An Overview of Coal Characterisation Research at The University of Nottingham

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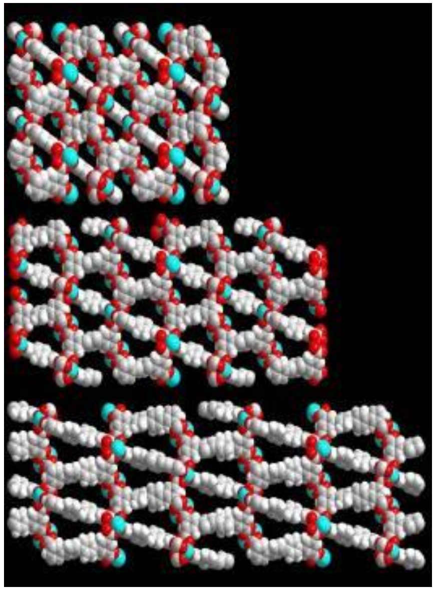
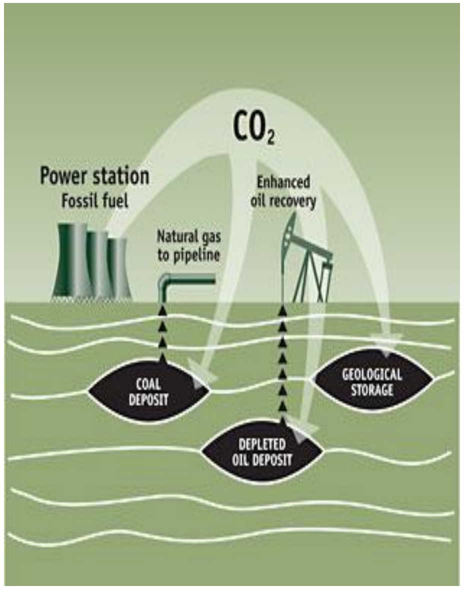
Outline:

- Energy Research at Nottingham
- Summary of facilities, capabilities and application
  - Maceral Analysis
  - Vitrinite Relectance
  - Image Analysis
  - Nuclear Magnetic Resonance
  - Rheometry
- Case study: Xuan Wei Cancer Epidemic

ETRI - Introduction

- Carbon Abatement
- Hydrogen and Fuel cells
- Renewable Energy
- Electrical Infrastructure
- Built Environment
- Environmental & Socio-economics





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Research Themes in Cleaner Fossil Energy and CO_2 Mitigation

- CO_2 adsorption and multi-pollutant control
- CO_2 phase behaviour
- Coal characterisation and conversion – carbonisation, combustion and liquefaction
- Applied geochemistry – black carbon, petroleum generation, biomass degradation
- Environment geoscience and health – PAHs, particulates, source apportionment

The EngD Centre also covers a number of themes in combustion and carbon capture/multi-pollutant technologies.

COAL CHARACTERISATION CAPABILITIES

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Facilities

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- Optical analysis
- SEM-EDAX MLA
- TGA-(MS)
- ^{13}C / ^{1}H NMR
- SOAS Rheometry
- Hydrogen Pyrolysis
- Calorimetry
- GC-IRMS

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Specific Questions that tend to arise

- Quality Assurance – *is this coal the one that we think we bought?*

- Combustion Performance Assessment – *will this new coal behave as per proximate spec?*

- Post Combustion 'Forensics' – *something has gone wrong, why?*

Standard Tests

- Maceral Analysis (Manual and Automated)
- Vitrinite Reflectance (Rank analysis)

Non-Standard Tests

- % Unreactives – *a measure for combustion potential*
- Mosaic Images – *good for 'seeing' the problem*

Q - Quality Assurance – *is this coal the one that we think we bought?*

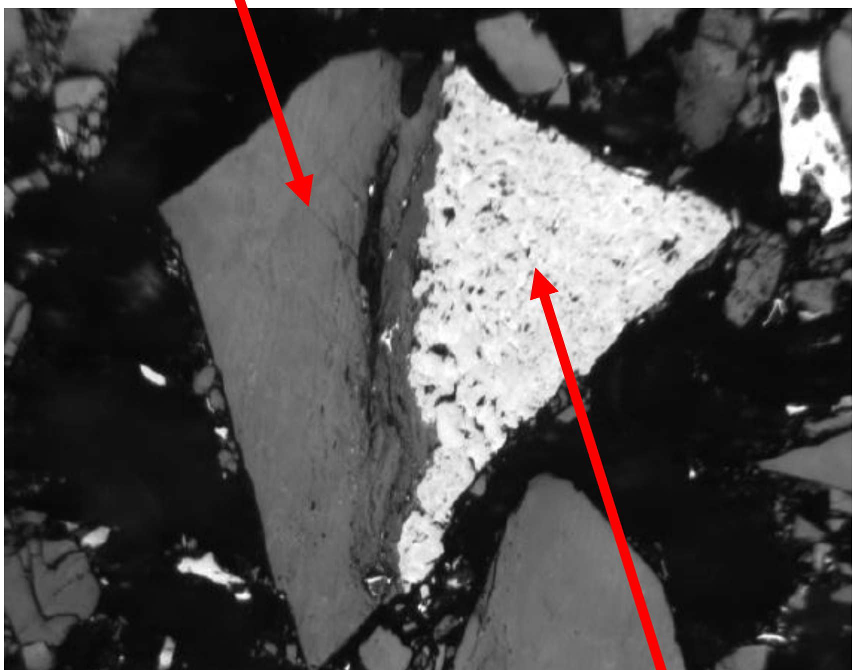
MACERAL ANALYSIS

Q - Quality Assurance – *is this coal the one that we think we bought?*

MACERALS

Liptinite (spores…) – GOOD

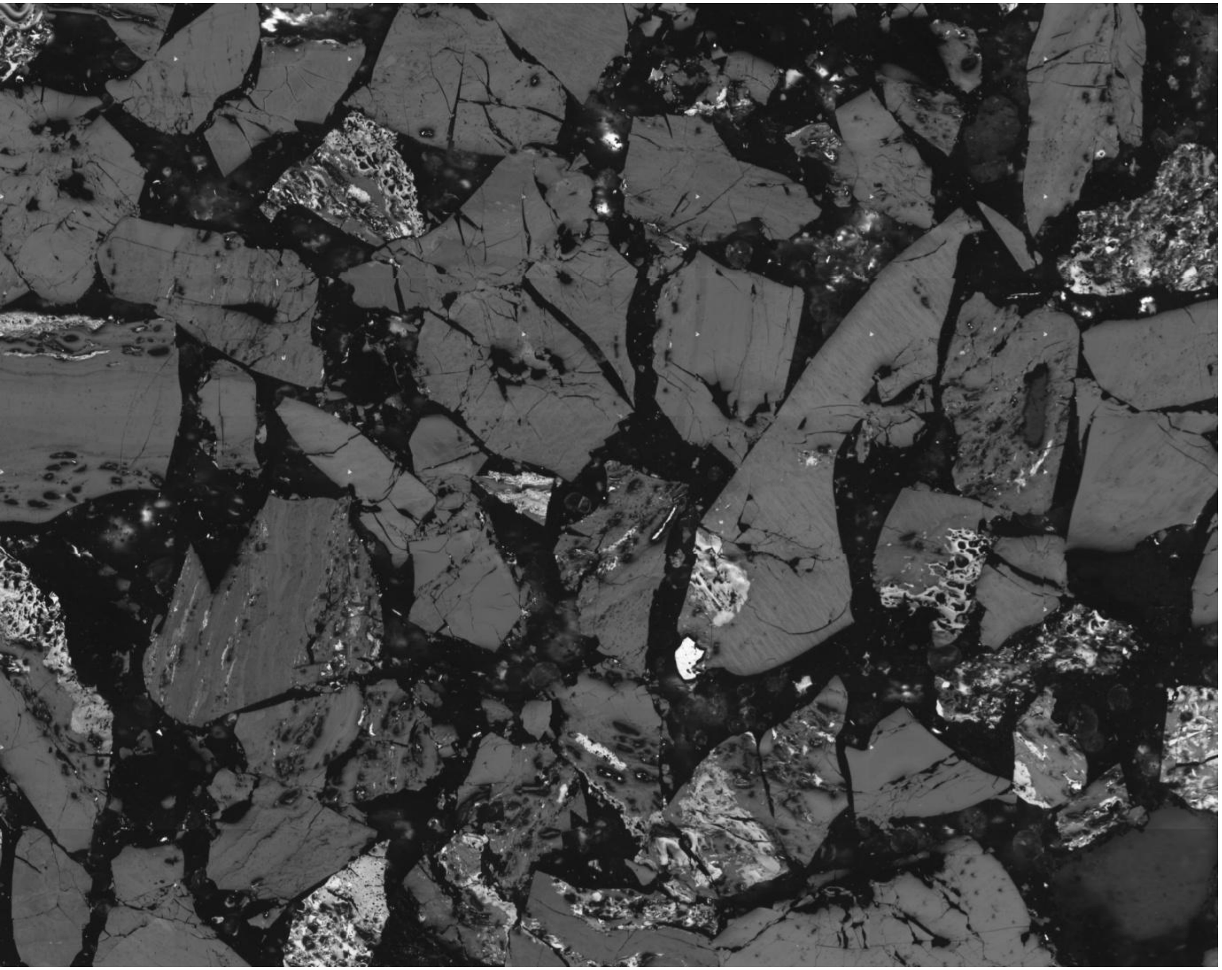
Vitrinite (cellulosic…) – GENERALLY GOOD



Inertinite (oxidised cellulosic) – CAN OFTEN BE BAD NEWS

Q - Quality Assurance – *is this coal the one that we think we bought?*

A good combustion coal



Why?

•High percentage of vitrinite

•Vitrinite has a low reflectance (∴ high volatile)

•Low proportion of high reflectance inertinite

•Low levels of unfavourable vitrinite/inertinite associations

Q - Quality Assurance – *is this coal the one that we think we bought?*

A poor combustion coal

Why?

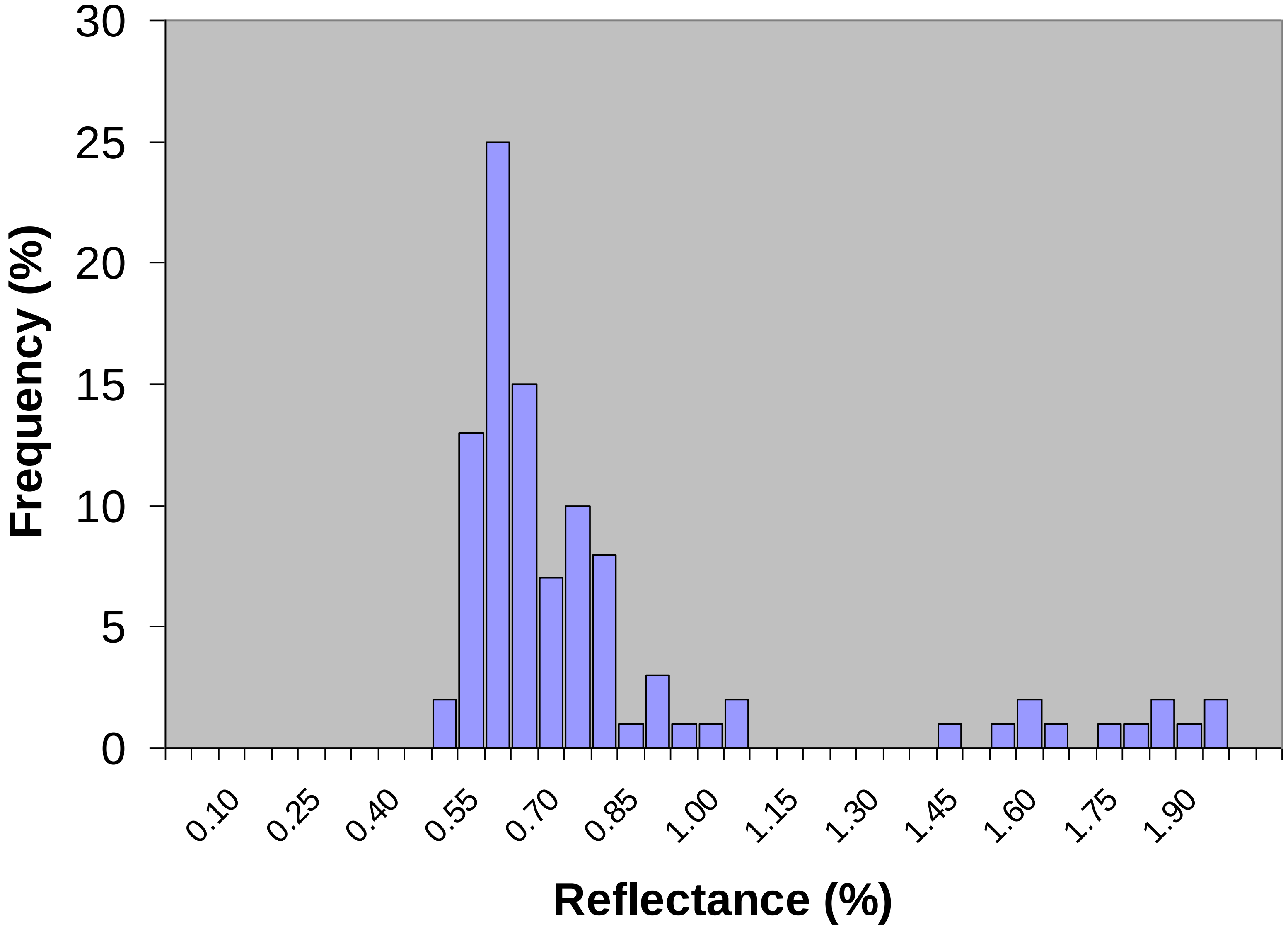
- High percentage of inertinite
- Vitrinite is blended($\therefore$ lower volatiles)
- High proportion of high reflectance inertinite
- Higher levels of unfavourable vitrinite/inertinite associations

Q - Quality Assurance – *is this coal the one that we think we bought?*

VITRINITE REFLECTANCE

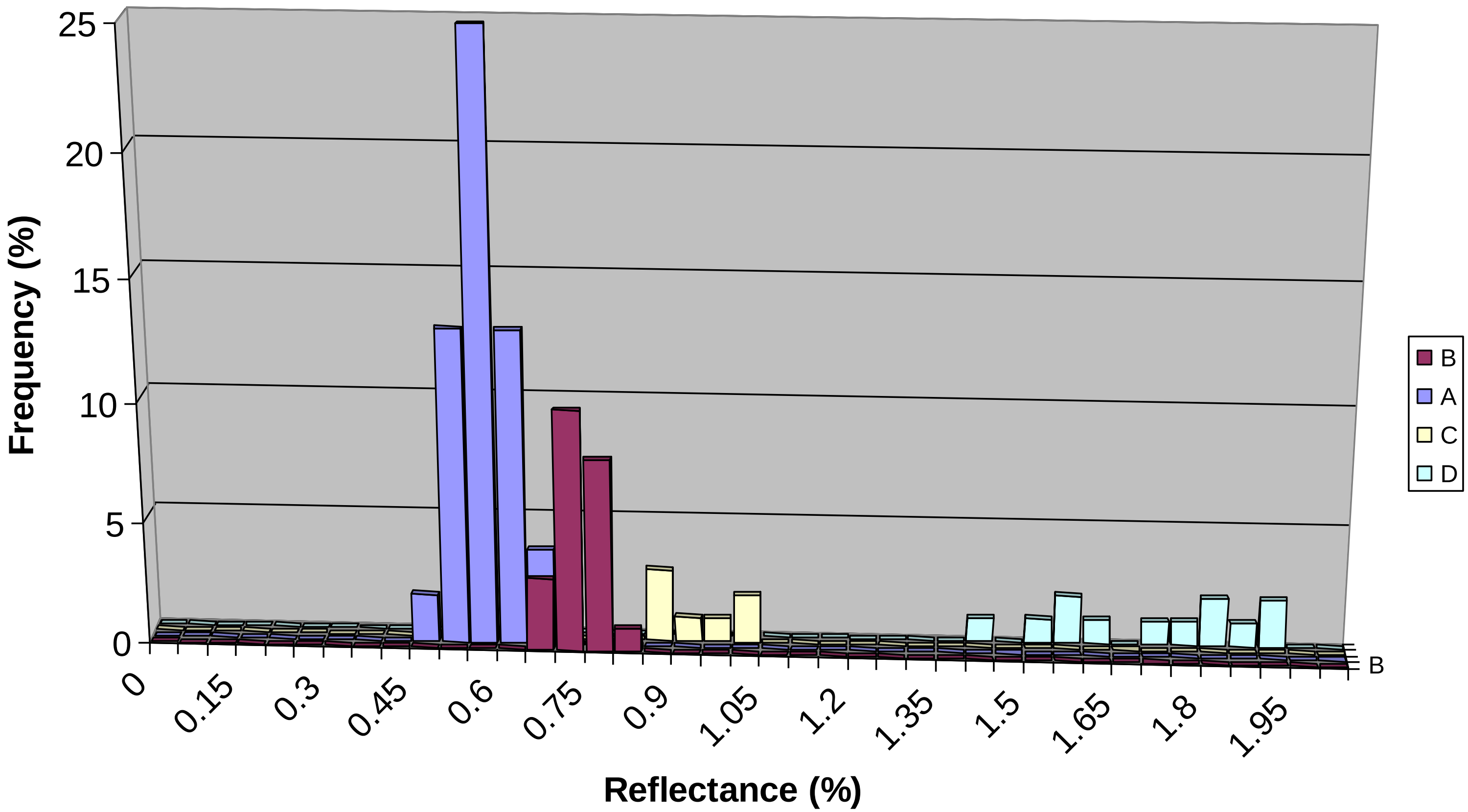
Q - Quality Assurance – *is this coal the one that we think we bought?*

Rank Analysis/Vitrinite Reflectance



Q - Quality Assurance – *is this coal the one that we think we bought?*

3-4 coals in a blend – but where the average volatile content still meets (just) specification

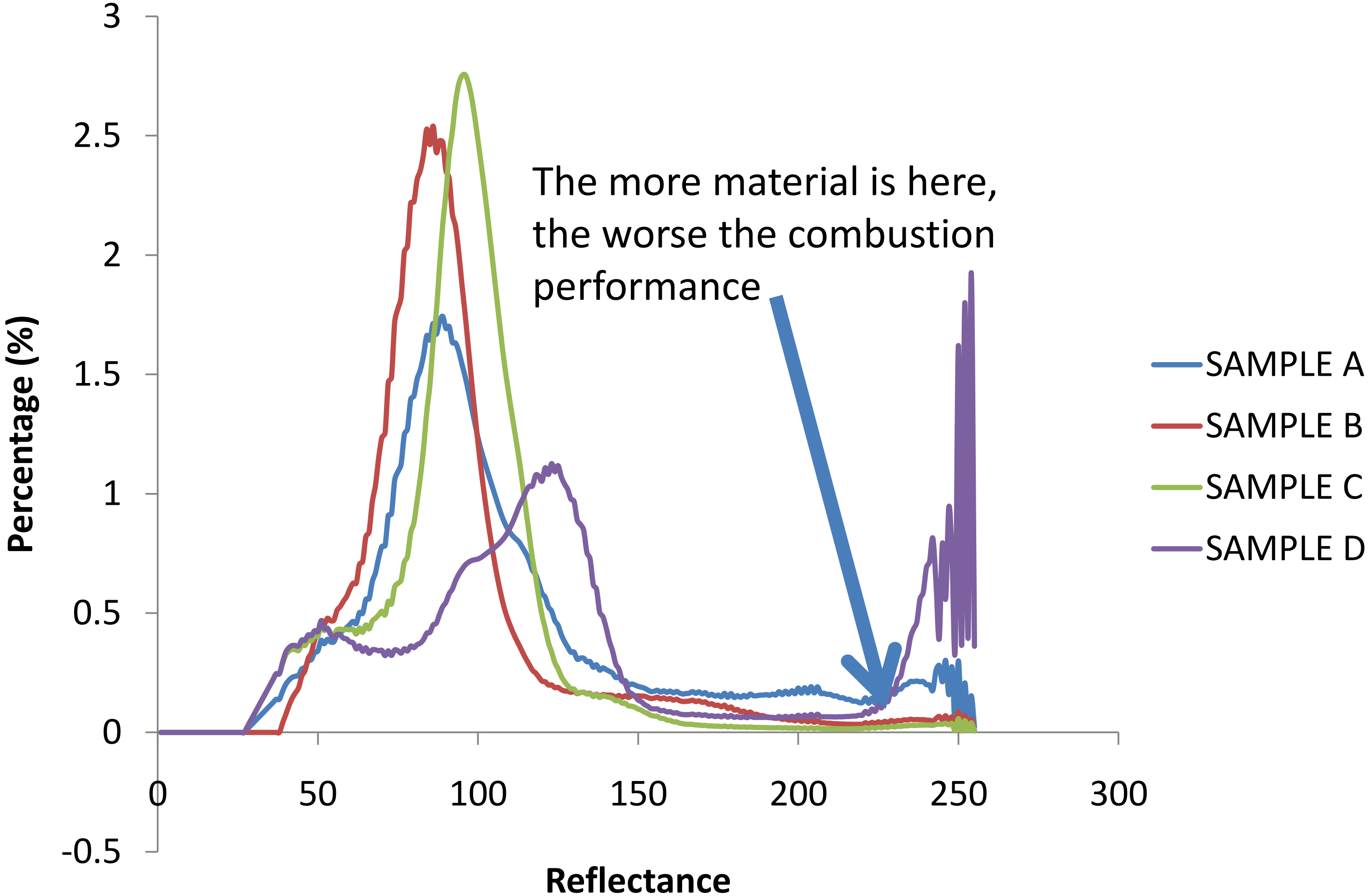


Q - Quality Assurance – *is this coal the one that we think we bought?*

IMAGE ANALYSIS
AN ADVANCED TOOL FOR FINGERPRINTING COALS

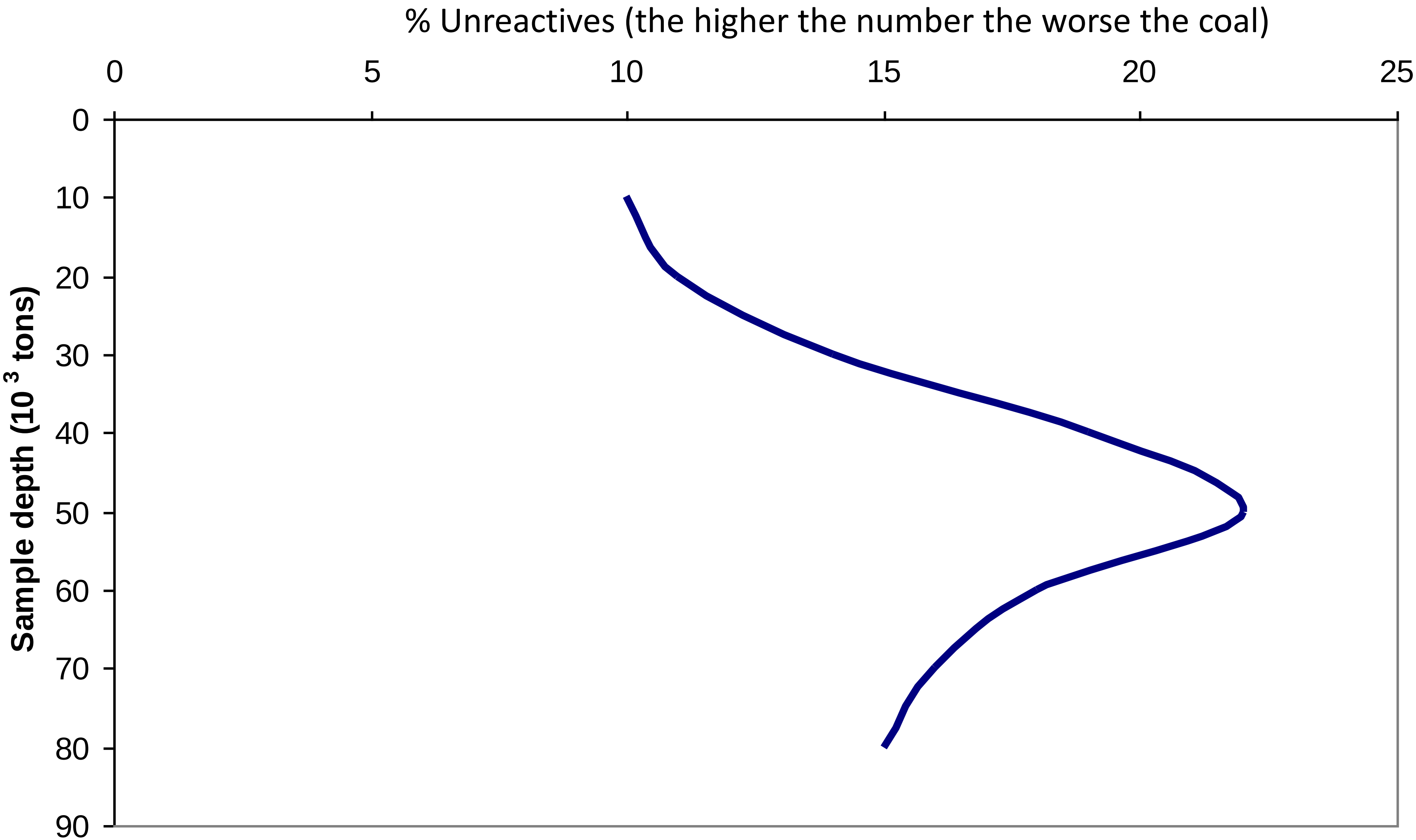
Q - Quality Assurance – *is this coal the one that we think we bought?*
Q - Combustion Performance Assessment – *will this new coal behave as per proximate spec?*

Coal Fingerprinting



with combustion predictions of B > C > A > D

QUALITY ACROSS A BOAT!



Char/Flyash Analysis

POST COMBUSTION FORENSICS

Post Combustion ‘Forensics’ – *something has gone wrong, why?*

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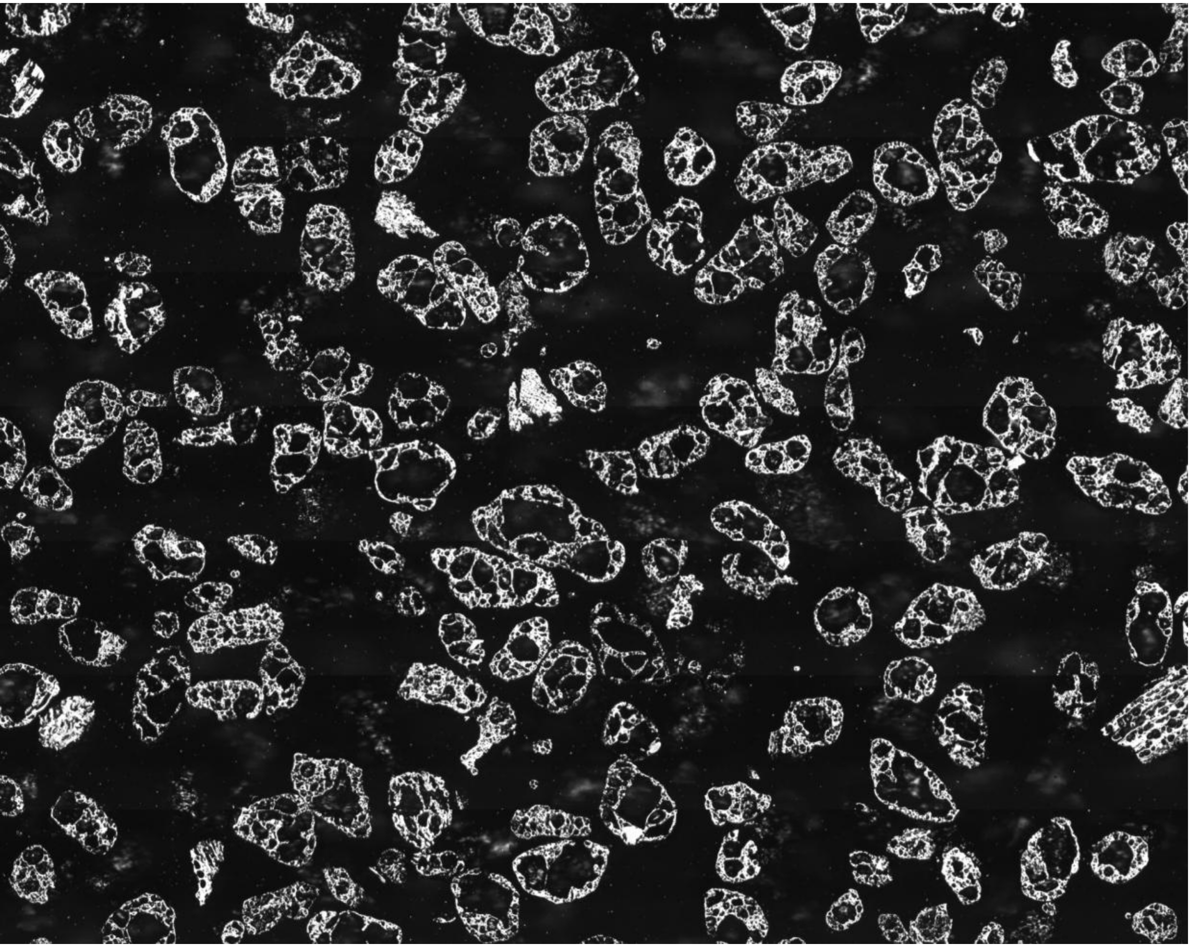
Good Combustion Intermediate



Why?

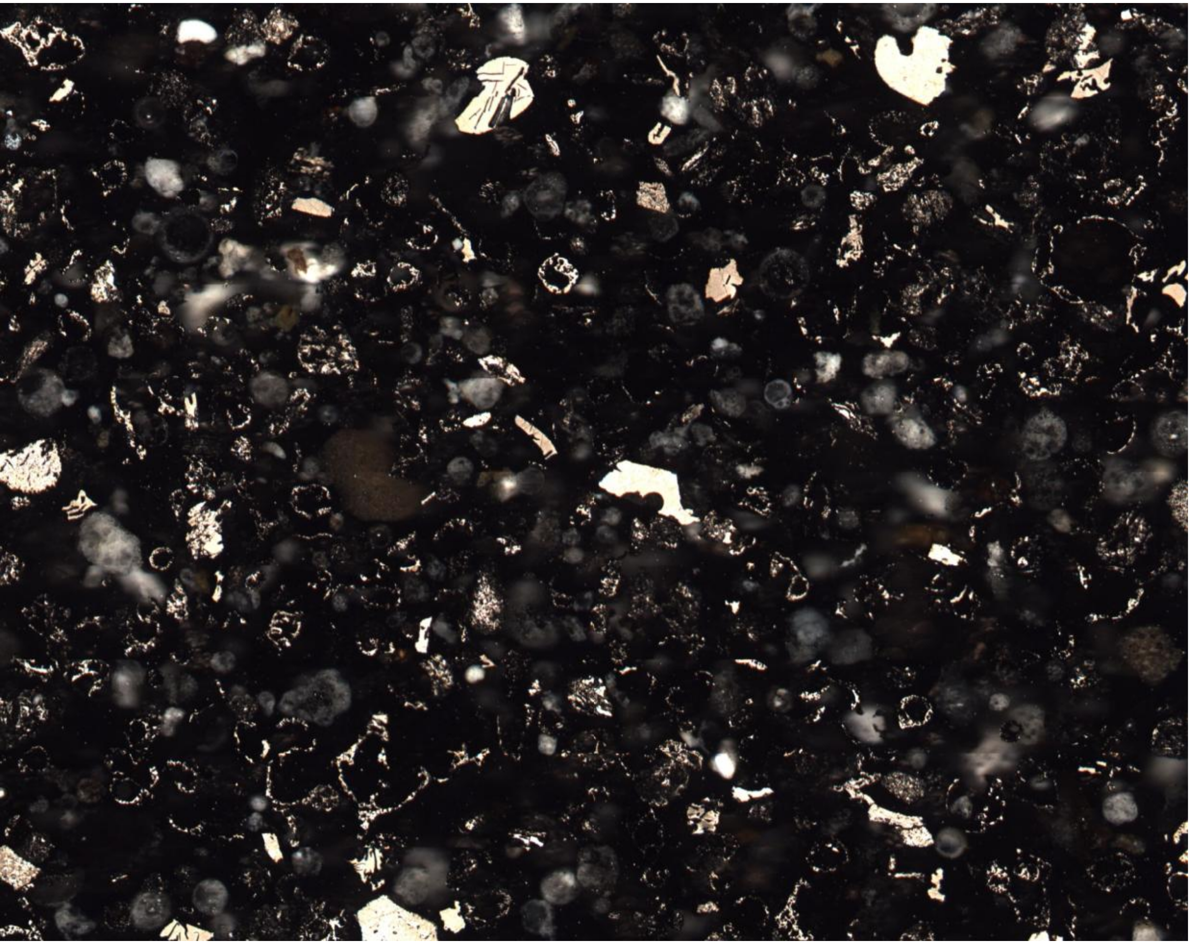
•Open Structures

•High Proportion of thin walled material

•Low proportion of dense non-porous char

Post Combustion 'Forensics' – *something has gone wrong, why?*

Poor Combustion residue



Why?

•Dense Structures

•High Proportion of non-porous structures

•Mixed thin and thick walled chars

Post Combustion 'Forensics' – *something has gone wrong, why?*

SEM, EDAX and Mineral Liberation Analysis

ASH CHARACTERISATION

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SEM of flyash particulates

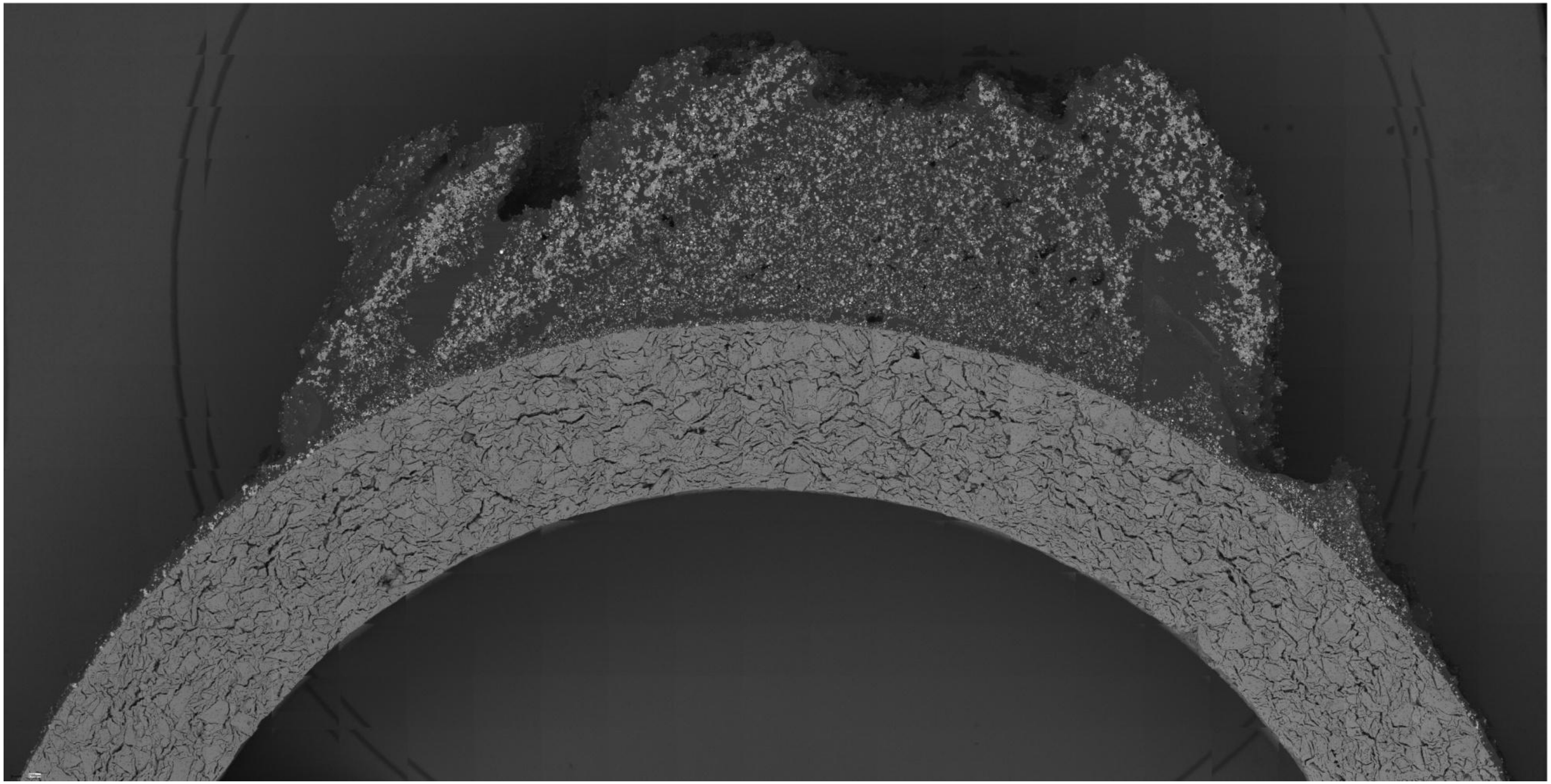
Why?

•Good imaging of post combustion residues in 3D

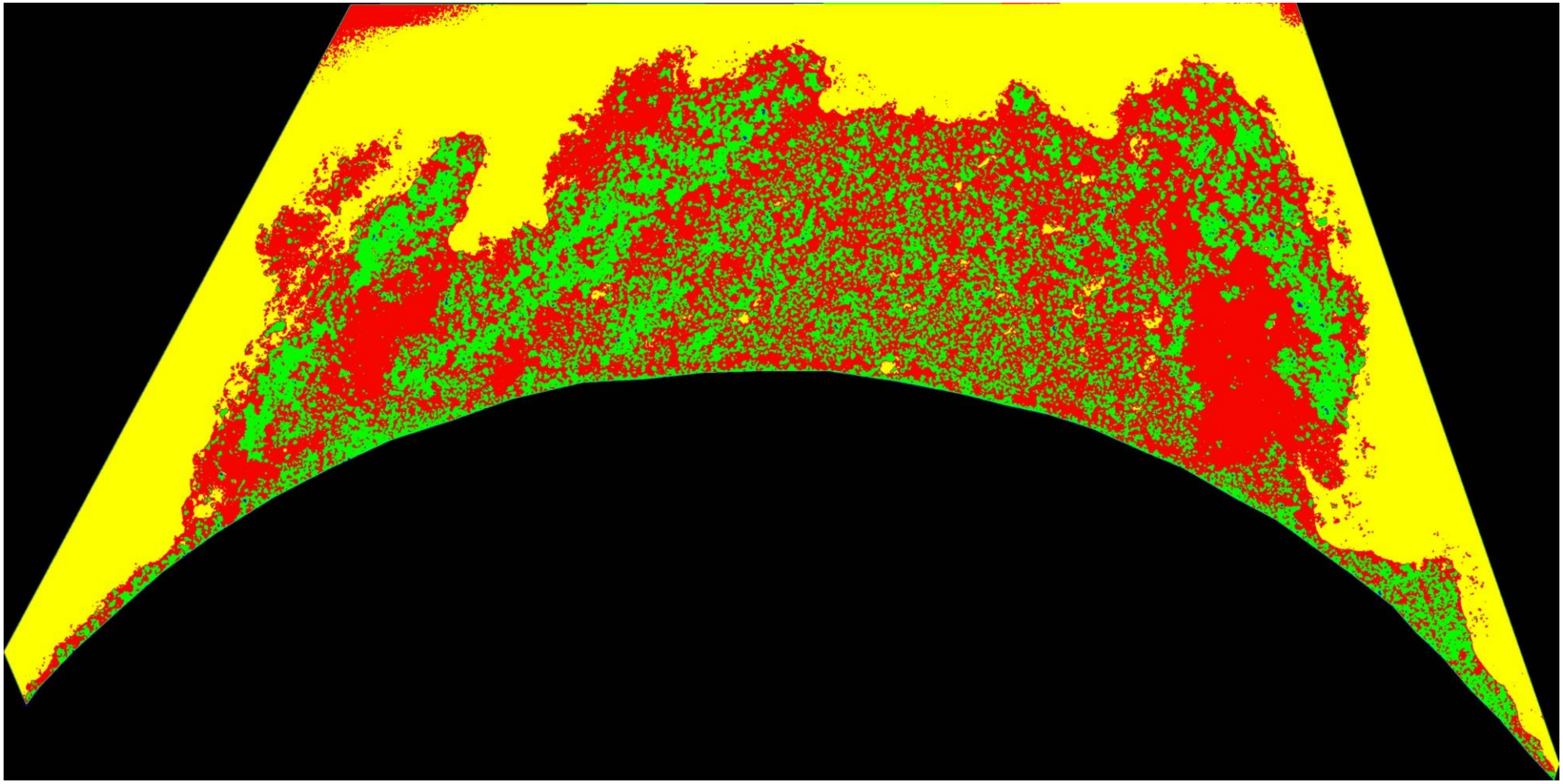
•Good way to compare morphologies that relate to maceral origins

•Good means of sizing carbon and ash particles

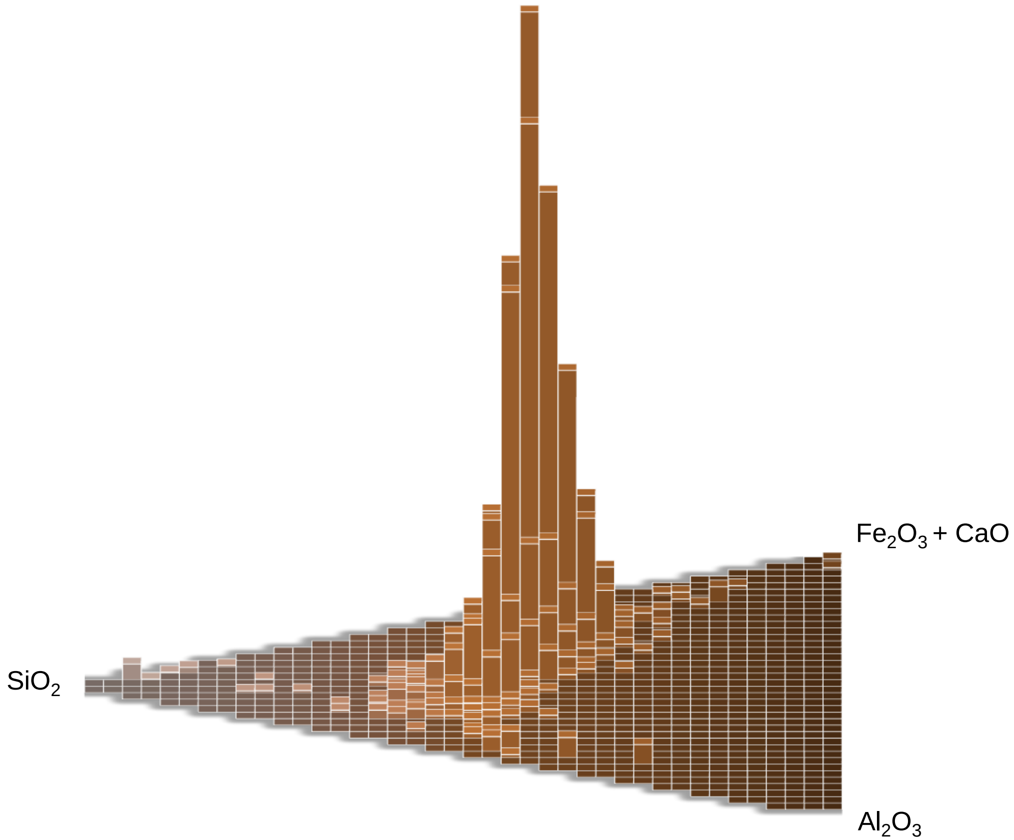
Ash Deposit Analysis



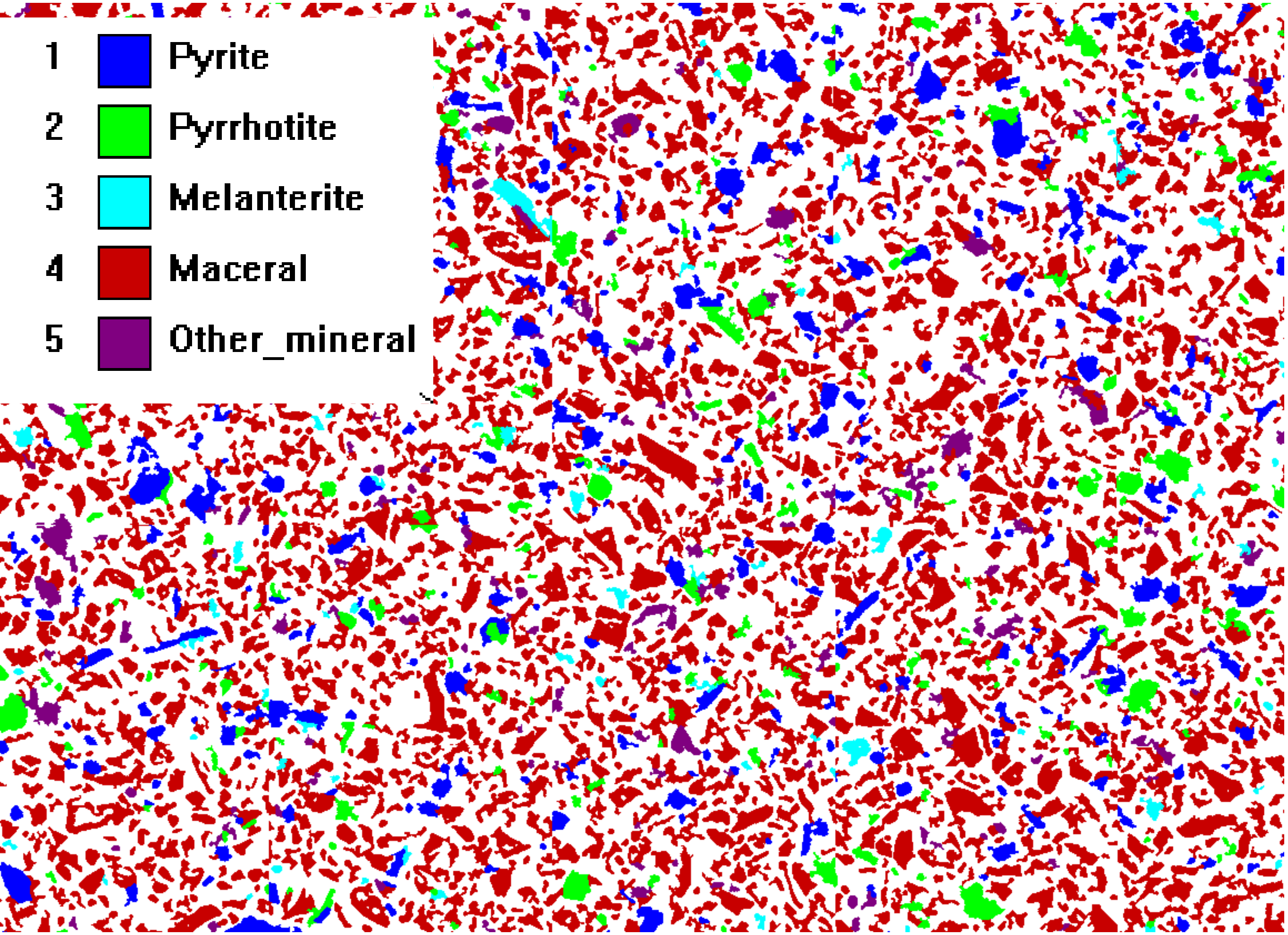
Separation of Ash Phase



Compositional analysis of ash deposit



Coal Mineral Analysis



- Coal **and** mineral analysis – useful for associations of minerals within coal particles – or degree of liberation within a coal sample

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Microstructural studies during combustion/ pyrolysis / carbonisation.

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Coal conversion – carbonisation, combustion and liquefaction

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- **Combustion – oxyfuel and additives**
  Oxyfuel – 2 recent Dti/BERR grants (£180k) and current EPSRC E.ON grant, EP/G062153/1: OxyCAP UK, £328k (01.08.09-31.07.12) investigating fundamental aspects.
  Additives – fully supported studentship and EngD project, Innospec, 2 Patents.

- **Carbonisation/coking**
  On-going RFCS projects, two new projects started July 2010 (£400k), combined use of rheology and NMR to predict coking behaviour.

- **Liquefaction of coal and biomass**
  BP supported project (£60k) on fundamental aspects of liquefaction, including conversion of biomass to produce low O heavy oils.

Some Recent Publications

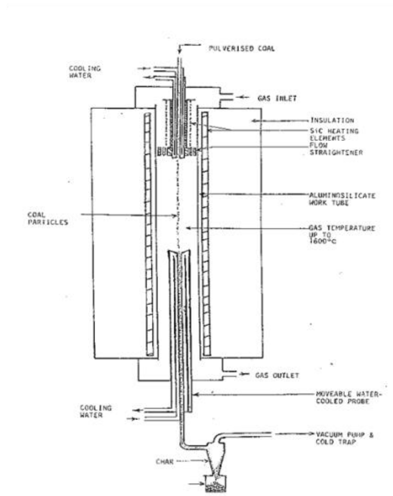
K.M. Steel, M. Castro Diaz, J.J. Duffy and C.E. Snape, Use of oscillatory shear rheometry and thermogravimetric analysis to examine the microstructural changes during coal pyrolysis/carbonisation for the prediction of IRSID strength indices, Energy & Fuels, 2009, 23, 2111-2117.
M.C. Diaz, L. Edecki, K.M. Steel, J.W. Patrick and C.E. Snape, Determination of the effects caused by different polymers on coal fluidity during carbonisation using high-temperature 1H NMR and rheometry, Energy & Fuels, 2008, 22, 471-479.
K.U. Ogbuneke, C.E. Snape, J.M. Andrésen, S. Crozier, C. Russell and R. Sharpe, Identification of a polycyclic K. Le Manquais, C.E. Snape, I. McRobbie, J. Barker and V. Pellegrini, Comparison of the combustion reactivity of TGA and drop tube furnace chars from a bituminous coal, Energy & Fuels, 2009, 23(9), 4269-4277.

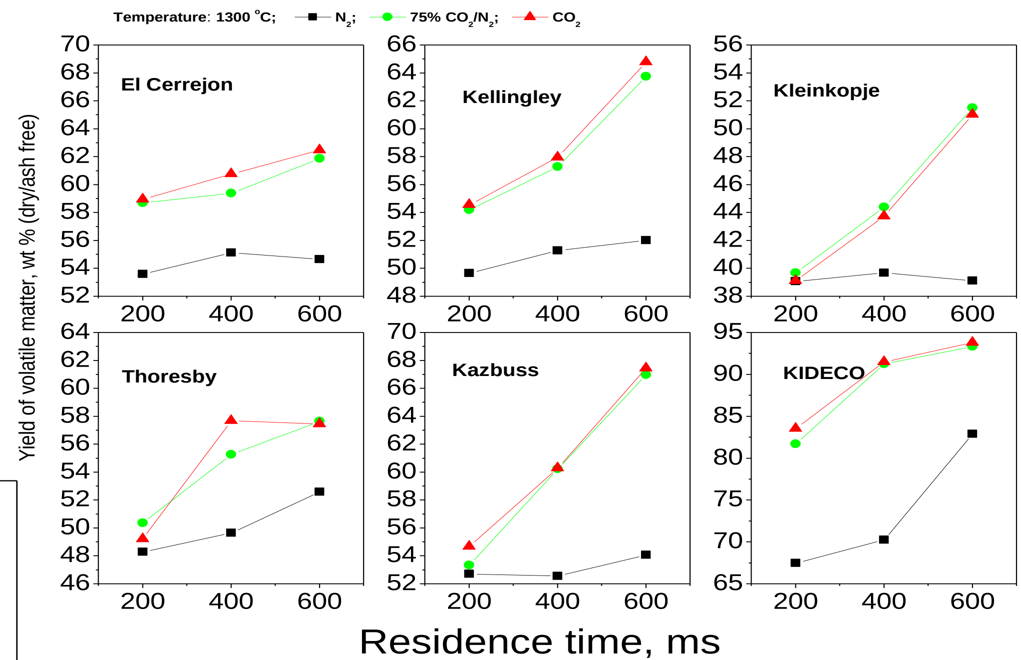
Oxyfuel and normal combustion using a drop tube furnace

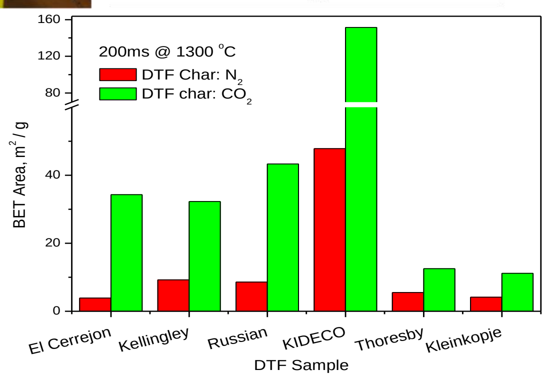
Chenggong Sun, Donglin Zhao and Colin Snape

(EPSRC and BERR/DEC, Oxycoal UK projects)

Oxy-fuel conditions give higher yields of total volatiles (5 ~ 20 wt%), attributable to the contribution of the CO_2/char reaction for a number of coals.

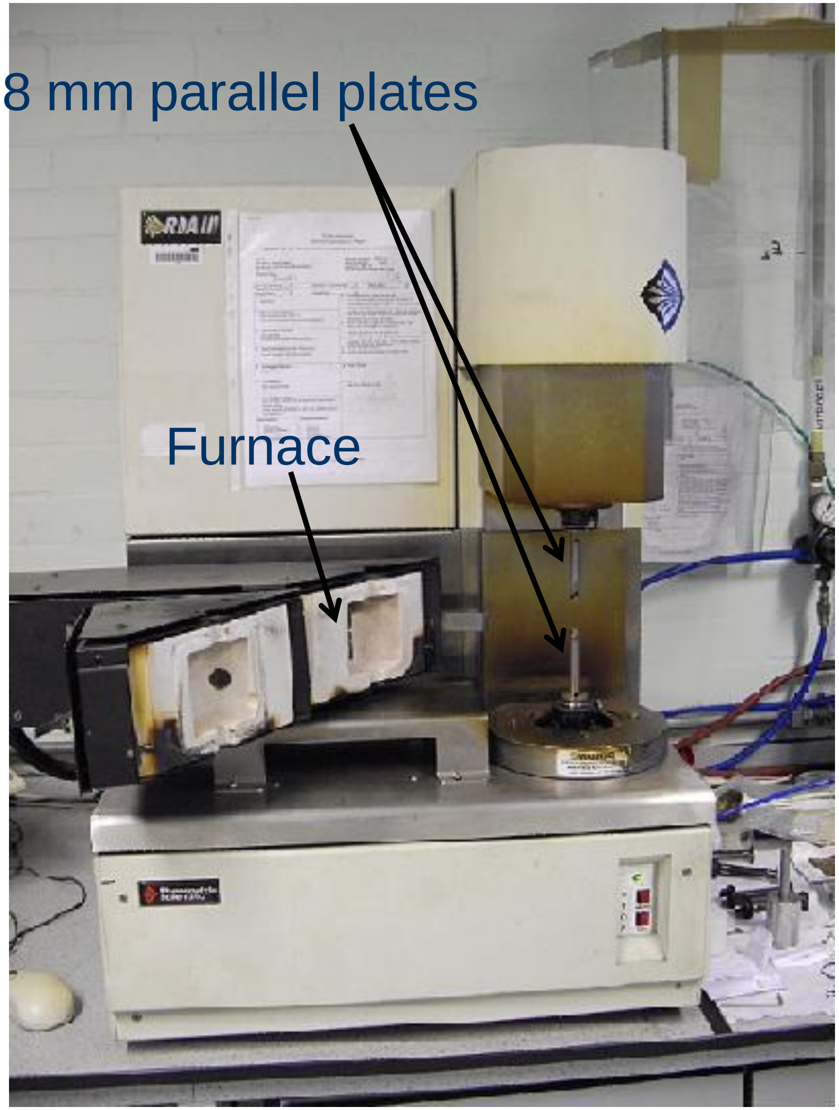






Increases in BET surface area arise at 1300°C due to char activation in CO_2.

High-torque, high-temperature SAOS rheometry

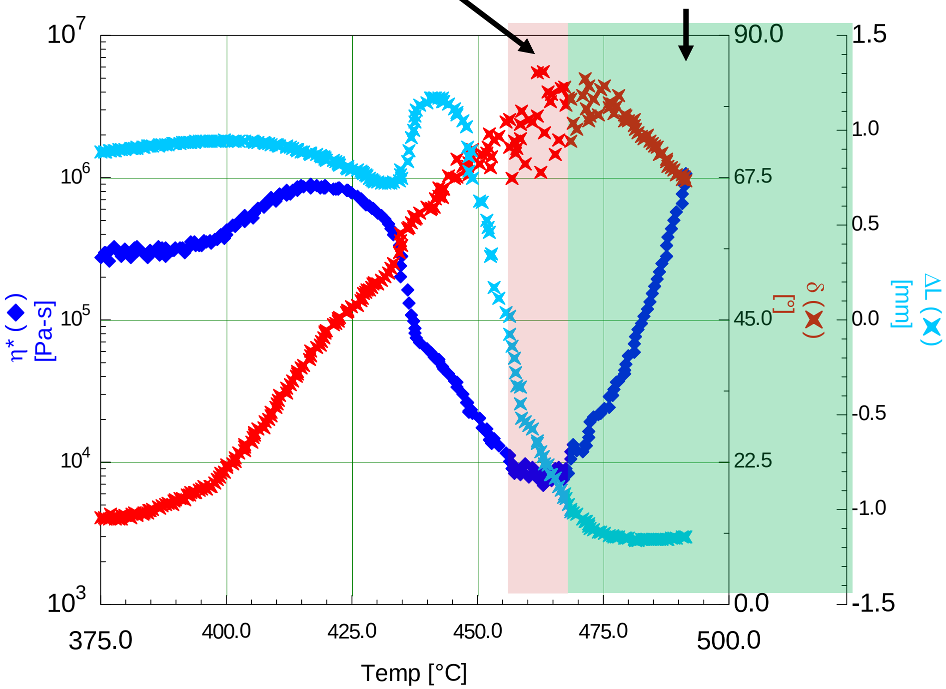


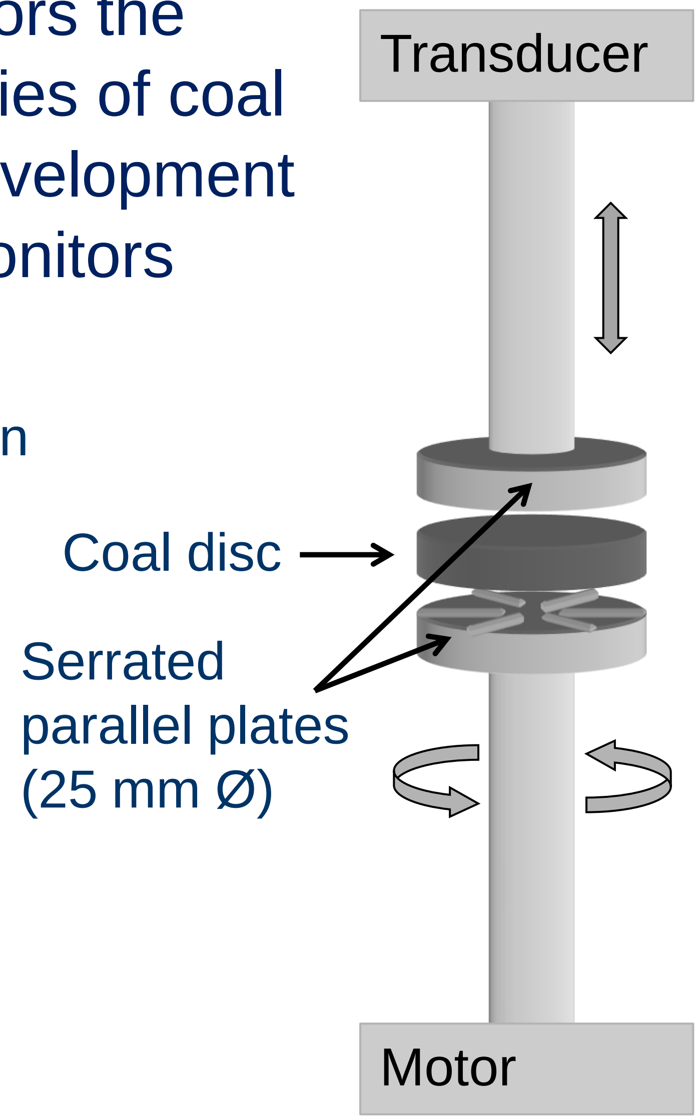
- Rheometrics RDA-III rheometer.
- Parallel plates of either 8 mm or 25 mm in diameter.
- Tests can be carry out from room temperature up to 600° C.
- Sample size is 0.1 g (8 mm plates) and 1.5 g (25 mm plates).

High-torque, high-temperature SAOS rheometry

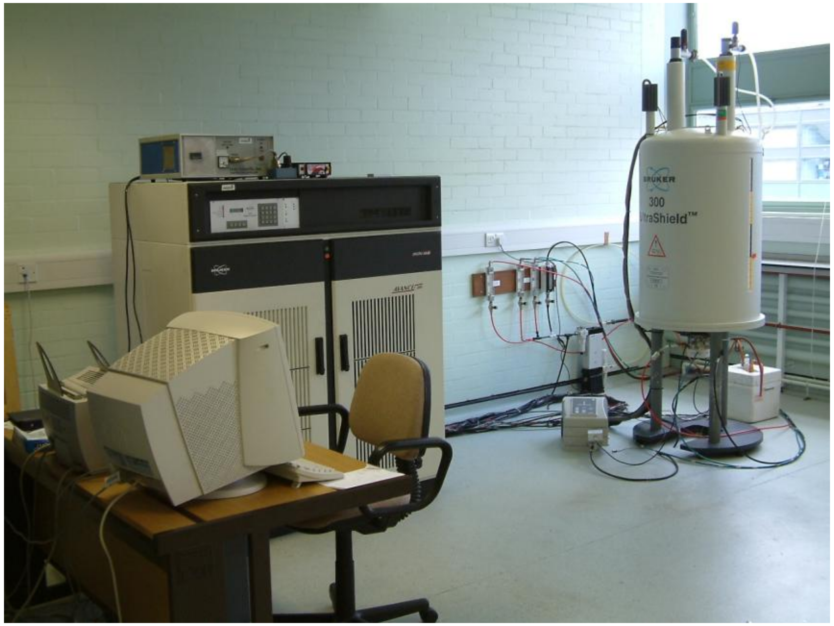
- High temperature rheometry monitors the changes in the viscoelastic properties of coal with temperature to quantify the development of fluidity in the sample mass ⇨ monitors macroscopic phenomena.

Expansion Collapse & Resolidification

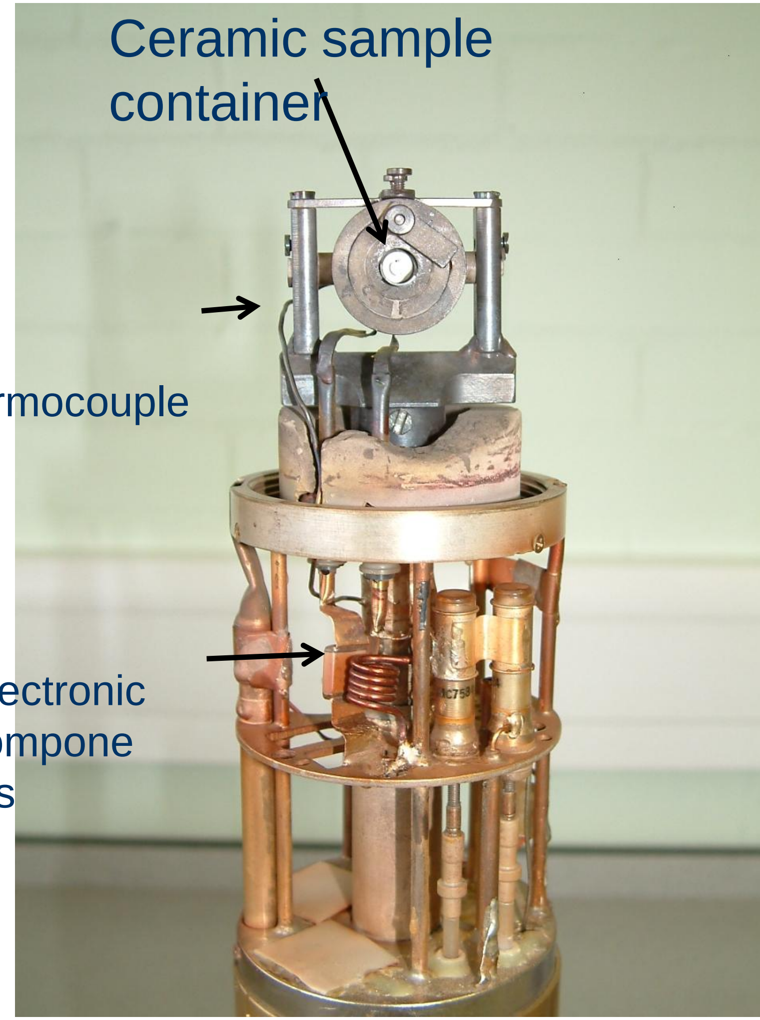




Solid-state NMR spectrometer



- 200 MHz field strength (4.7 Tesla).
- Equipped for high resolution ^{13}C and broadline ^{1}H measurements.
- ^{1}H NMR tests can be carry out from room temperature up to 520° C.



High-temperature ^{1}H NMR spectra of coals

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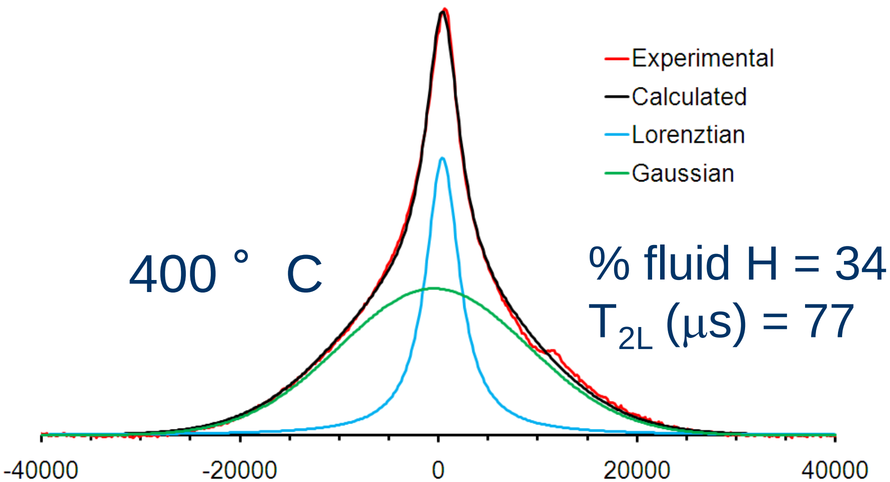
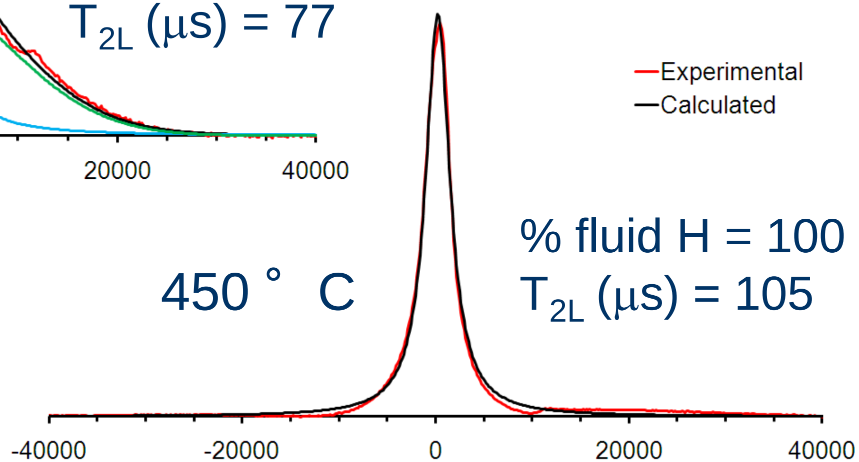
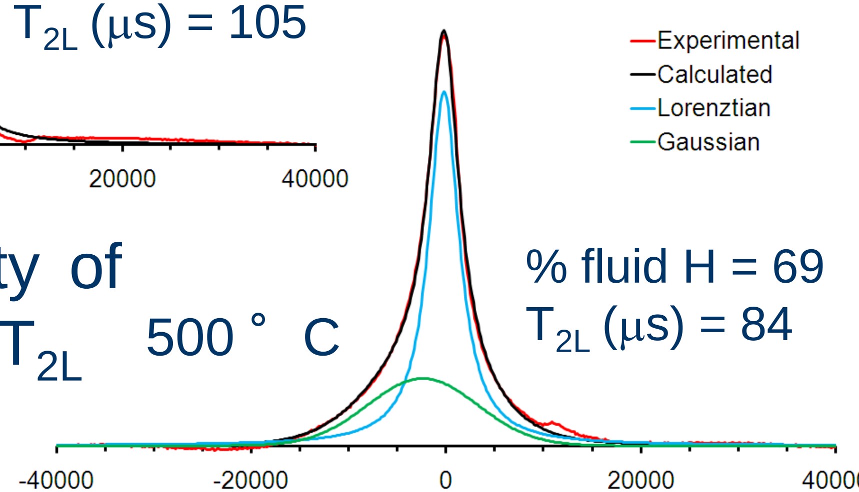
Carter Roag

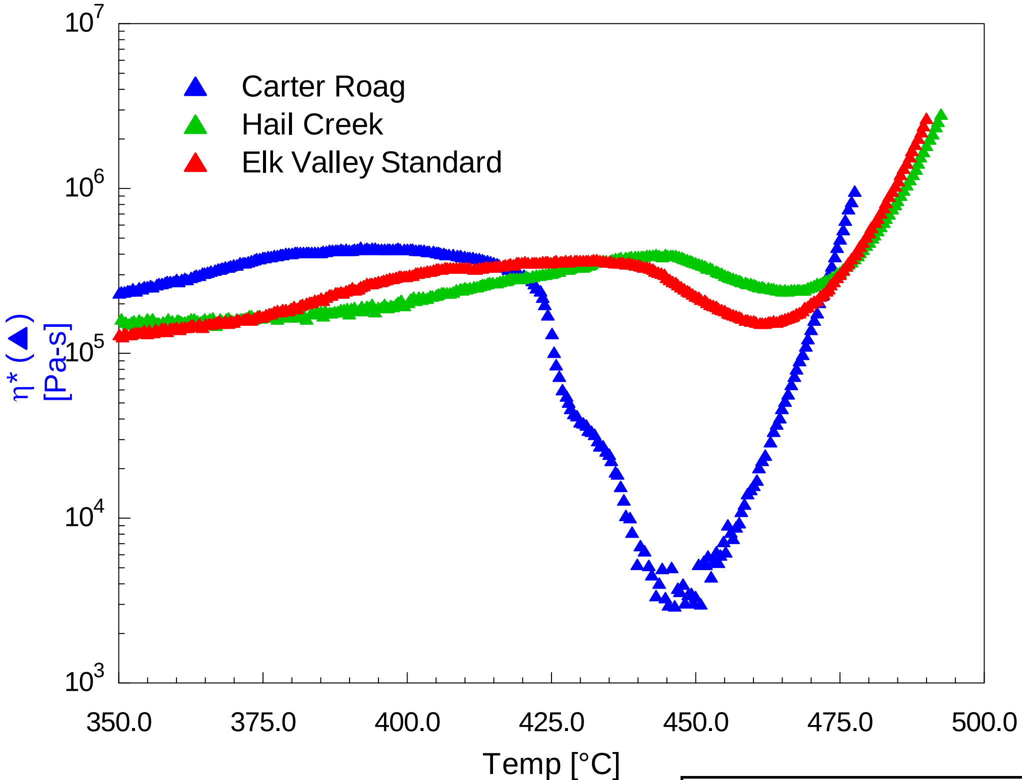






T_{2L} correlates with the mobility of the fluid phase, i.e. the higher T_{2L} the higher the mobility.

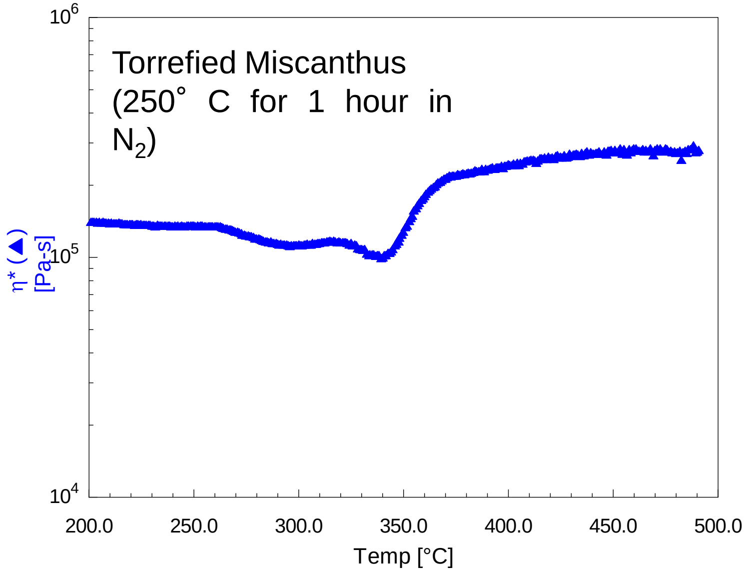
SAOS rheometry results coal

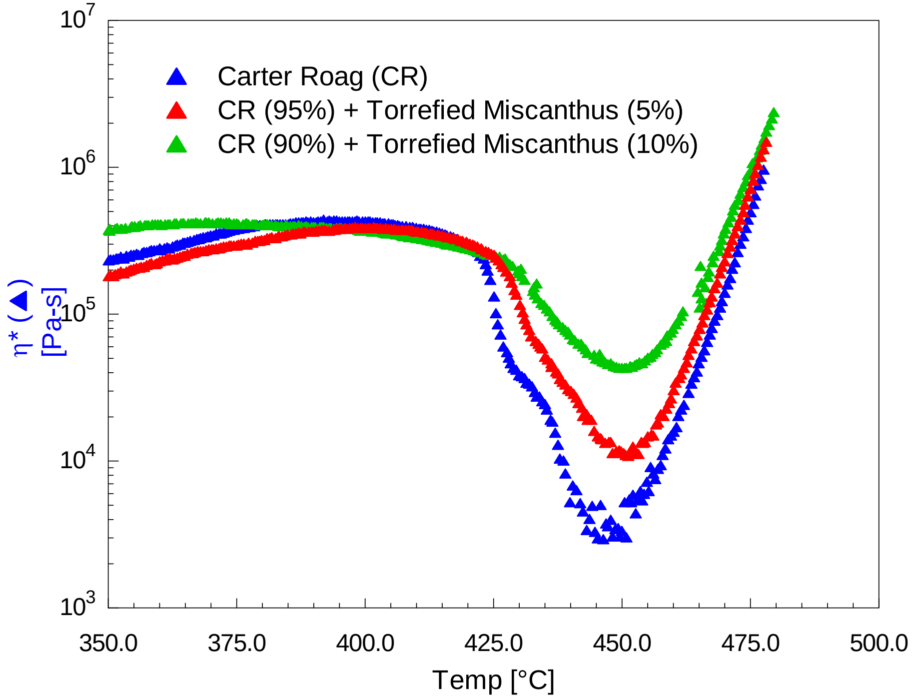


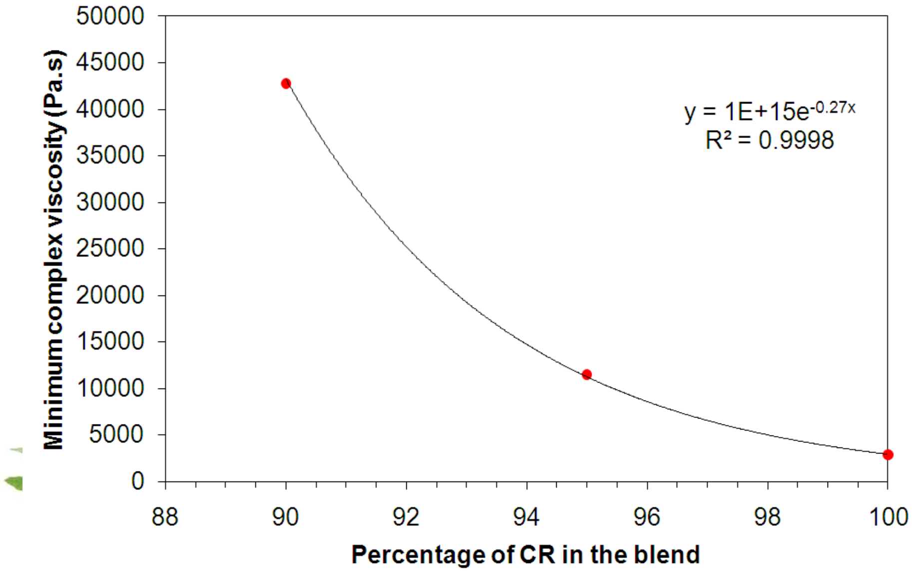
- Hail Creek and Elk Valley Std develop similar viscoelastic properties.
- Gieseler and rheometry are in agreement although the softening temperatures are higher in the rheometer.

Gieseler Data	Carter Roag	Hail Creek	Elk Valley Std
Softening T (° C)	412	436	430
T maximum fluidity (° C)	447	466	459
Max. fluidity (ddpm)	534	31	48
Resolidification T (° C)	479	486	482

Addition of torrefied biomass







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

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

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

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

High-temperature ^{1}H NMR results showing how biomass suppresses fluidity

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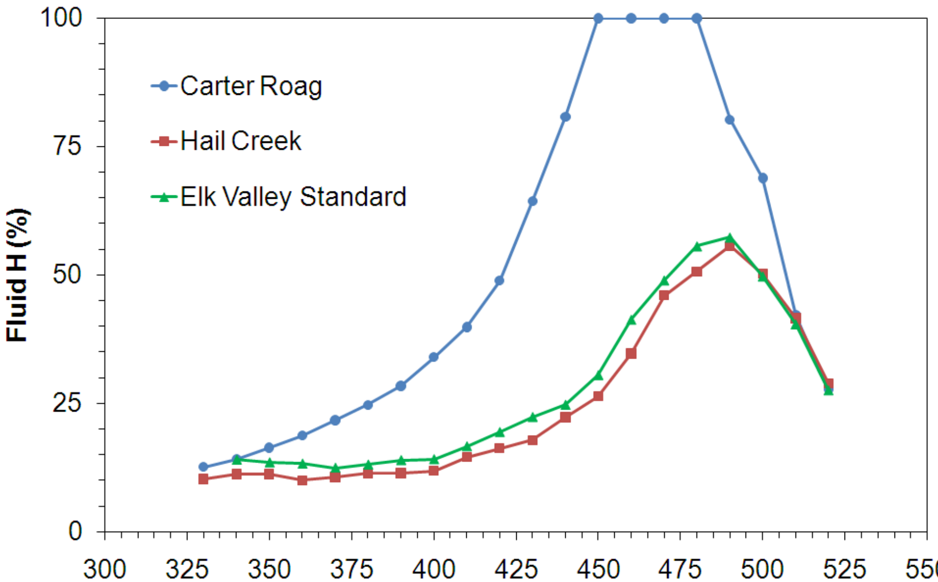
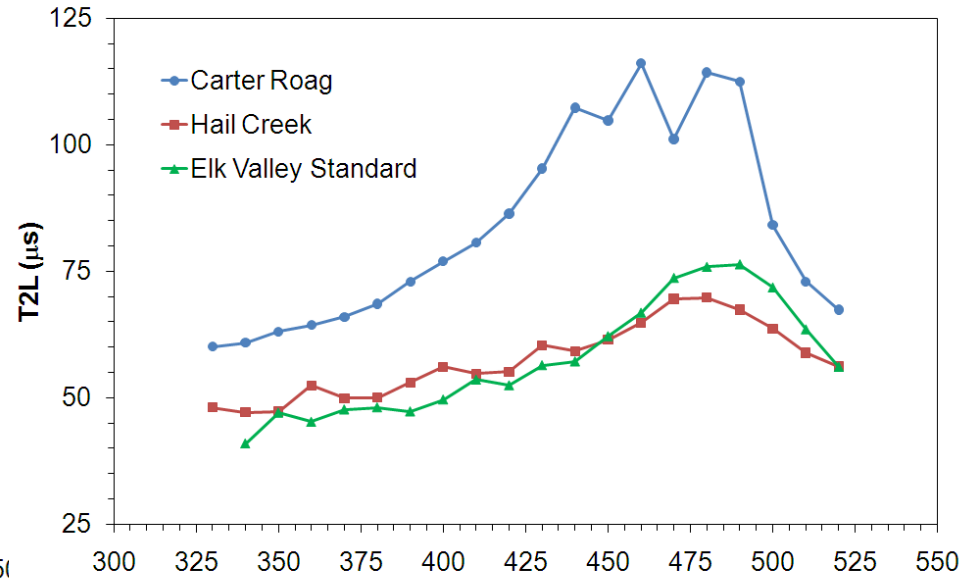
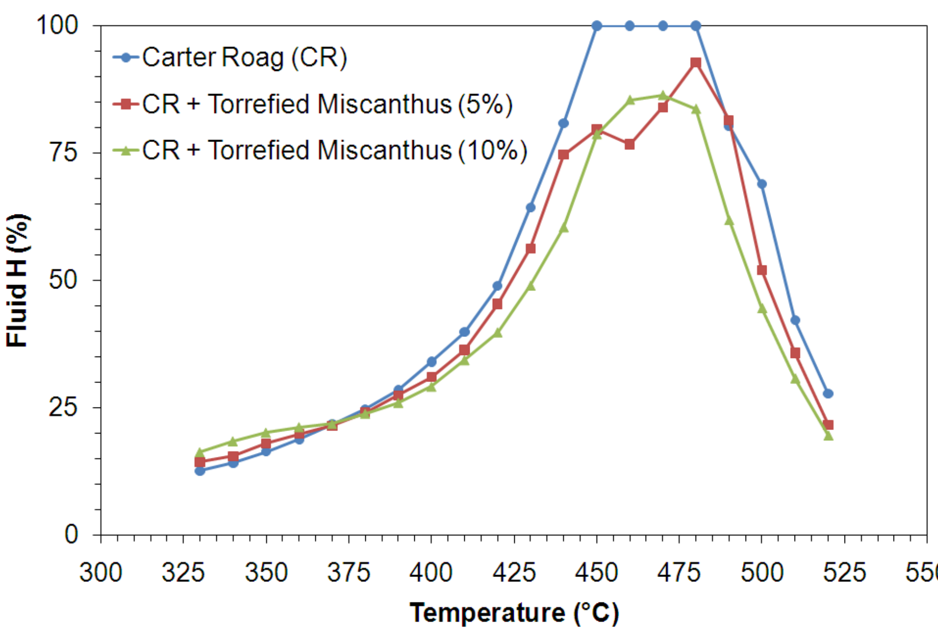
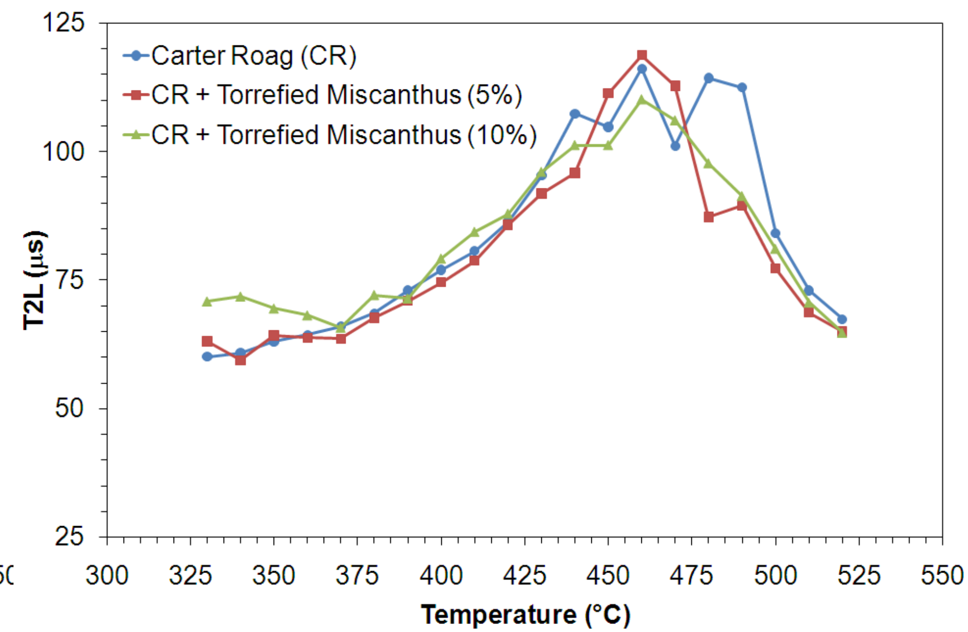
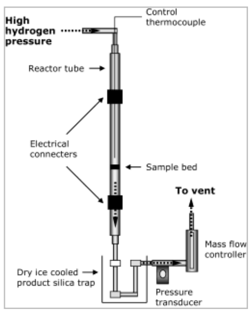




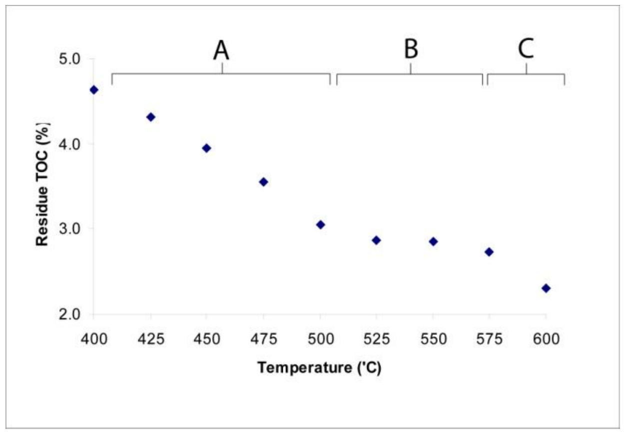




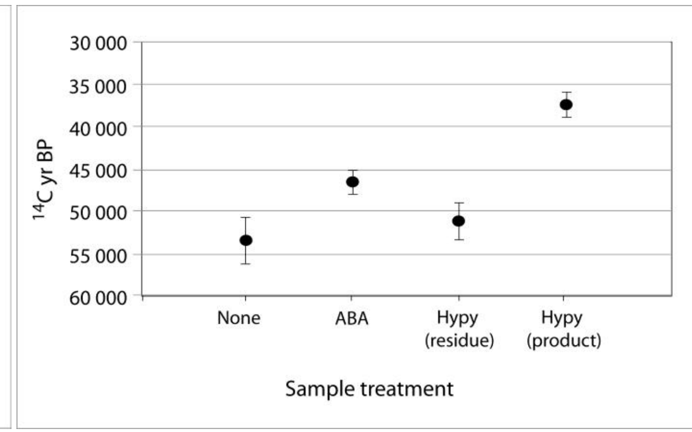
Black carbon measurement and purification by hydropyrolysis



Hydropyrolysis is a commercially available pyrolysis technique



Example of residual TOC variation from hypy for a typical soil sample. BC content is the carbon remaining when the plateau in carbon loss is reached at *ca*. 550° C.



Results for ^{14}C measurement compare favourably with results from more time consuming clean up methods

Hydropyrolysis shows great potential as a new tool for rapid BC isolation and quantification, with benefits in for ^{14}C age determination

100% conversion for biomass means that contents in coal blends can easily be quantified from the remaining inertinite content.

CASE STUDY: Xuan Wei lung cancer epidemic

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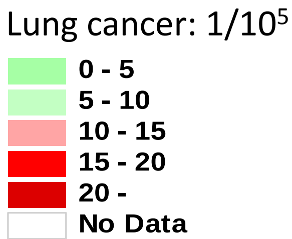
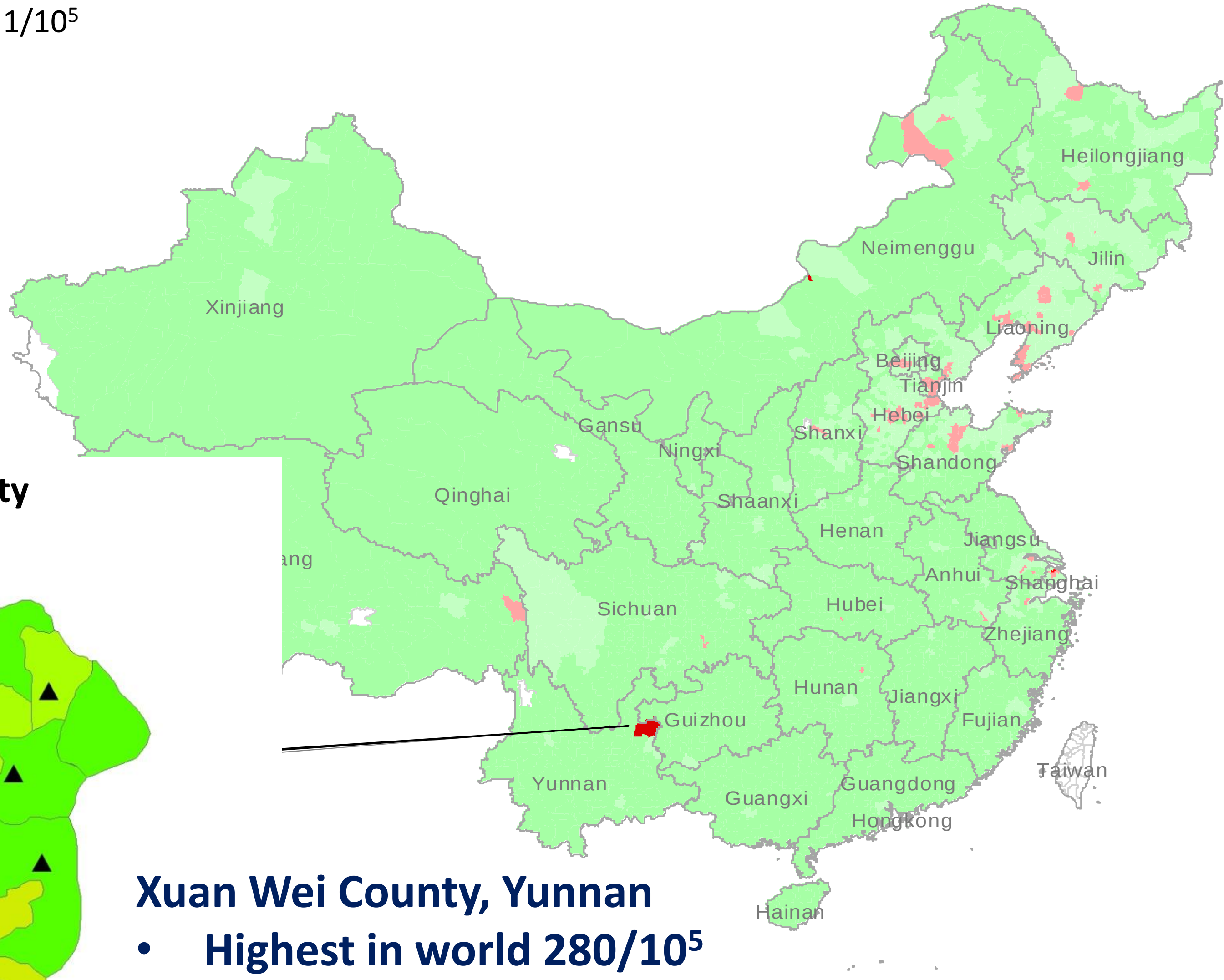
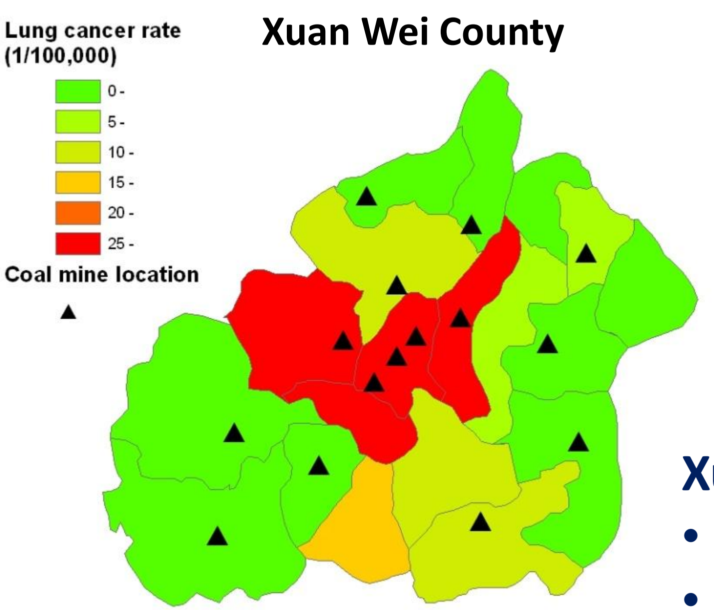
Xuan Wei lung cancer epidemic





Women lung cancer mortality in China, 1973-75

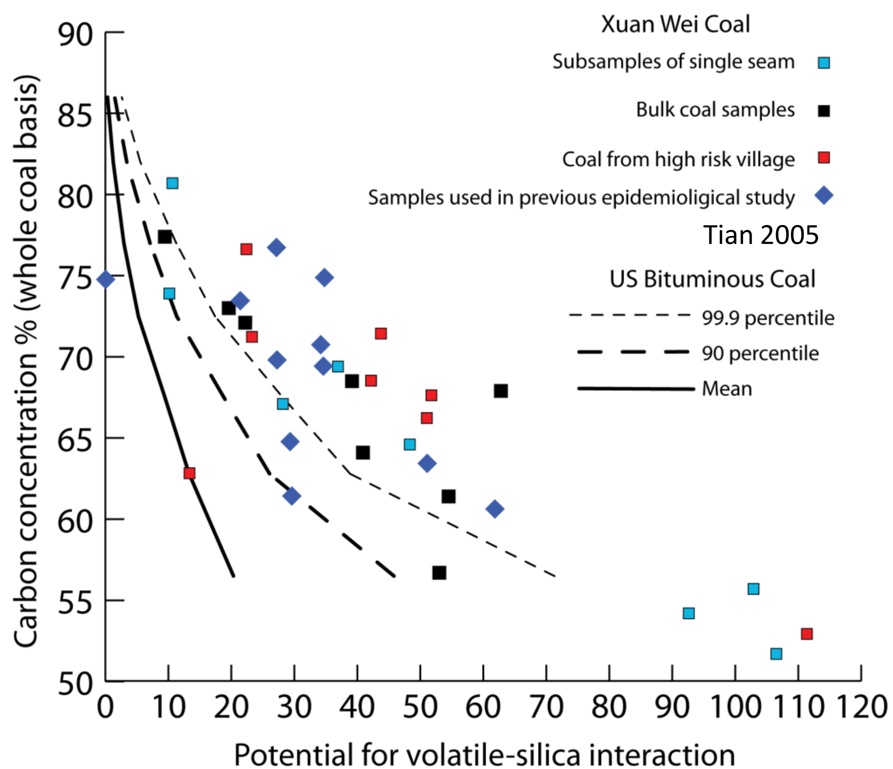


Xuan Wei County, Yunnan

- Highest in world $280/10^5$
- Highest in women
- Women don’t smoke in this area.
- Attributed to local bituminous coal

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

ANY QUESTIONS?

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