sulphur forms in some coals and kerogens by high pressure temperature programmed reduction, *Fuel*, 1994, **73**, 1159-1166.

# Hydropyrolysis oil yields by kerogen type



- **Conversions > 90% TOC for Type I and II kerogens, only inertinite remains for high volatile bituminous coals( type III kerogens).**
- ***Optimal pressure for all applications is 150 bar***

C. Bolton, C. Riemer, C.E. Snape, F.J. Derbyshire and M.T. Tetter, Effect of low temperature hydrogenation on pyrolysis and hydropyrolysis of a bituminous coal, *Fuel*, 1988, **67**, 901-905.

M.J. Roberts, C.E. Snape and S.C. Mitchell, Hydropyrolysis: fundamentals, two-stage processing and PDU operation, pp 277-294.

C.E. Snape, C.J. Lafferty, G. Eglinton, N. Robinson and R. Collier, The potential of hydropyrolysis as a route for coal liquefaction, *Int. J. Energy Res.*, 1994, **18**, 233-242

# Hydropyrolysis – a versatile analytical pyrolysis technique

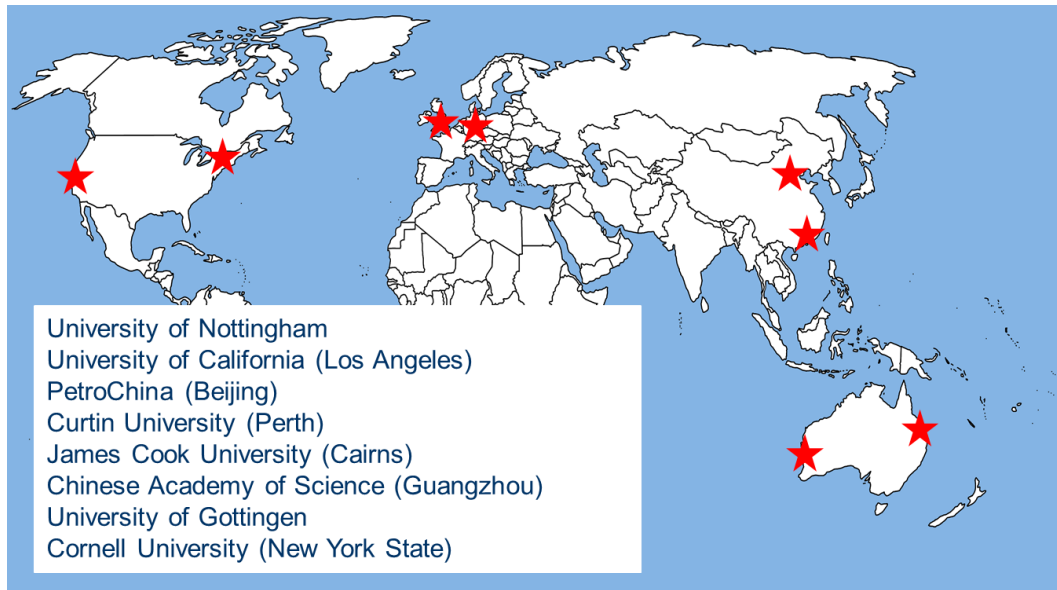
- Applications include:
  - quantifying **black or pyrolytic carbon** in environmental matrices
  - understanding the earliest life forms from severely altered organic material
  - fingerprinting biodegraded oils and over mature petroleum source rocks.
- The Engineer 2008 award winner for collaboration with Strata Technology.
- 7 systems including Petrochina, Curtin and James Cook Universities.



1. P.L. Ascough, M.I. Bird, F. Brock, T.F.G. Higham, W. Meredith, C. E. Snape and C.H. Vane. Hydropyrolysis as a new tool for radiocarbon pretreatment and the quantification of black carbon. *Quaternary Geochronology*, 2009, 4, 140-147.
2. W. Meredith, P.L. Ascough, M.I. Bird, D.J. Large, C.E. Snape, Y. Sun and E.L. Tilston, Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials, *Geochim Cosmochim Acta*, 2012, **97(15)**, 131-147
3. G.D. Love, E. Grosjean, C. Stalvies, D.A. Fike, A.S. Bradley, A.E. Kelly, M. Bhatia, W. Meredith, C.E. Snape, Fossil steroids record the appearance of Demospongiae during the Cryogenian Period, *Nature*, 2009, 457, 718-721.

# Hydropyrolysis Commercialisation (Will Meredith)

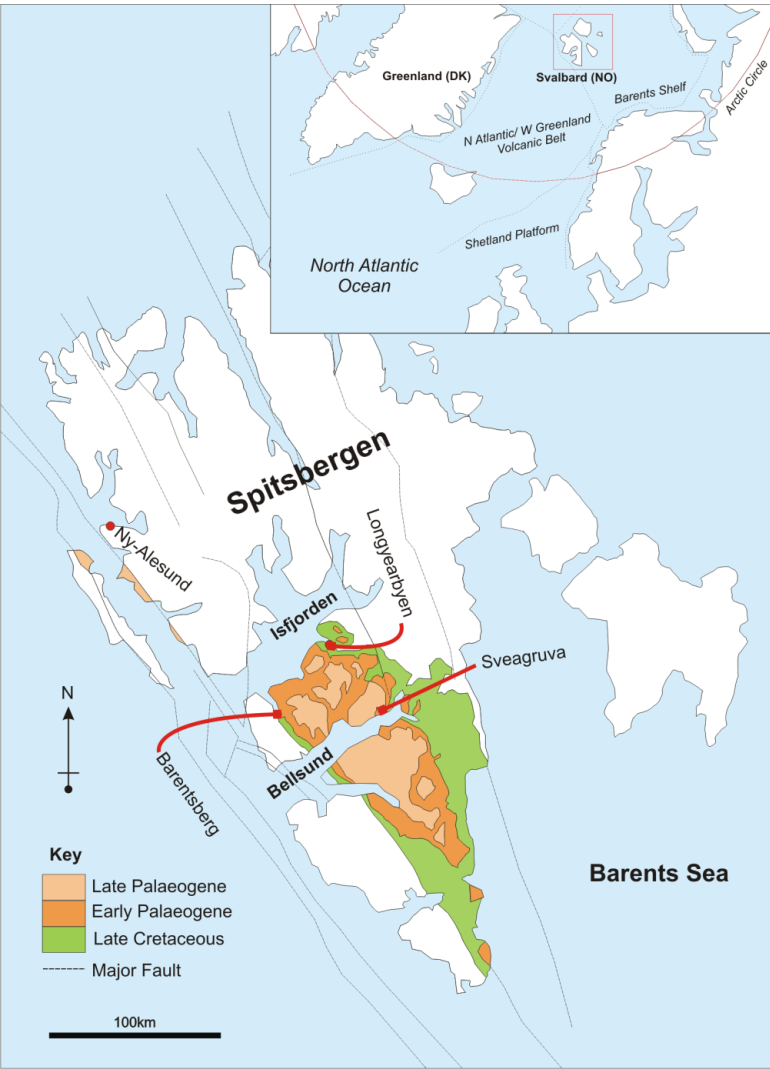
- Licensing agreement got the system designed, built (and sold)
- Collaborative approach recognised at the Technology and Innovation Awards 2008





# Hydrogen Rich (Perhydrous) Coals – ideal candidates for liquefaction (David Large and Chris Marshall)

## Central Tertiary Basin in the Archipelago of Svalbard Palaeocene Stratigraphy (ca. 60 Ma)

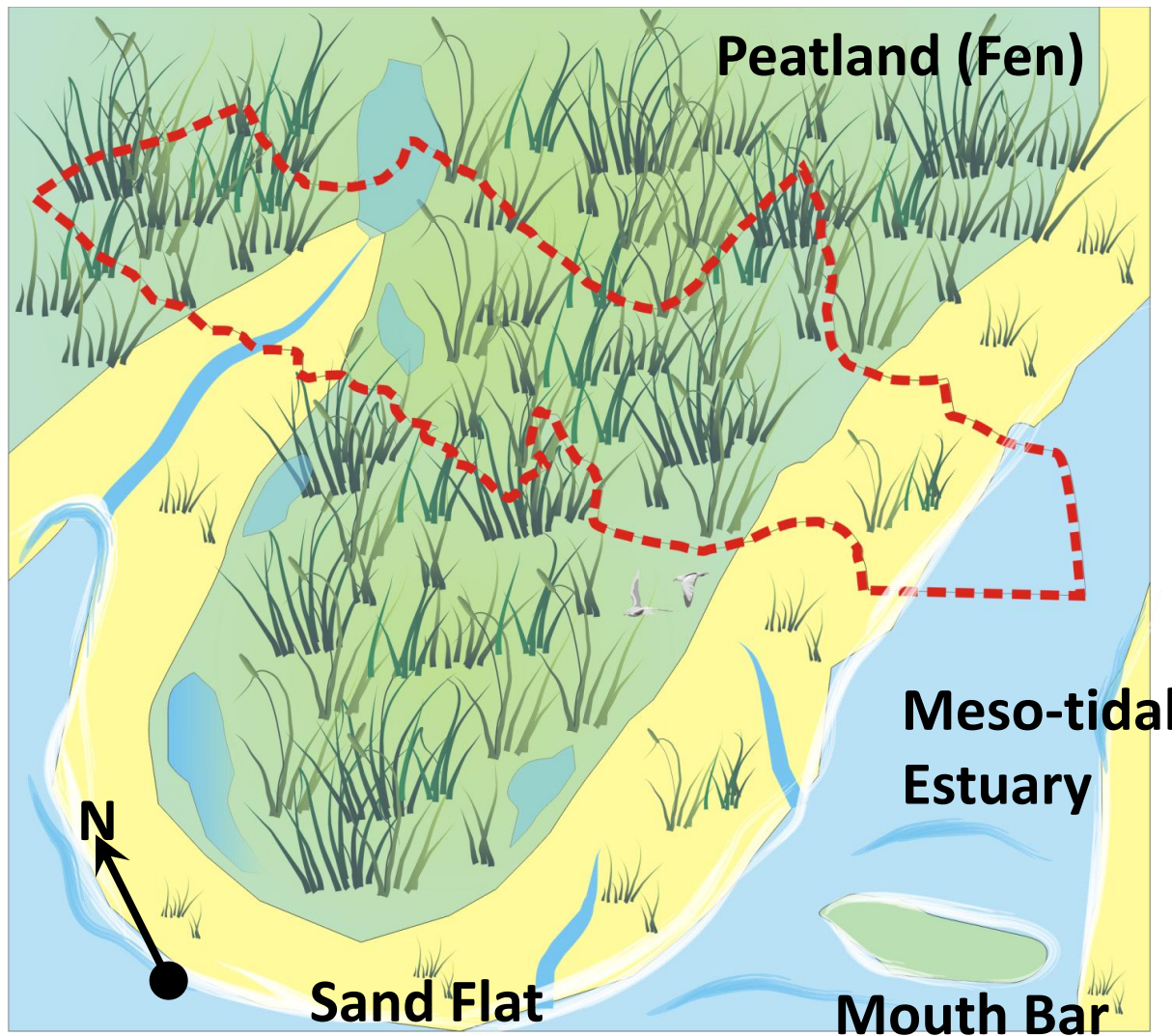


- 5 Seams found within the Mid-Palaeocene Todalen Member.
- Lowest Svea Seam is less oil prone
- 4 seams are oil prone named (oldest-youngest)
  - Todalen
  - Longyear
  - Svarteper
  - Askeladden
- Total resource size up to 61 million tonnes (SNSK). Longyear only seam mined
- Seams characterised by variable sulfur contents.

50m



# Depositional Estuarine Setting



- Estuarine setting - with peatland forming between channels
- Marine Influence – supply of S and alkalinity decreases away from the channels

## Key

Longyear seam  
outline at  
Lunckefjellet  
mountain

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# Longyear free and bound bacterial hopane distributions are synergistic

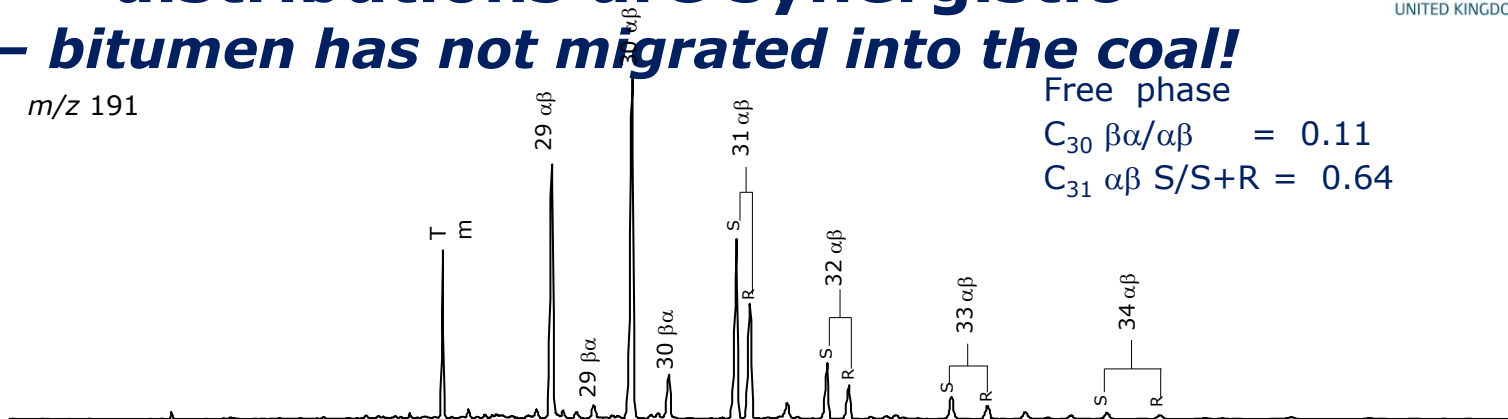


The University of  
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– *bitumen has not migrated into the coal!*

$m/z$  191

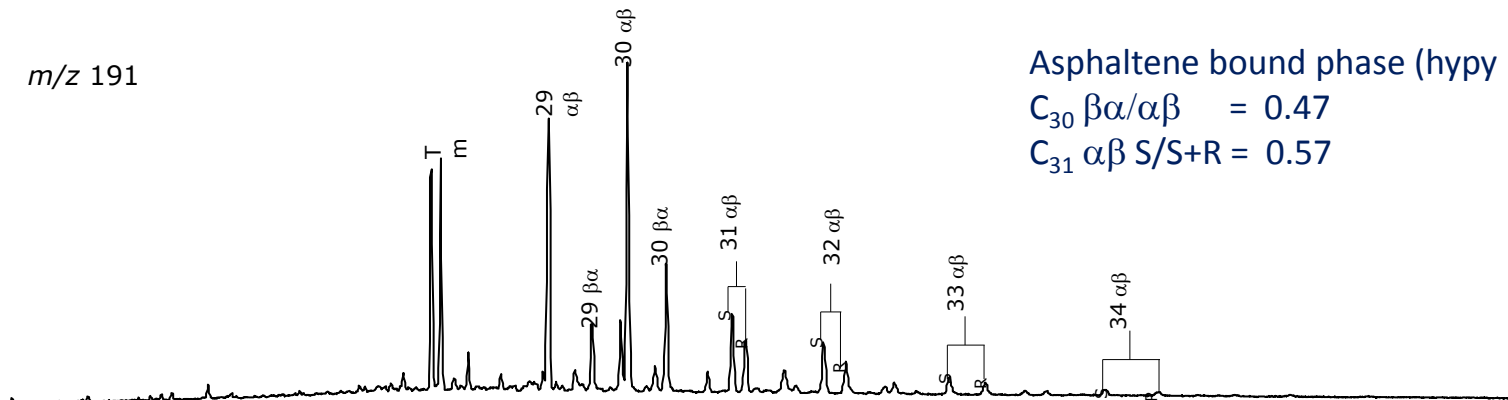


Free phase

$$C_{30} \beta\alpha/\alpha\beta = 0.11$$

$$C_{31} \alpha\beta S/S+R = 0.64$$

$m/z$  191

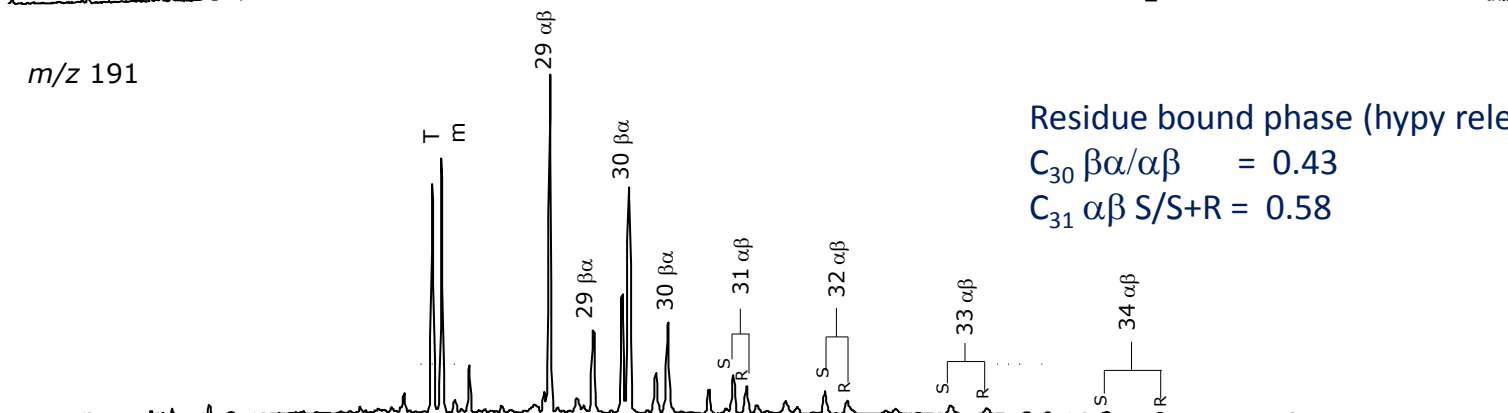


Asphaltene bound phase (hypy released)

$$C_{30} \beta\alpha/\alpha\beta = 0.47$$

$$C_{31} \alpha\beta S/S+R = 0.57$$

$m/z$  191

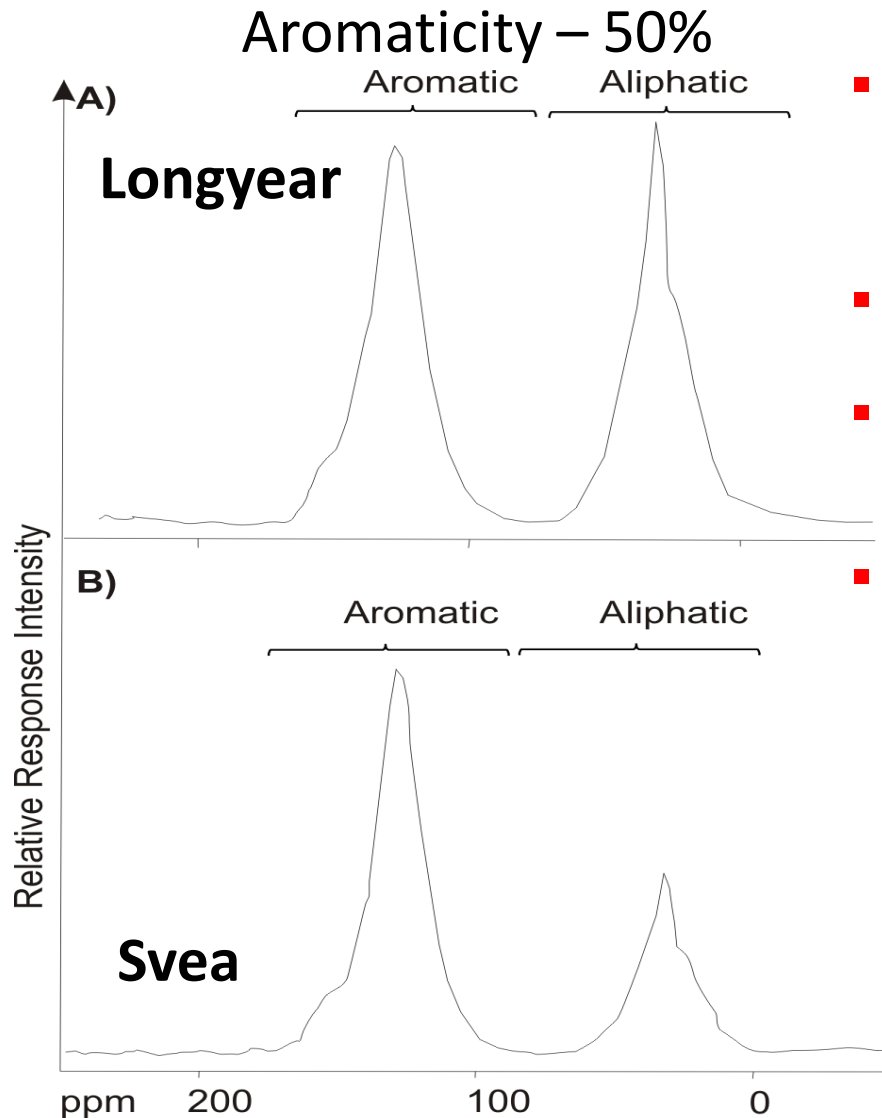


Residue bound phase (hypy released)

$$C_{30} \beta\alpha/\alpha\beta = 0.43$$

$$C_{31} \alpha\beta S/S+R = 0.58$$

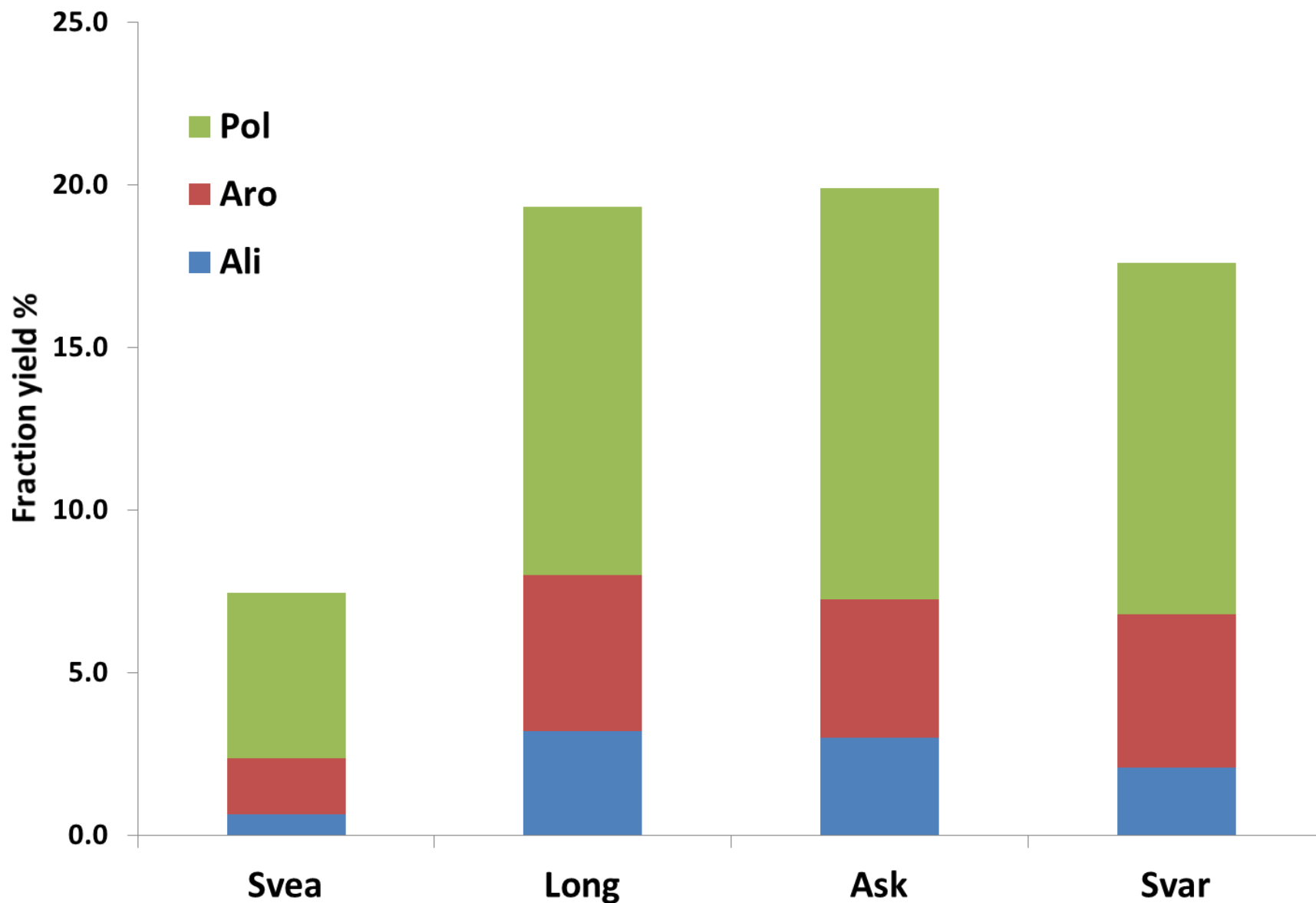
# Aromaticity $^{13}\text{C}$ NMR



**Aromaticity – 72%**

- Aromaticity indicates that the Longyear seam contains significant amounts of aliphatic (bacterial, microbial) non coaly material.
- This causes reduced of the vitrinite reflectance.
- The Svea seam which is not oil prone exhibits an aromaticity consistent with the observed maturity.
- Taking a normal bituminous coal (Svea) to be 75 parts aromatic and 25 parts aliphatic carbon, this requires another 50 parts of aliphatic carbon from microbial input to give an aromaticity of 0.5.

# Gray King Retorting oil yields





# Coal carbonisation

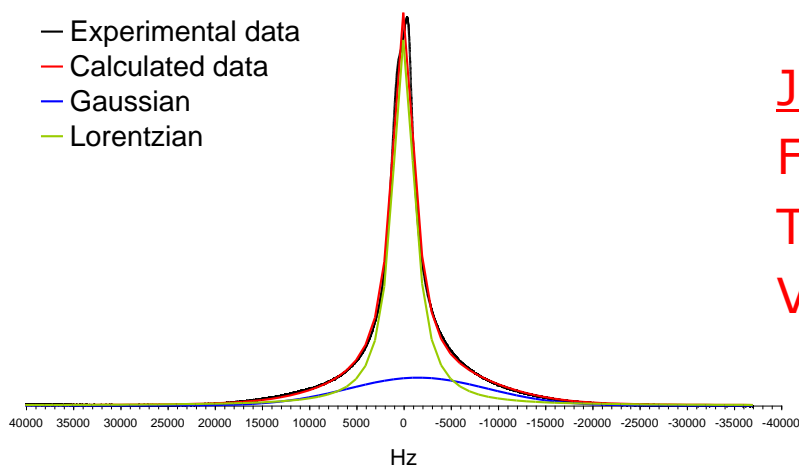
(Ron Willmers, Ruth Poultney & Colin Atkinson  
– B. Steel, Corus, Tata)

- After decades of investigation, uncertainty still surrounds a number of key phenomenon – coal blending, oven wall pressure,
- Empirical tests to gauge softening but do not easily relate to e.g. Gieseler fluidity.
- Define softening from a structural standpoint and so much more will be understood regarding coke making.



# Deconvoluted Broadline $^1\text{H}$ NMR spectra at maximum fluidity – 450°C

Coal gives an inert component - broad Gaussian peak and a narrower Lorentzian peak from mobile (softened) material.

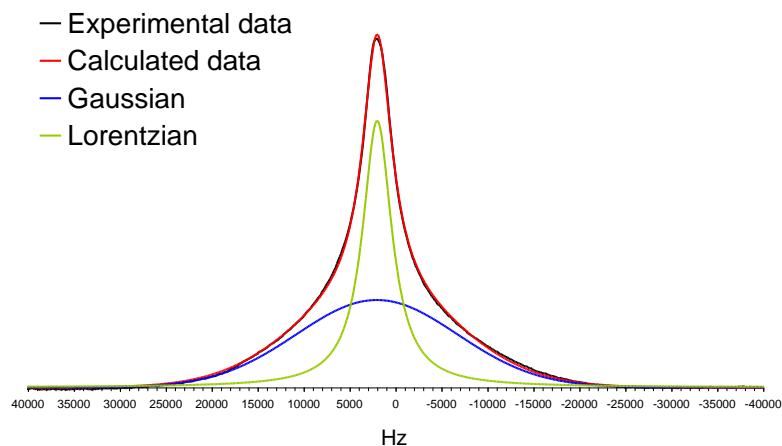


Jaeger coal

Fluid H = 73 %

$T_{2L} = 103$  ms

Viscosity =  $6.2 \times 10^3$  Pa.s



Jaeger (80%) + Charcoal (20%)

Fluid H = 51 %

$T_{2L} = 91$  ms

Viscosity =  $8.8 \times 10^4$  Pa.s

*Charcoal addition reduces fluid  
phase and shortens  $T_{2L}$*

# Some well-known (qualitative) facts about carbonisation

## *Quantification by in-situ $^1\text{H}$ NMR*

- Mild air oxidation is detrimental
- Fluidity generation is reversible with rapid heating.
- Pitch additives enhance fluidity.
- Semi-fusinite is reactive, contributes to fluidity.
- Biomass generally suppresses fluidity

## *Other debatable points answered*

- Influence of particle size? Reduces  $T_2$  not % fluid H.
- How much fluid phase is derived from pyridine extractables? *ca.* 50%.

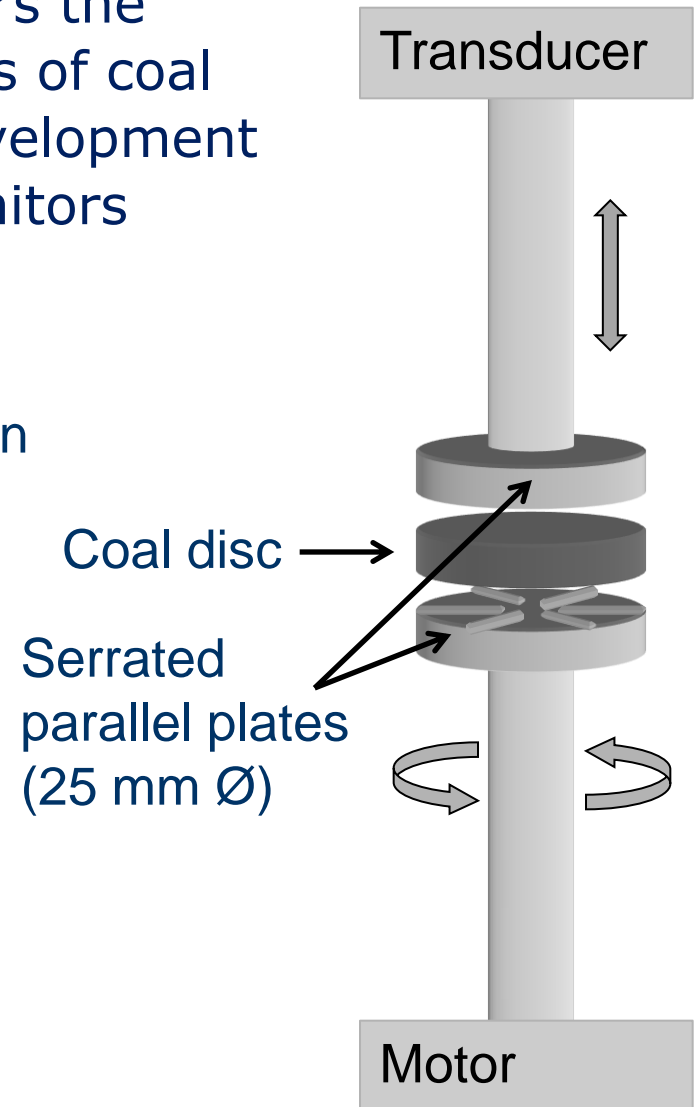
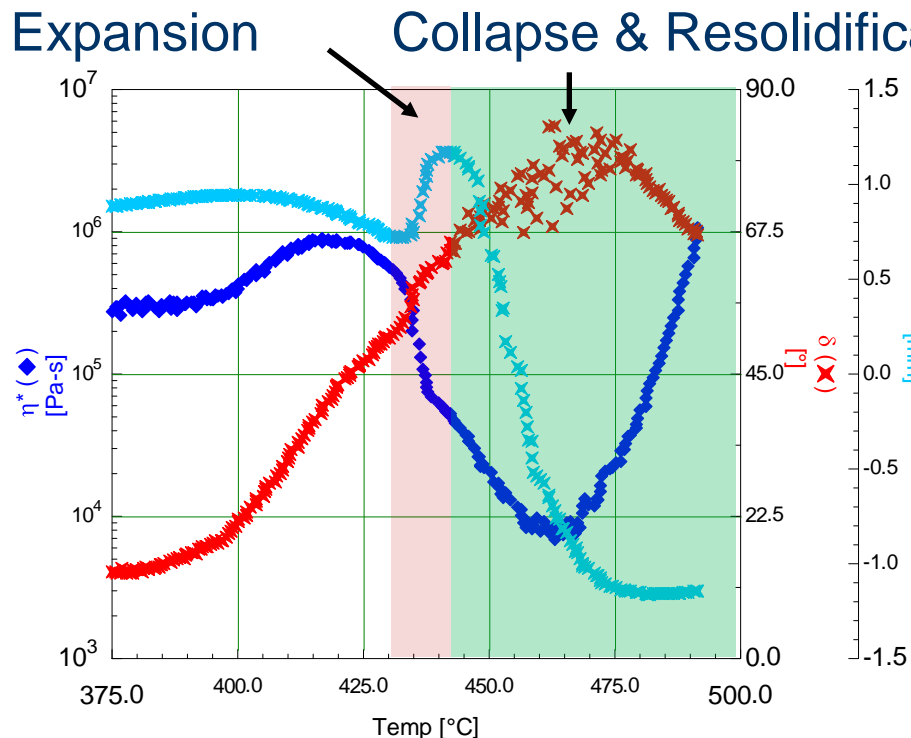
M.M. Maroto-Valer, J.M. Andrésen and C.E. Snape, In-situ  $^1\text{H}$  NMR investigation of particle size, mild oxidation and heating regime effects on fluidity development during coal carbonisation, *Energy & Fuels*, 1997, 11, 236-244.

M.M. Maroto-Valer, D.N. Taulbee, J.M. Andrésen, J.C. Hower and C.E. Snape, The role of semifusinite in plasticity development for a coking coal, *Energy & Fuels*, 1998, 12, 1040-1046.

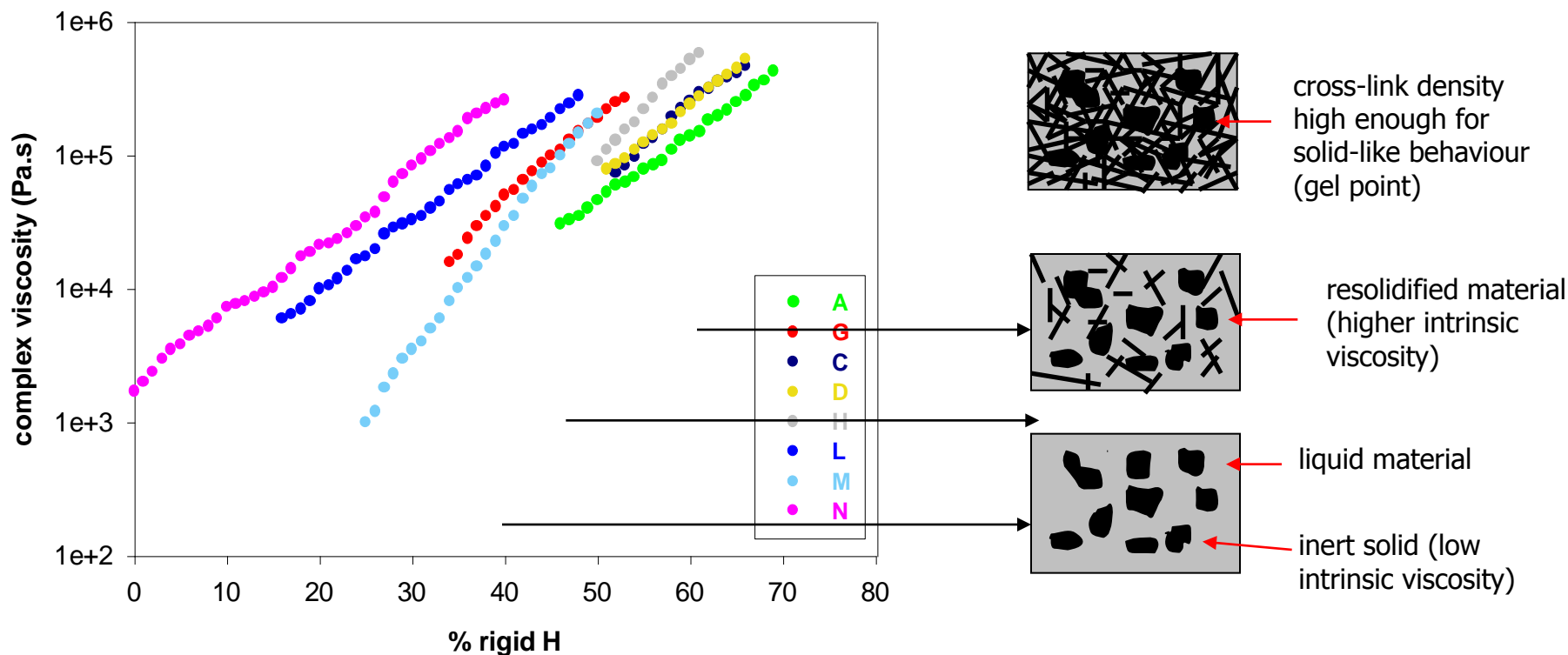
M. Castro Díaz, H. Zhao, S. Kokonya, A. Dufour and C.E. Snape, The effect of biomass on coal fluidity development in coking blends using high temperature rheometry, *Energy & Fuels*, 2012, **26**(3), 1767-1775.

# High-torque, high-temperature SAOS rheometry

- High temperature rheometry monitors the changes in the viscoelastic properties of coal with temperature to quantify the development of fluidity in the sample mass  $\Rightarrow$  monitors macroscopic phenomena.



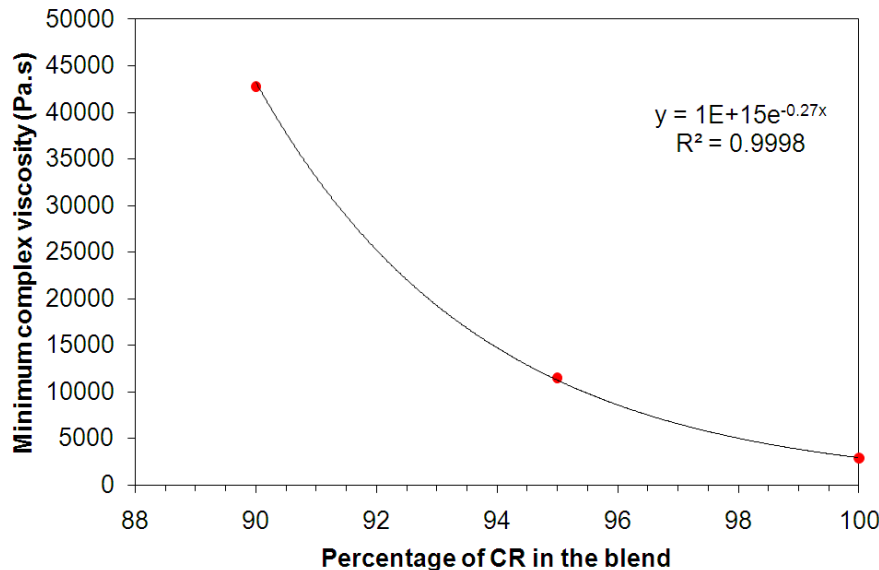
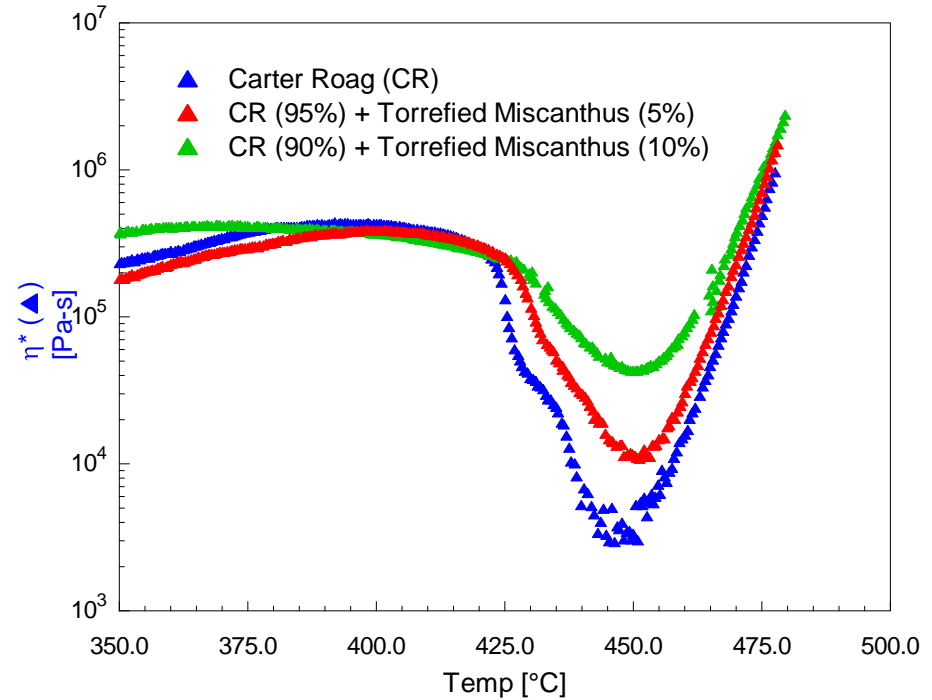
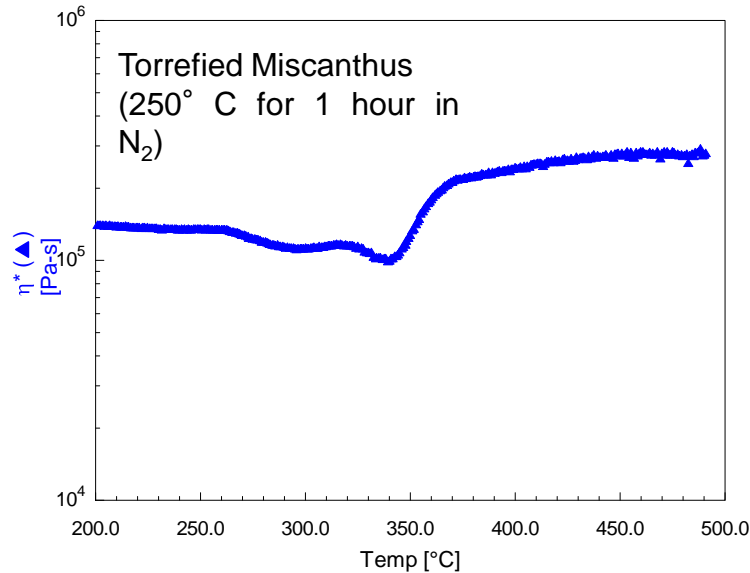
# Combining rheometry with $^1\text{H}$ NMR (resolidification)



- Exponential relationship occurs for all the coals studied.
- Position of curve (horizontal shift) depends largely on how much rigid H is present as inert solid, and how much is resolidified material (have different intrinsic viscosities).



# Addition of torrefied biomass



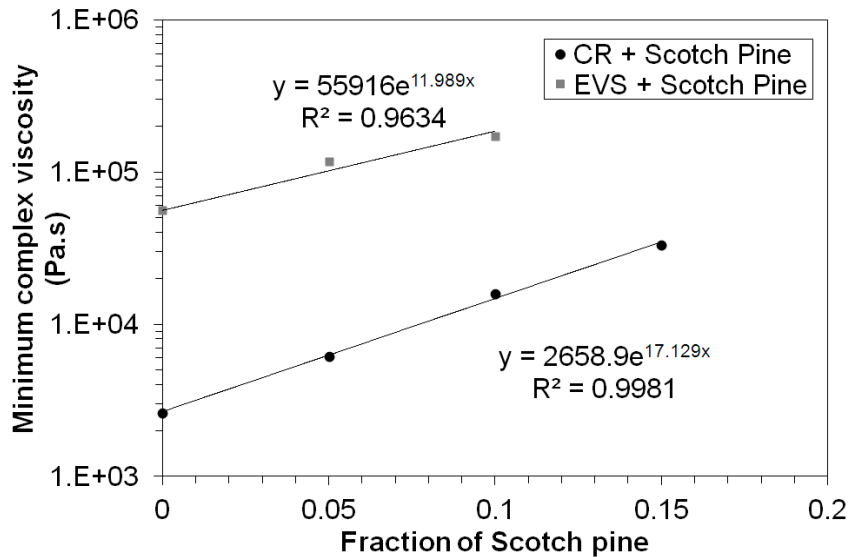
Follows polymer blending rule  
when  $\phi_{CR} \gg \phi_{TM}$ :

$$\eta^* = A \exp(B \phi_{CR})$$

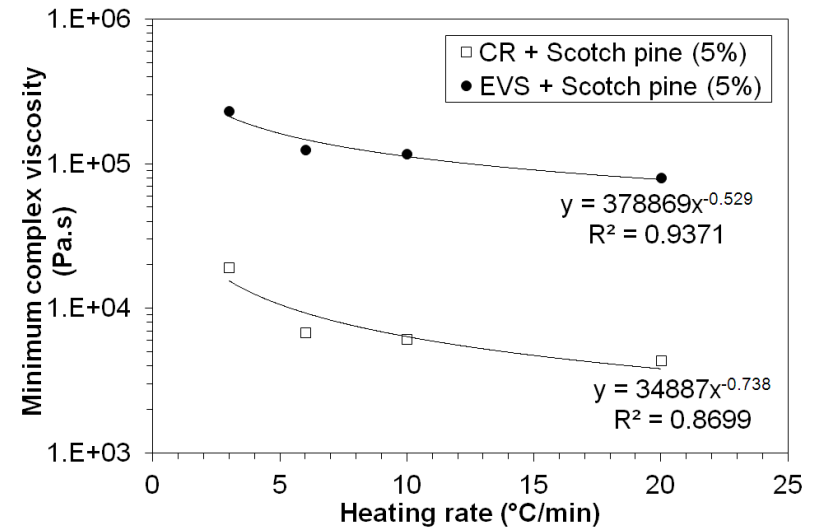
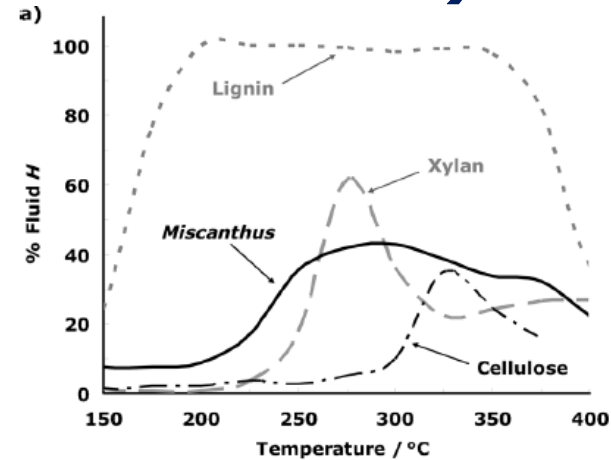
$$\ln(\eta^*) = \ln A + B \phi_{CR}$$

$$\ln(\eta^*) = \phi_{TM} \ln \eta^*_{TM} + \phi_{CR} \ln \eta^*_{CR}$$

# Faster heating enables more biomass to be incorporated into coking blends (RFCS Densicharge project – Tata Steel)



- Log complex viscosity increases linearly with biomass addition.
- Biomass fluidity arises predominately from lignin.
- Faster heating reduces time lag between fluidity development from biomass and coal.



M. Castro Díaz, H. Zhao, S. Kokonya, A. Dufour and C.E. Snape, The effect of biomass on coal fluidity development in coking blends using high temperature rheometry, *Energy & Fuels*, 2012, **26(3)**, 1767-1775.

A. Dufour, M. Castro Diaz, N. Brosse, N. Bouroukba and C.E. Snape, Origin of molecular mobility during biomass pyrolysis as revealed by in-situ  $^1\text{H}$  NMR analysis, *ChemSusChem*, 2012, **5**, 1258-1265.

# STABLE CARBON AND HYDROGEN ISOTOPES

## A powerful for source apportionment

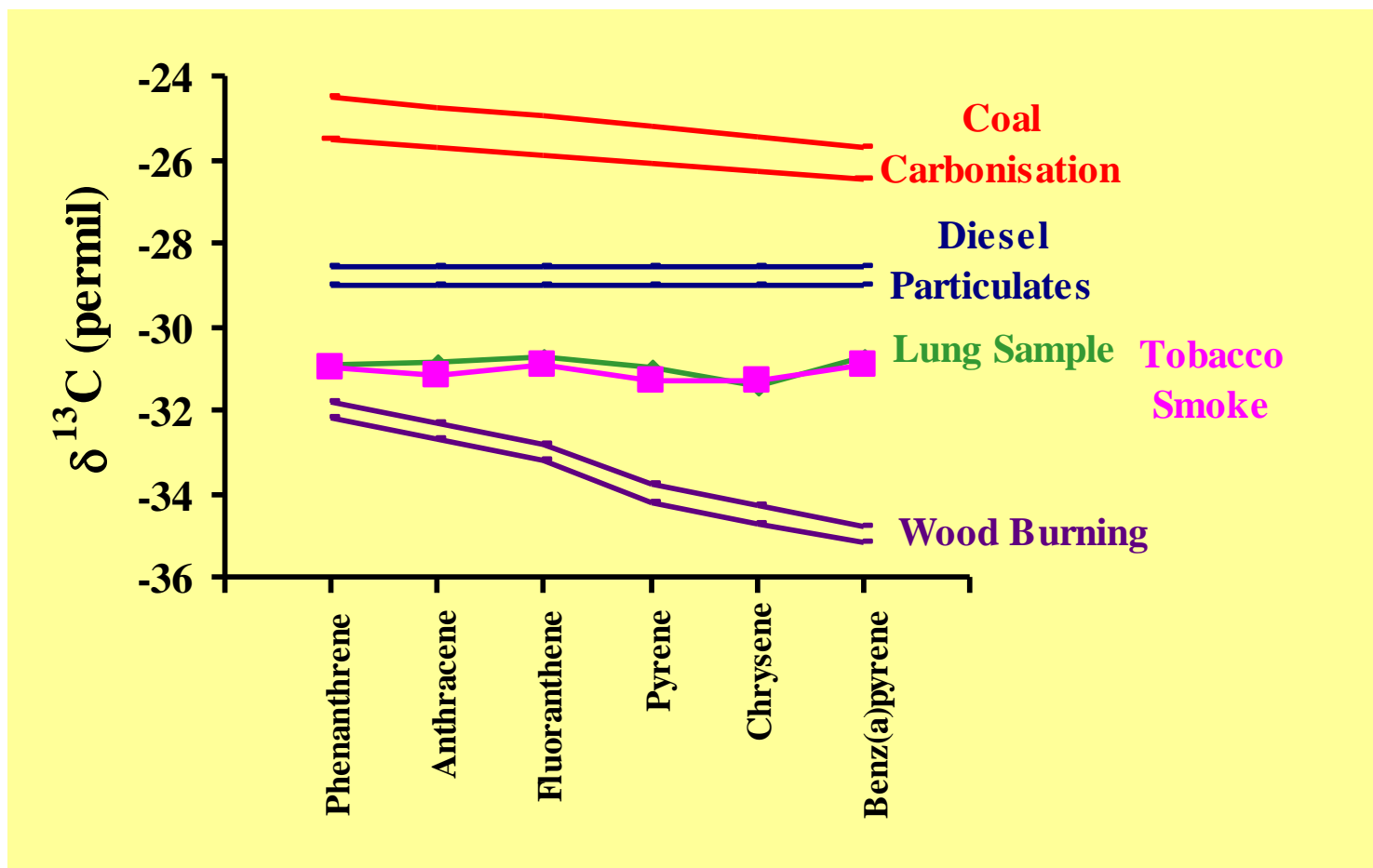
- Compounds of biological origin are always enriched in the lighter  $^{12}\text{C}$  isotope as opposed to the heavier  $^{13}\text{C}$ .
- Fossil fuels, i.e. coal, petroleum and natural gas, are often isotopically distinguishable:

	$\delta^{13}\text{C}$ (‰, PDB)	$\delta\text{D}$ (‰, SMOW)
Crude oil: mainly	-27 ~ -28‰	-90 ~ -180
Coal:	-23 ~ -25‰	-60 ~ -120
Natural gas ( $\text{CH}_4$ ):	-55 ~ -110‰	-170 ~ -400

- Ubiquitous compounds from different sources may exhibit varying isotopic compositions relative to each source.

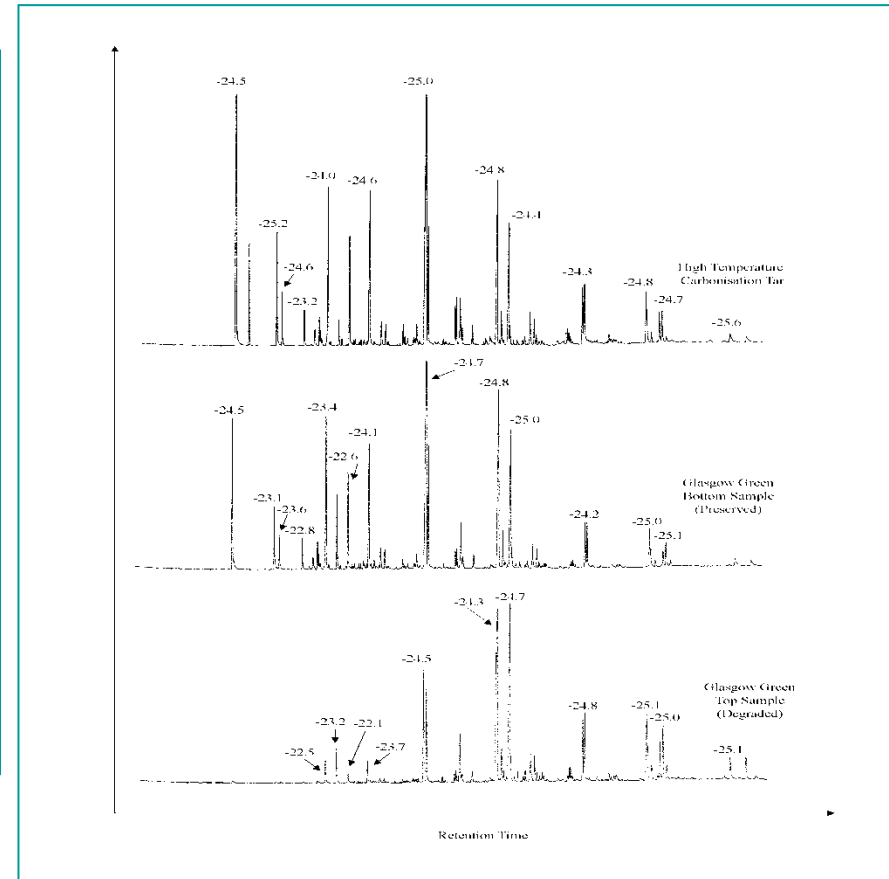
# Selected carbon isotopic ratios for PAHs obtained from a human lung, tobacco smoke, coal tars and wood burning

(Tony Fallick, Chenggong Sun and Carole McRae)



1. C. McRae, C.E. Snape and A.E. Fallick, Variations in the stable isotope ratios of specific aromatic and aliphatic hydrocarbons from coal conversion processes, *The Analyst*, 1998, **123**, 1519-1523.
2. C. McRae, C-G Sun, C.E. Snape and A.E. Fallick,  $\delta^{13}\text{C}$  values of coal-derived PAHs from different processes and their application to source apportionment, *Organic Geochem.*, 1999, **30**, 881-889.

# Glasgow Green Site



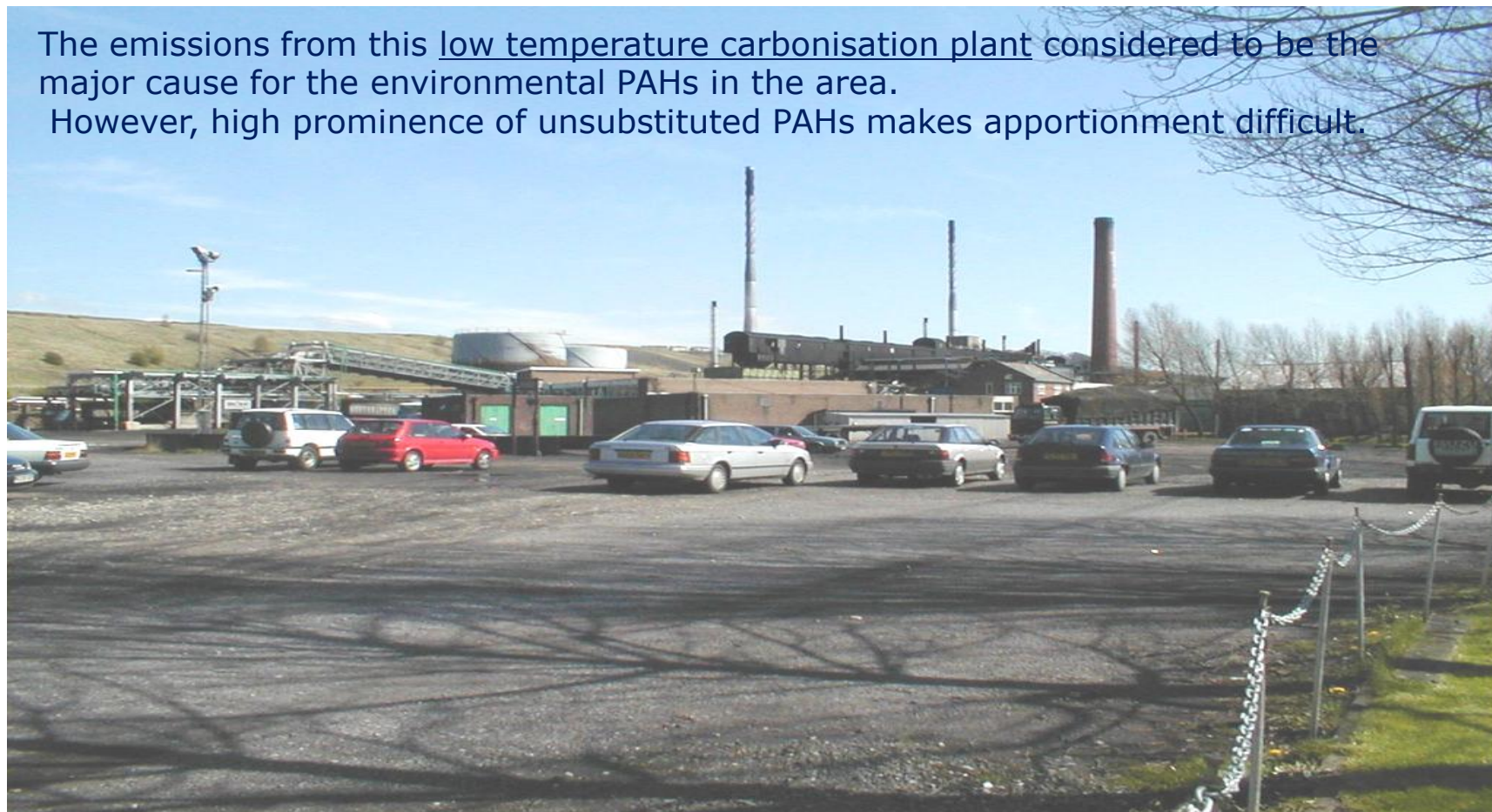
- Illegal tar dumping – either from gas works or coking plant in a former air swimming pool.
- Close match to high T coal tar in PAH distribution and isotopic ratios (-25 ‰).



# Low temperature carbonisation plant, Bolsover, North Derbyshire

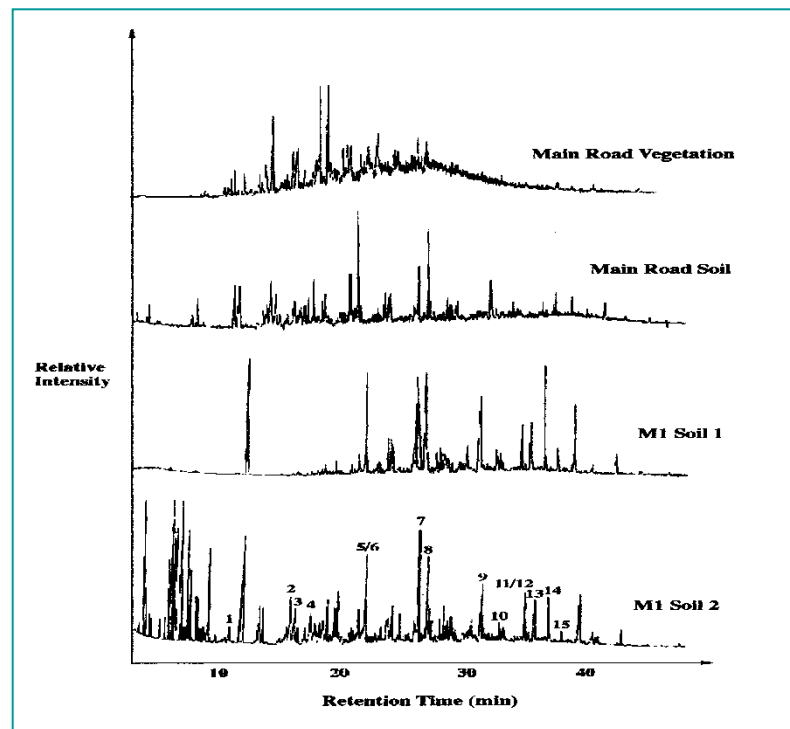
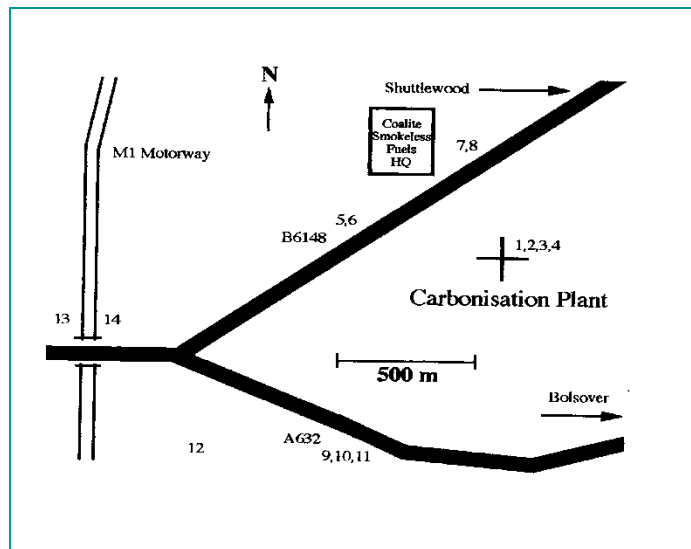
The emissions from this low temperature carbonisation plant considered to be the major cause for the environmental PAHs in the area.

However, high prominence of unsubstituted PAHs makes apportionment difficult.



C-G Sun, C.E. Snape, C. McRae and A.E. Fallick, Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints, Fuel, 2003, 82, 2017-2023.

# GC profiles of aromatics from vegetation and soil samples

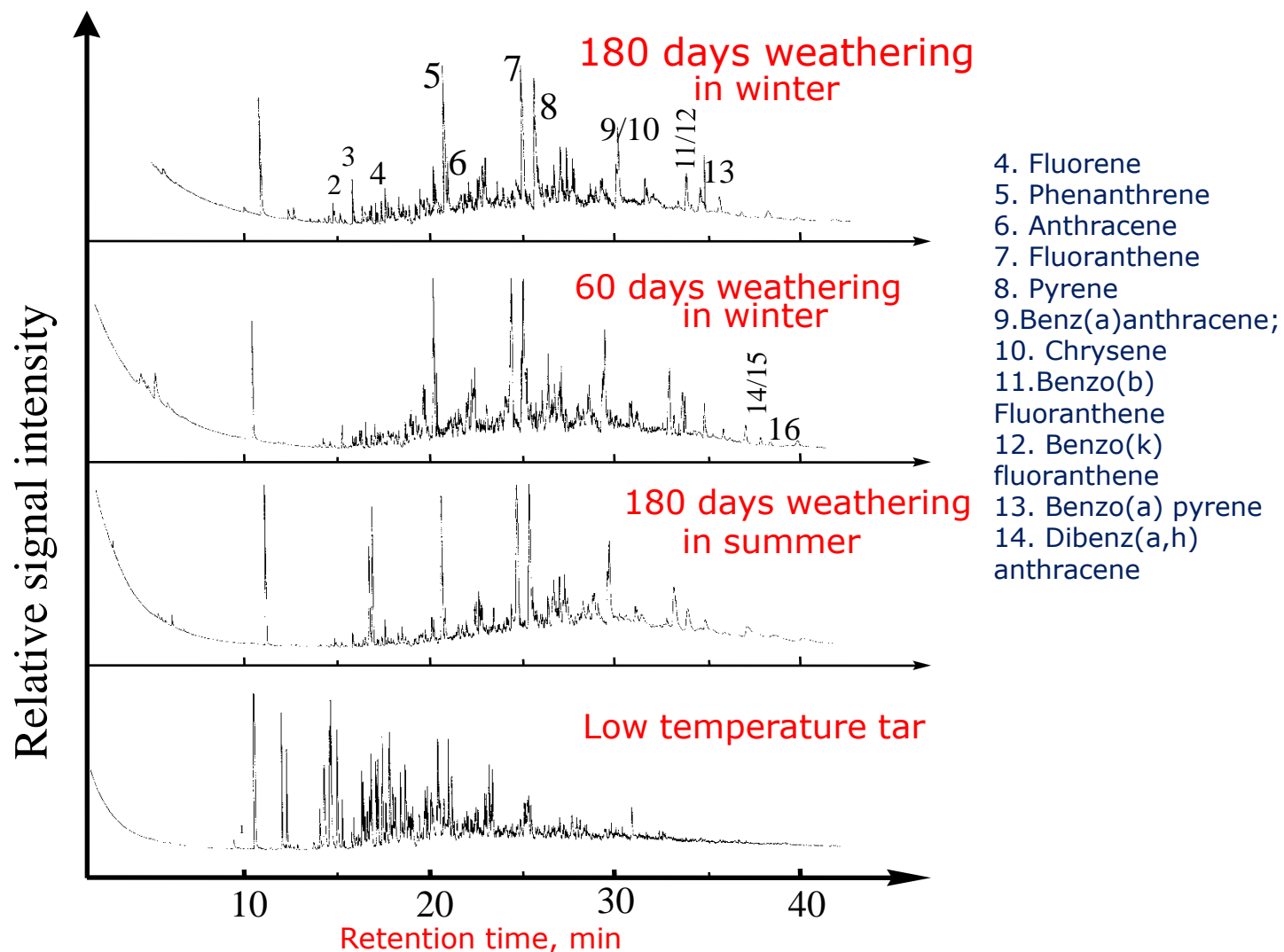


Generally, little resemblance to low T coal tar

- However, many isotopic values in range  $-24$  to  $-26$  ‰.
- Parent PAH present – may suggest another source , e.g. high T carbonisation?
- High MM PAH exhibit isotopically lighter signatures ( $< -28$  ‰) suggesting transport fuel/biomass contribution.

# GC profiles of neutral aromatics from weathered and initial low temperature coal tar

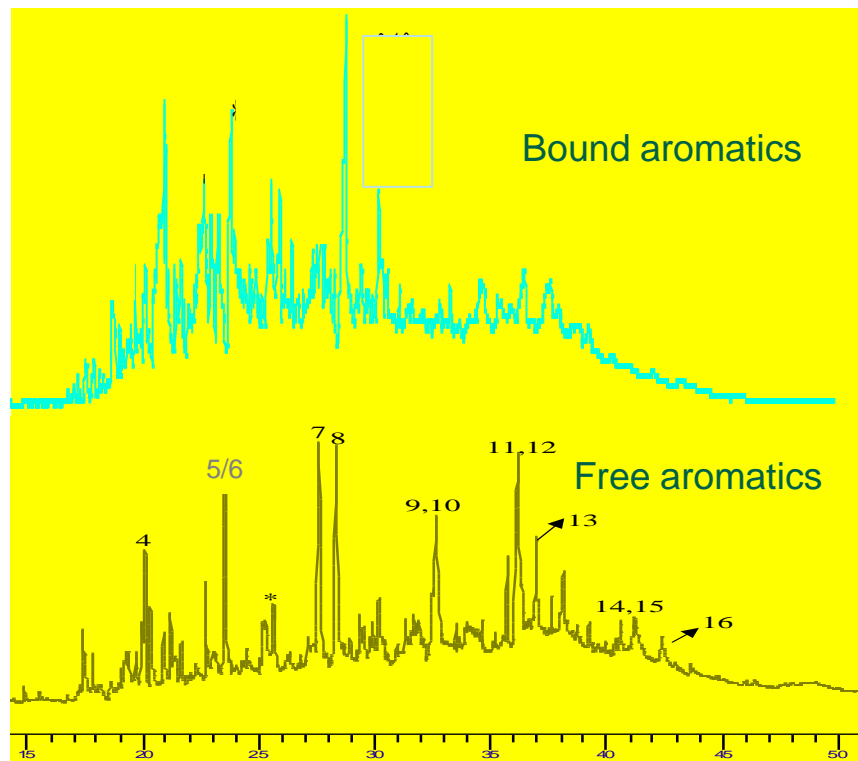
Alkyl substituted PAHs degrade faster than parent PAHs over short periods, but carbon stable isotopic values remain constant close to  $-25$  permil.



# A soil sample close to the low temperature carbonisation plant

- The inconsistency between the molecular and isotopic profiles for free and bound PAHs indicate a multiplicity of the input sources:
- oil and/or traffic related emissions, and mixed input of low temperature coal tar.
- However, the prominent free parent PAHs appear again to occur mainly from degradation of low T coal tar.

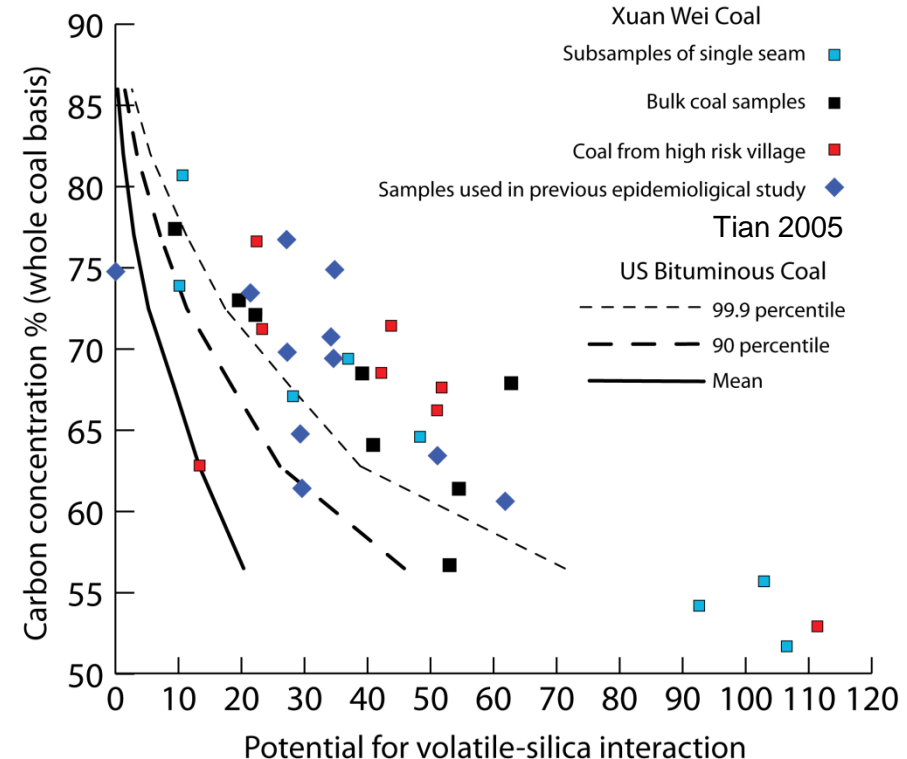
## $\delta^{13}\text{C}$ isotopic values for parent PAHs



Name and No of PAHs	Free aromatics	Bound aromatics
4. Flurene	-23.2	-23.6
5. Phen	-23.3	-23.7
6. Anthr	-23.3	-23.7
7. Fluoranth	-23.4	-26.3
8. Py	-23.8	-25.6
9. Benz(a)anthr	-24.0	-26.7
10. Chry	-24.0	-26.7
11. B (b)fluoranth	-24.6	-27.3
12. B(k)fluoranth	-24.6	-27.3
13. B(a)py	-24.3	-26.0
14. Ind(cd)py	-24.3	-26.1
15. Dib (a,h)anthr	-24.3	-26.1
16. B(ghi)peryl	-24.3	-26.1

# Xuan Wei lung cancer epidemic

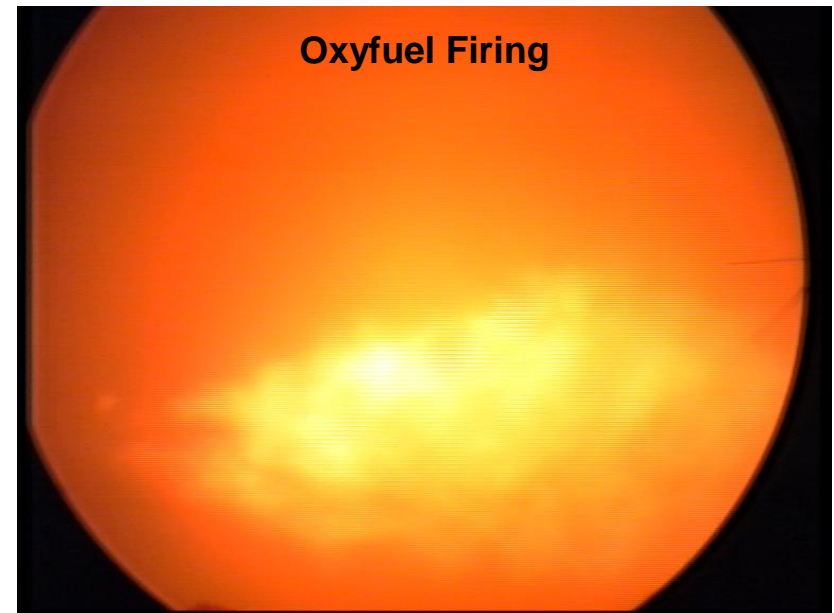
- Highest lung cancer mortality in the world
- Lead a new multidisciplinary approach to this problem
- Coal unusually enriched in silica
- Mortality correlates with the interaction of silica and volatiles
- Resulting Environmental Science and Technology paper received global media coverage.



D.J. Large, S. Kelly, S., B. Spiro, L. Tian, L. Shao, L., Finkelman, *et al.* Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. *Environmental Science & Technology*, 2009, doi: 10.1021/es902033j



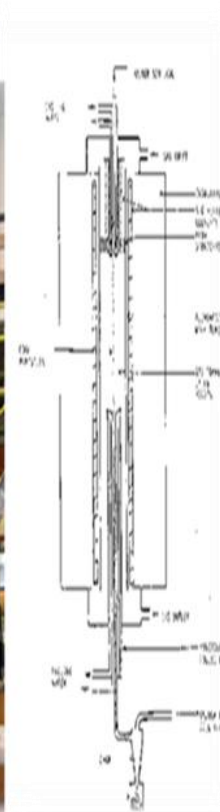
# Oxyfuel 1 MW Burner Testing



Flame structure and shape were found to be similar for Air and Oxyfuel firing operation but need oxygen levels of 30-35%.

# Drop-tube furnace test (DTF) programme

- DTF tests under conditions of different temperatures (up to  $1500^{\circ}\text{C}$ ), residence times (down to 50 ms) and combustion atmospheres simulating typical oxy-combustion operations.
  - Devolatilisation
  - Large batches of char production
  - Char re-firing tests
- TGA and other characterisation (BET, SEM/EDAX etc.) of the chars.

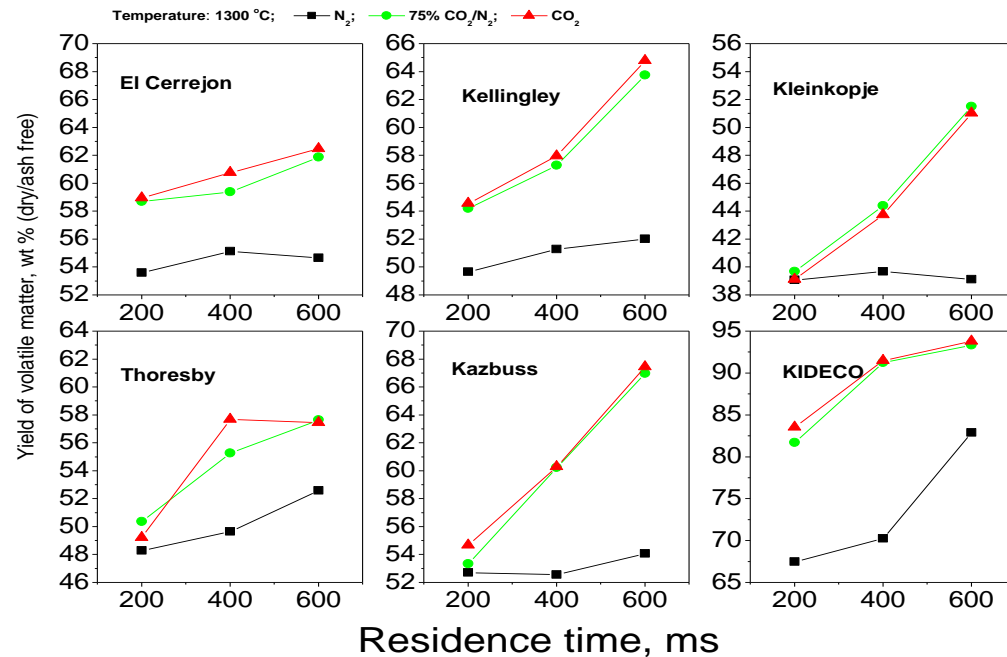
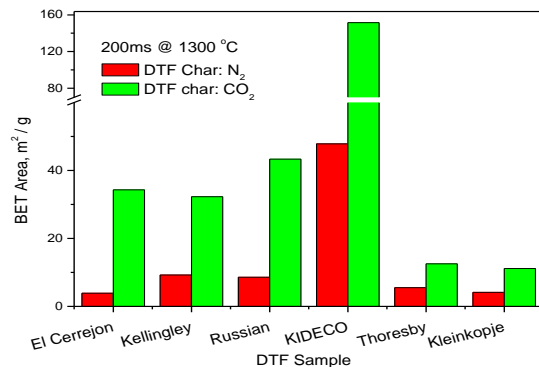


# Oxyfuel and normal combustion using a drop tube furnace



The University of  
Nottingham

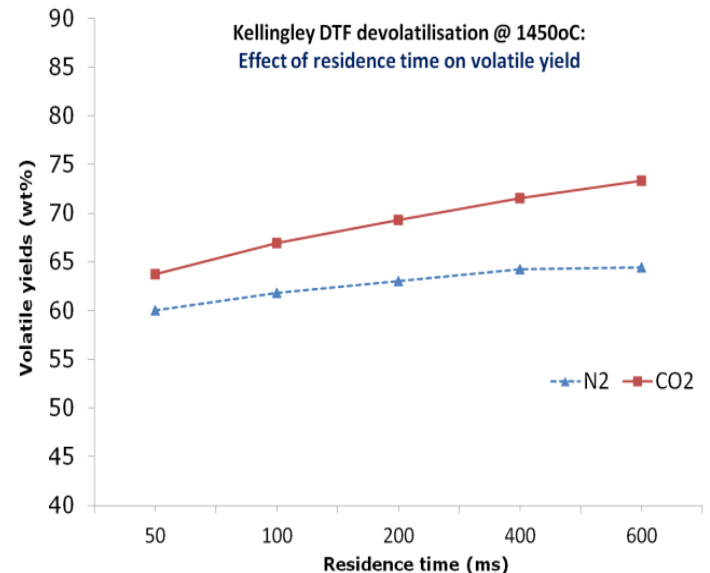
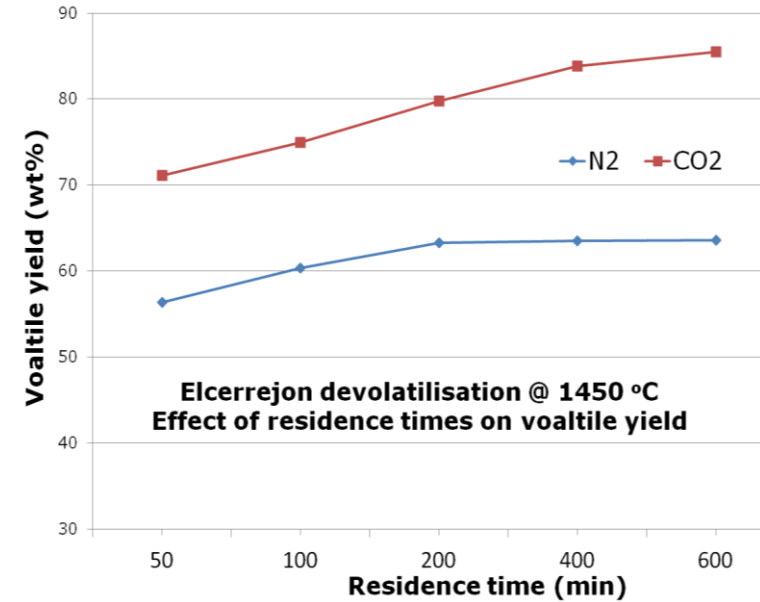
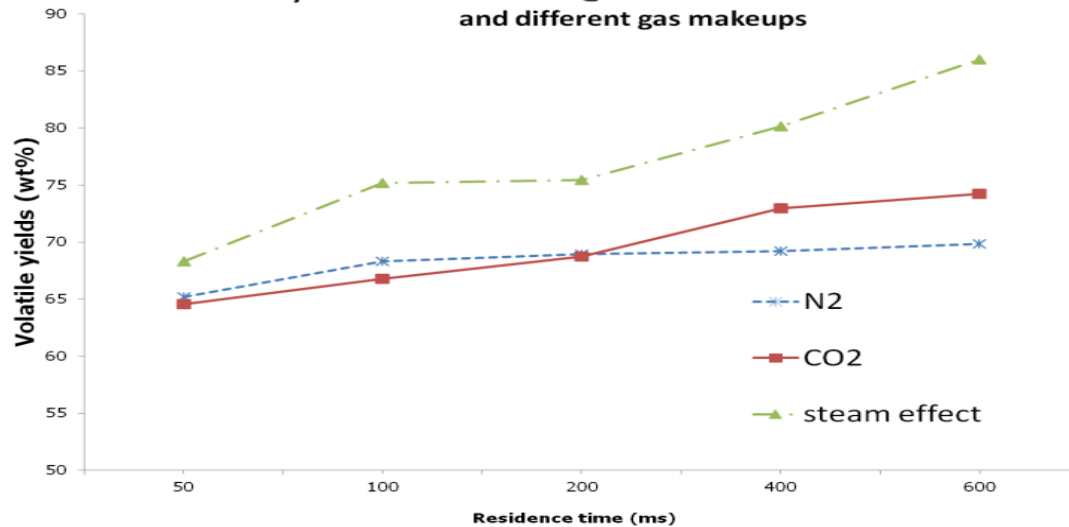
Oxy-fuel conditions give higher yields of total volatiles (5 ~ 20 wt%), attributable to the contribution of the  $\text{CO}_2$ /char reaction for a number of coals.



Increases in BET surface area arise at 1300°C due to char activation in  $\text{CO}_2$ .

# Limiting volatile yields at high temperature (1450°C)

Thoresby DTF devolatilisation @ 1450 °C at different residence times and different gas makeups

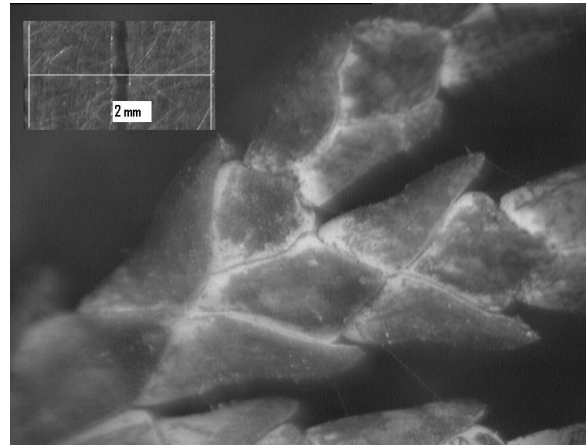


- The contribution of CO<sub>2</sub> gasification reactions was evident for all 3 coals investigated.
- Effect of steam (30%) is larger than CO<sub>2</sub>, giving rise to even higher volatile yields with increasing residence times.

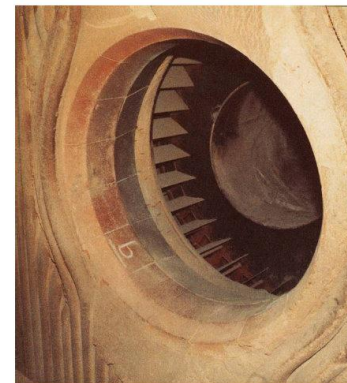


# Biomass handling and quality

- Biomass degrades quite quickly on storage.
- Tilbury to closes following fire in 600 tonne feed hoppers.
- Slagging and fouling due to more alkali/alkaline metals in ash.



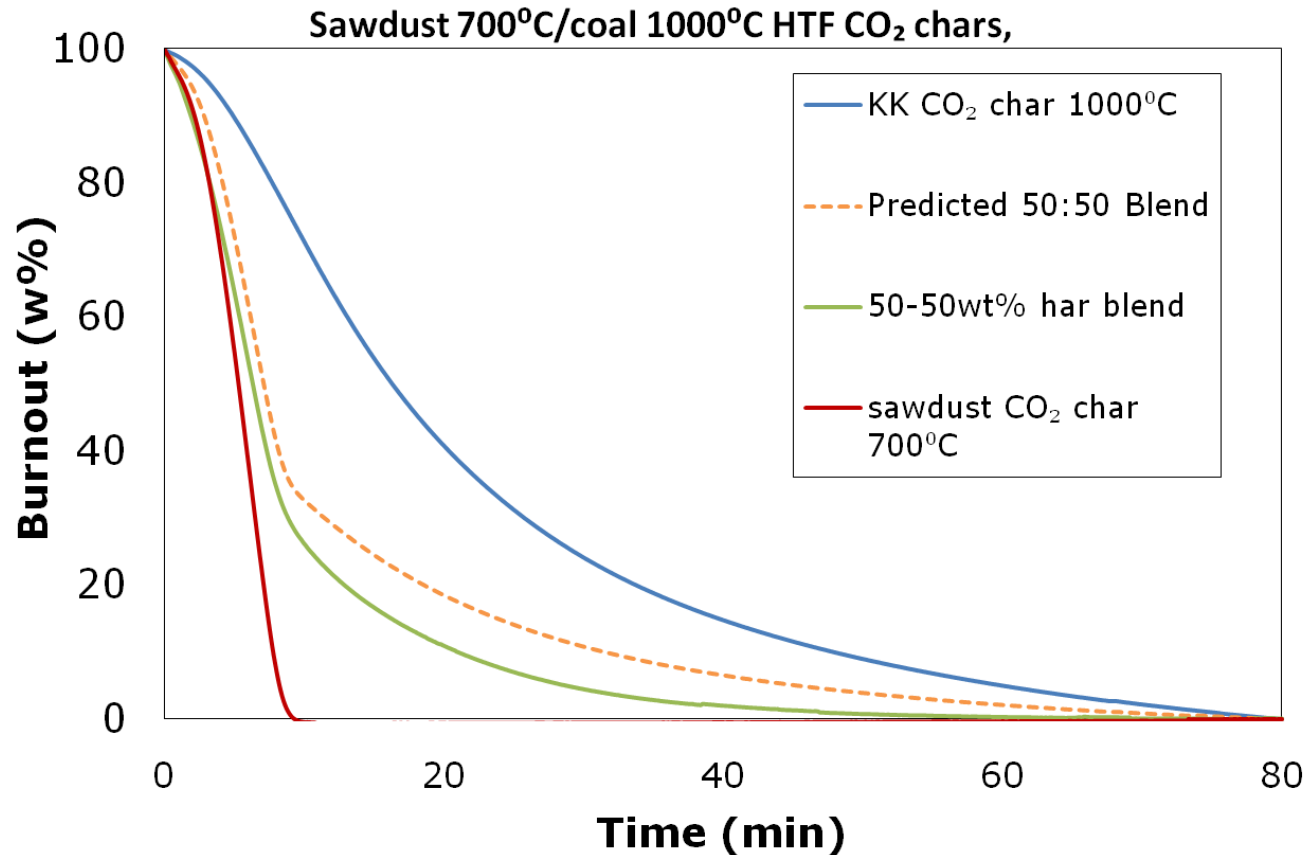
- 15 weeks in storage
- Fungal growth but also structural damage and stickiness



Slag deposits

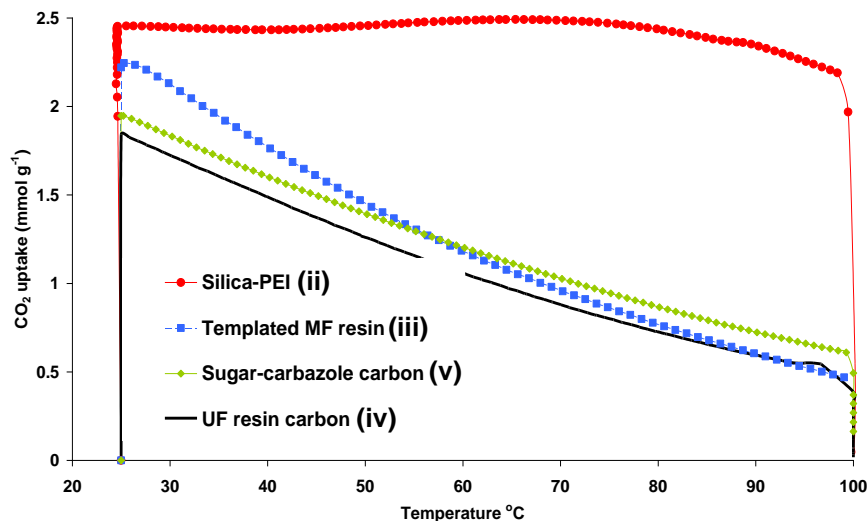


# TGA co-combustion of sawdust and coal chars showing synergistic effect



S. Timipere Farrow, D. Zhao, C. Sun and C.E. Snape, Impact of biomass on char burn-out under air and oxy-fuel conditions, *Fuel*, 2012, in press, [doi.org/10.1016/j.fuel.2012.07.073](https://doi.org/10.1016/j.fuel.2012.07.073).

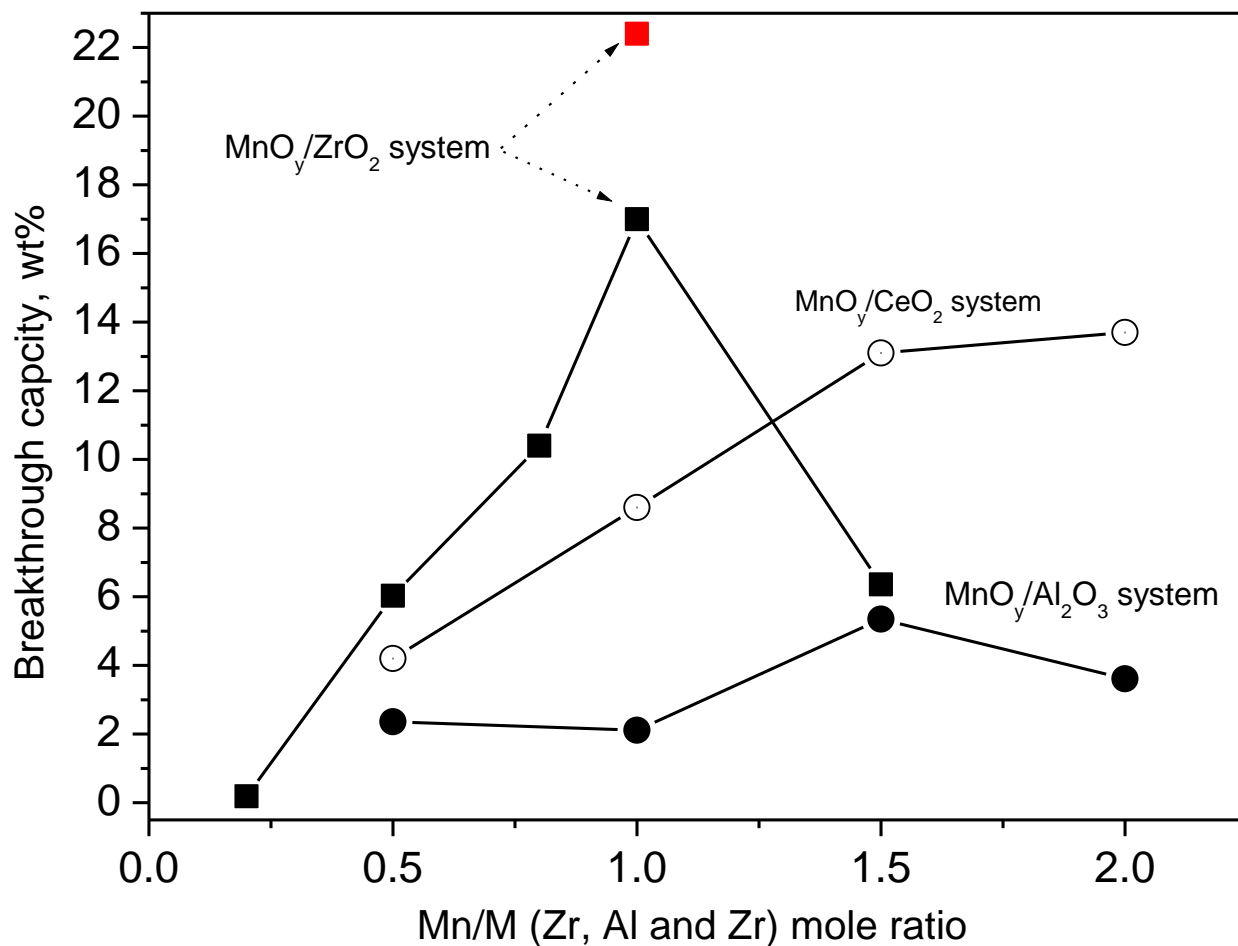
# Novel Adsorbents for CO<sub>2</sub> Capture



- Pre and post-combustion capture application (£3M programme).
- One of best performing materials in independent worldwide study ADA-ES (US-DOE DE-NT0005649)
- Novel regeneration techniques and mechanisms published
- Leading large R&D activity to develop and scale-up technology

(i) Drage T.C. Blackman J.M. Pevida C. and Snape C.E. 2009. Energy & Fuels, 23, 2790–2796.  
(ii) Drage T.C., Arenillas A., Smith K.M. And Snape C.E. Micropor. & Mesopor. Mats. 2008, 116, 504-512.  
(iii) Drage T.C., Pevida C. and Snape C.E. Carbon, 2008, 46, 1464-1474.  
(iv) Drage T.C., Arenillas A., Smith K.M., Pevida C., Piippo S. and Snape C.E., 2007. Fuel 86, 22-31.  
(v) Arenillas A., Drage T.C., Smith K. and Snape C.E., 2005. J. Anal. and Appl. Pyrolysis, 74, 298-306.

# Ultra high capacity co-precipitated $\text{MnO}_2$ sorbents for Hg capture (Janos Lakatos)



■ **Oxidative capture,  
 high mesoporous  
 surface area.**

■ Capacity achieved for bed  
 packed by sorbent at 50°C  
 and a N<sub>2</sub> flow of 130  
 ml/min.

■ Patents awarded

# Proven Global Coal, Oil and Gas Reserves are Increasing

■ Europe & Eurasia  
■ Asia Pacific  
■ North America  
■ Middle East & Africa  
■ S. & Cent. America

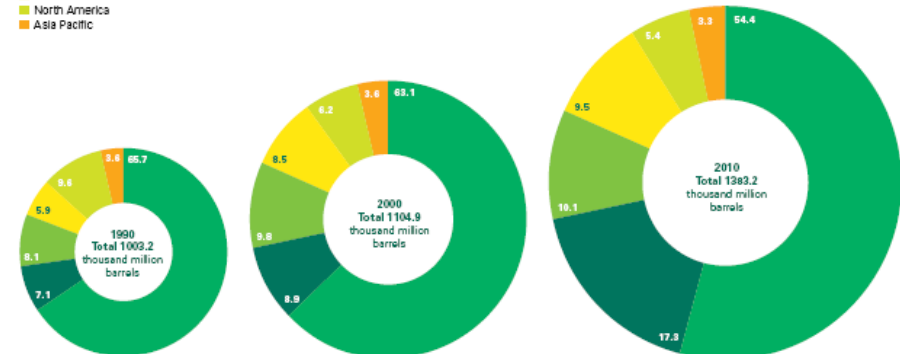


Source: Survey of Energy Resources, World Energy Council.

## Oil

Distribution of proved reserves in 1990, 2000 and 2010  
Percentage

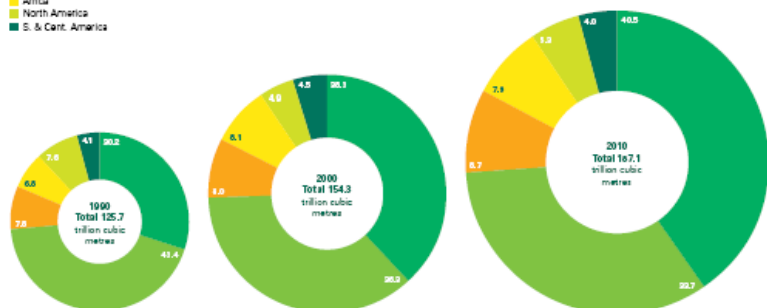
■ Middle East  
■ S. & Cent. America  
■ Europe & Eurasia  
■ Africa  
■ North America  
■ Asia Pacific



## Natural Gas

Distribution of proved reserves in 1990, 2000 and 2010  
Percentage

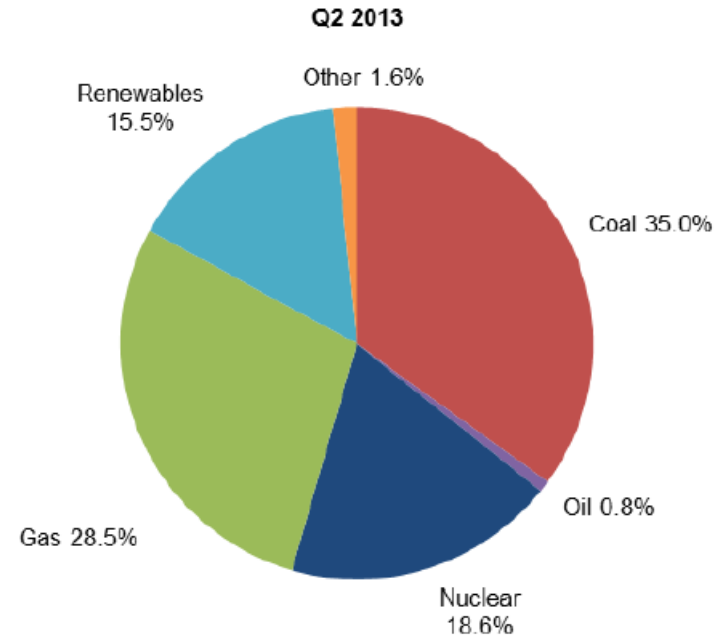
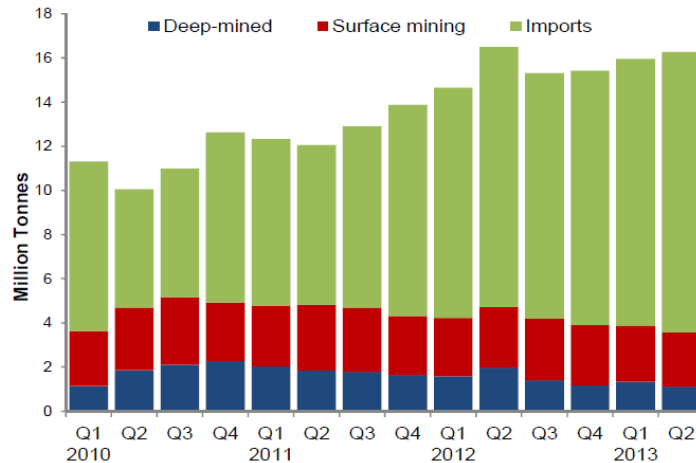
■ Middle East  
■ Europe & Eurasia  
■ Asia Pacific  
■ Africa  
■ North America  
■ S. & Cent. America



# UK Future for Coal

## COAL: QUARTER 2 2013

### Coal production and imports



- Electricity Q2 2013

	2013 Q2 Thousand tonnes	Percentage change on a year earlier
Coal production	3,572	-24.3
Coal imports	12,688	+7.7
Coal demand	13,507	-5.6
- Power stations	10,093	-11.1
- Coke ovens & blast furnaces	1,604	+1.4
- Final users	663	+13.6

# **The UK Future for Coal – technology and the best young talent**

- Globally, watch China – lead the way with CCSU during the 2020s
- CCS demonstrated and commercialised, a given for any new coal power generation
- CCS – cement, iron & steel including renewable coke
- Which technology is best?
  - Gasification – deal with intermittent renewable, gas distribution and storage
  - Energy security, forget shale gas and look at 4 billion tonnes of coal reserves ideally situated for underground coal gasification.
- Future talent, overcoming the generation gap.

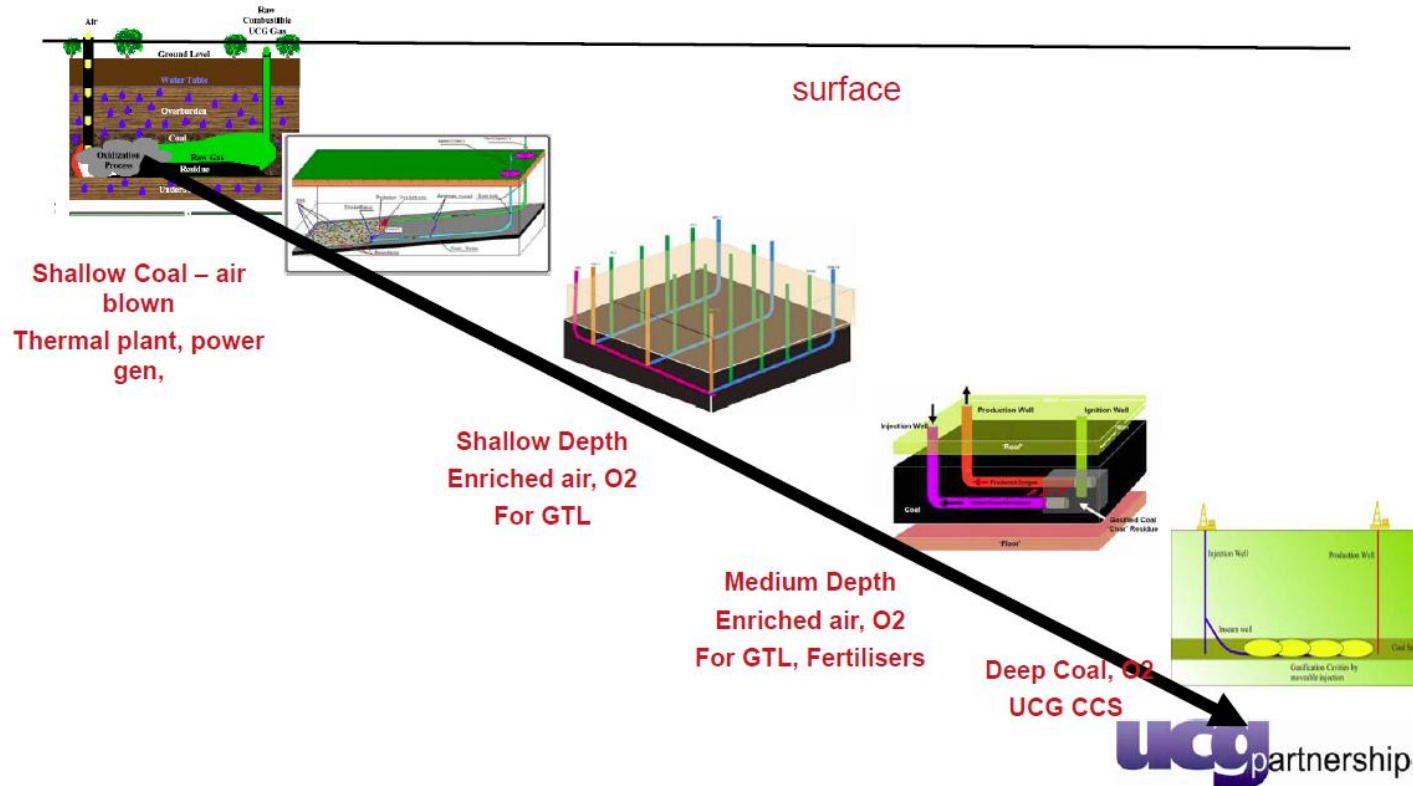


# Trend is to deeper UCG and oxygen blown

Underground Coal Gasification

4th UCGP Conference, London February 2009

## Technology Trends for UCG



# UK Coal Reserves and UCG Licenses



Approximate distribution of main Carboniferous coal-bearing units of the United Kingdom Continental Shelf

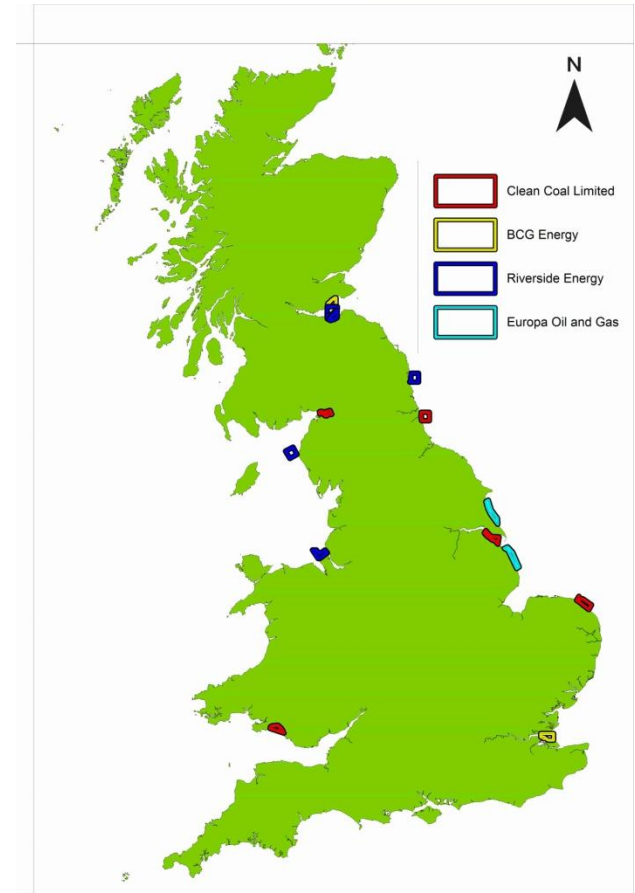


Approximate distribution of main Mesozoic coal and lignite-bearing units of the United Kingdom Continental Shelf



Approximate distribution of main Tertiary lignite-bearing units of the United Kingdom Continental Shelf

© NEIC and the Coal Authority 1999



- Five Quarters, Northumberland
- Clean Coal licences include Sunderland

# ***EPSRC Engineering Doctorate Centre*** **Efficient Power from Fossil Energy and Carbon Capture Technologies**

***The EngD Centre is essential to producing the highly trained personnel for implementing cleaner fossil energy technologies with CCS.***

- Highlighted in the recent RCUK Energy review as being “world class”.
- International summer schools – India and China
- Ningbo campus has set up a similar centre.





# EngD Centre: First Four Cohorts

2009



2010



2011

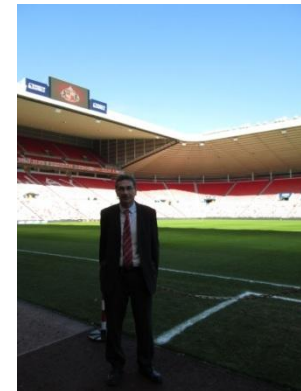
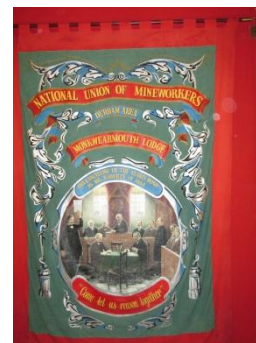
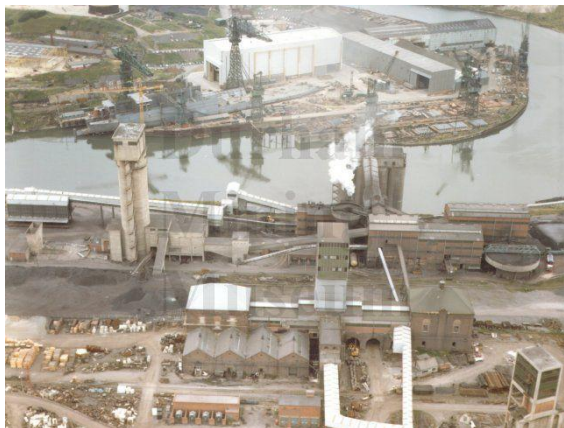


2012



# Positive legacy of mining

## What else could I have done....



Wearmouth Colliery, 1992      Stadium of Light 1997



- I've been around longer (1995). First Harry Potter novel, 1997 (The Philosopher's Stone)
- I've only broken large molecules down into smaller ones.



# Acknowledgements

- Funding – Research Councils -EPSRC/NERC, European Union - RFCS/ECSC, Dti (UK Government), BCURA/BF2RA and industry.
  - Worked on first ECSC project, 1975
- Nottingham colleagues
  - John Patrick, Ha Liu, Carol Eastwick, Trevor Drage, Chenggong Sun, David Large,
  - Miguel Castro Diaz, Salome Farrow, Will Meredith, Clement Uguna
- Former colleagues and PhD students
- Current PhDs/EngDs
  - Luke Morris, Philip Jenkinson, Hui Deng
- Family - Anne, researching the Snape family tree.