Experimental validation of coal gasification with neutron imaging

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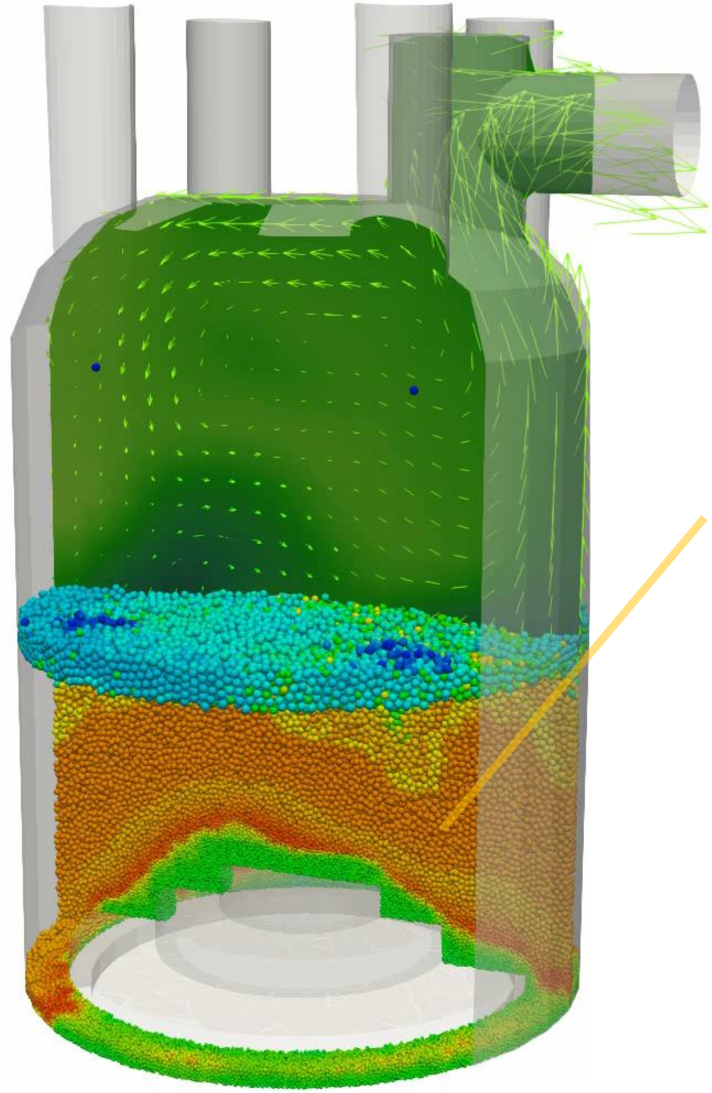
Coal samples

Joe Sheets (3J Enterprises, Newburg WV) – Sample A (anthracite)
Jim Mullins, **Shelby Howard** (Covol Fuels No. 3, Beverly KY) – Sample B (Blue Gem bituminous)
Cosmin Dumitrescu (West Virginia University, Morgantown WV) – Sample C (Pittsburgh #8 bituminous)
Jeff Barron (WWC Engineering, Sheridan WY) – Sample D (sub-bituminous)
Mike Heger (BNI Inc., Center ND) – Sample E (lignite)
Chilkoot Ward (Usibelli Coal Mine), **Brent Sheets** (University of Alaska, Fairbanks) – Sample U (Usibelli sub-bituminous)

Research sponsored by the U.S. Department of Energy Office of Fossil Energy

This project aims to obtain nonintrusive model validation data from inside operating gasifiers



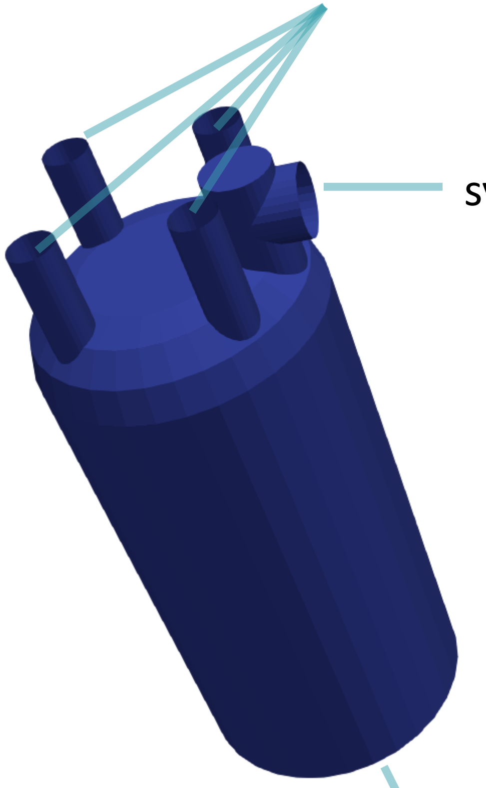
No known nonintrusive techniques to dynamically track coal gasification progression *in situ*

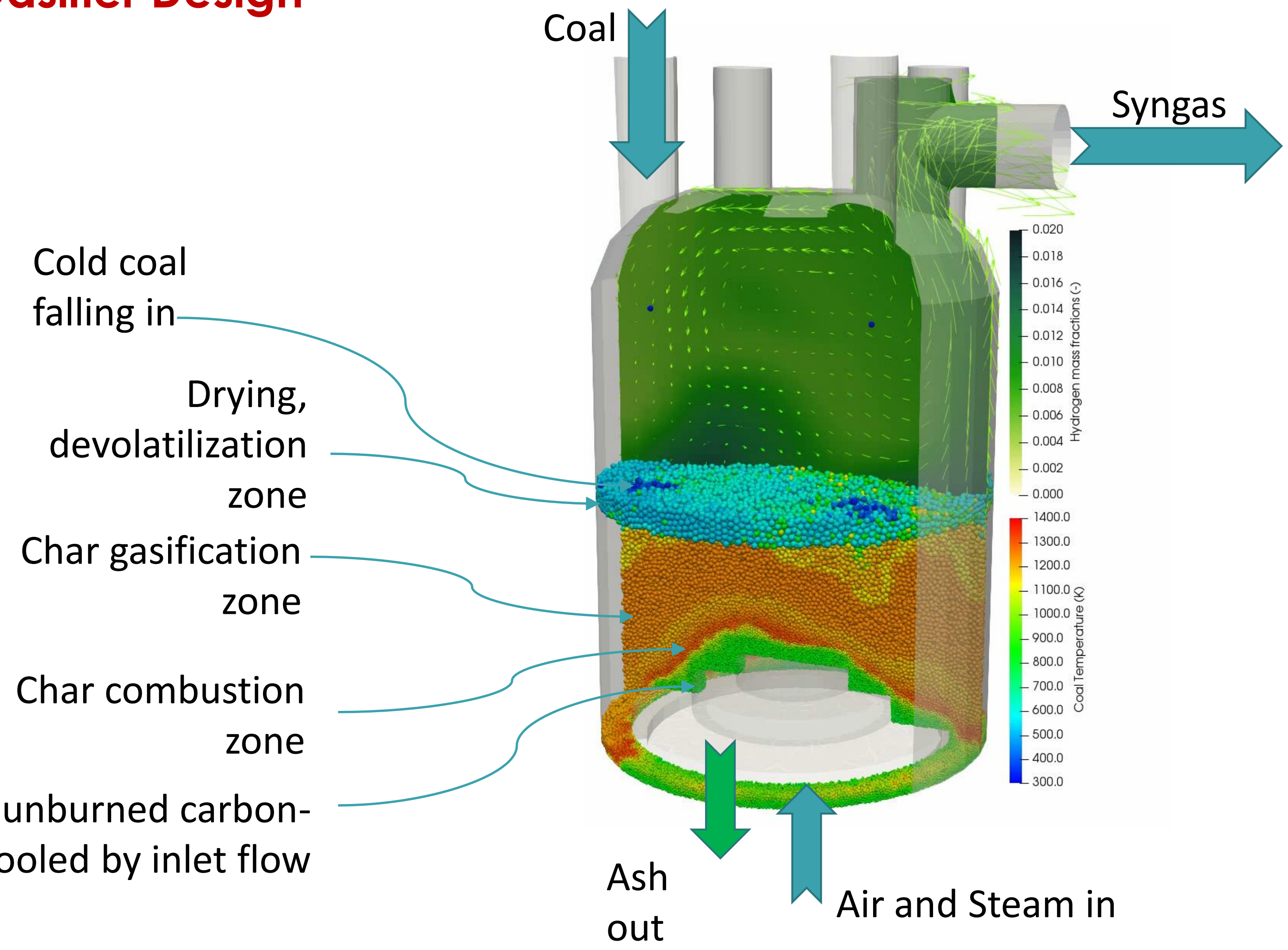
- Simulations are critical to designing next-generation advanced reactors
- Models such as MFiX rely on validation data for tuning and accuracy
- Measurement observations from inside operating gasifiers are difficult to obtain
- **Approach**: Use neutrons which interact strongly with H and weakly with metals, giving the ability to view coal pyrolysis and gasification *in situ*
- **Objective:** Obtain nonintrusive validation data from an operating gasifier, acquiring internal information and product-gas measurements to enable accurate simulations of coal gasification.

Graphics courtesy of W.A. Rogers (NETL)

An updraft, moving bed gasifier is our target design

See next presentation, “Advanced Gasifier Design” by Bill Rogers (NETL)





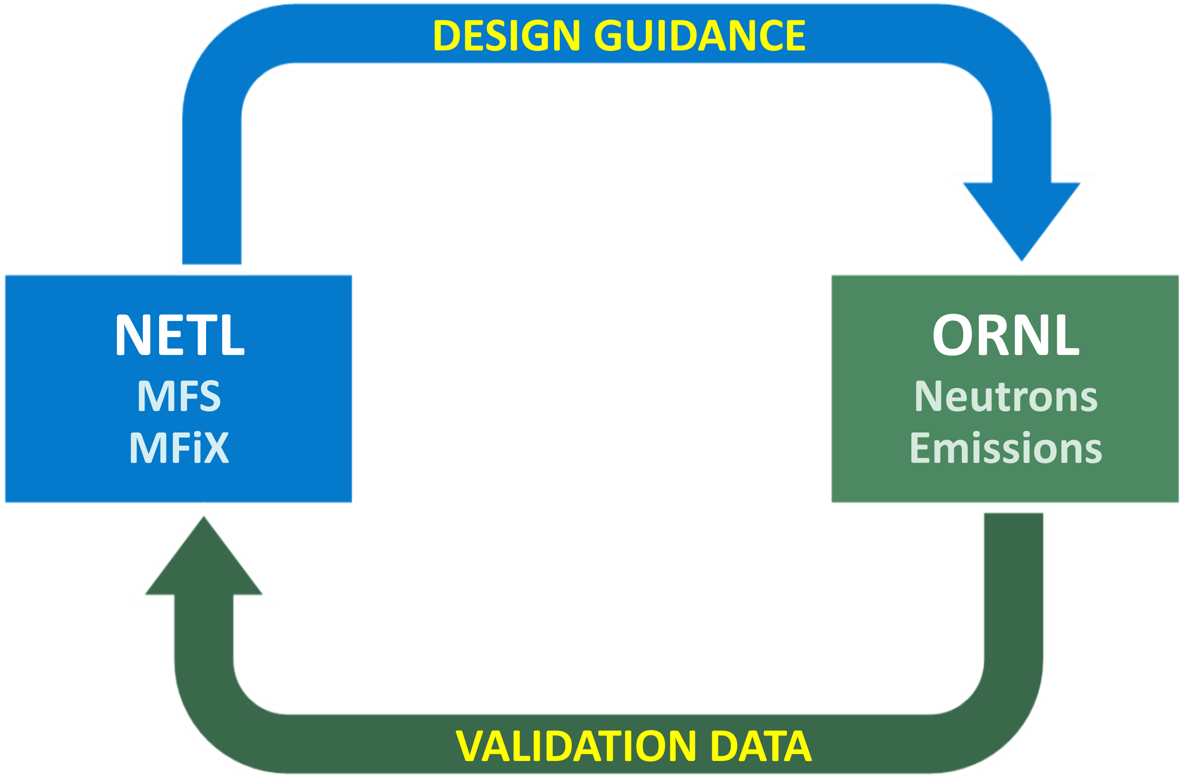
We aim to peer inside a similar reactor using neutrons to map the degree of gasification in space and time.

Graphics courtesy of W.A. Rogers (NETL)

ORNL research supports NETL in this project

NATIONAL ENERGY TECHNOLOGY LABORATORY

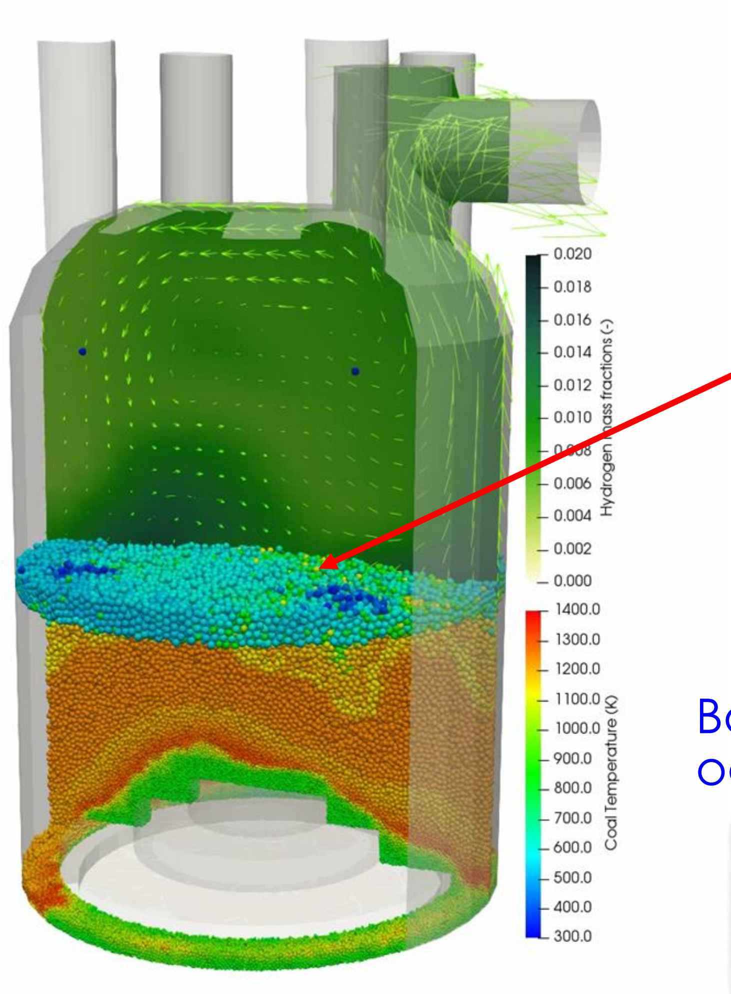
- Coal gasification expertise
- Multiphase flow experimental & computational expertise
- MFiX – Multiphase Flow with Interphase eXchange – CFD suite



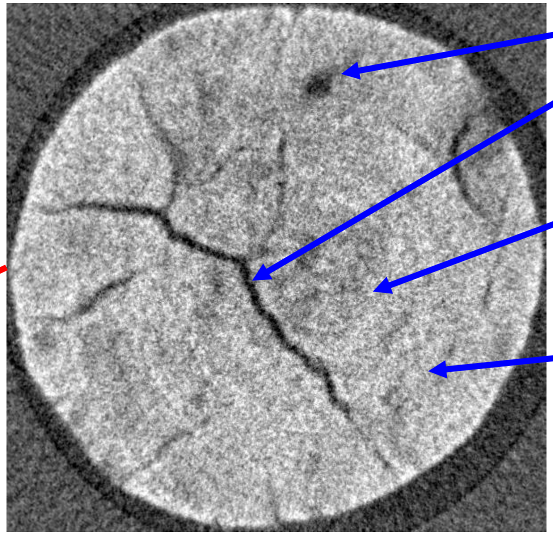
OAK RIDGE National Laboratory

- Neutron-scattering science facilities and expertise (High Flux Isotope Reactor, Spallation Neutron Source)
- Gaseous emissions facilities and expertise (National Transportation Research Center)

Science to Enable Accurate Reactor Modeling



neutron tomograph (slice)

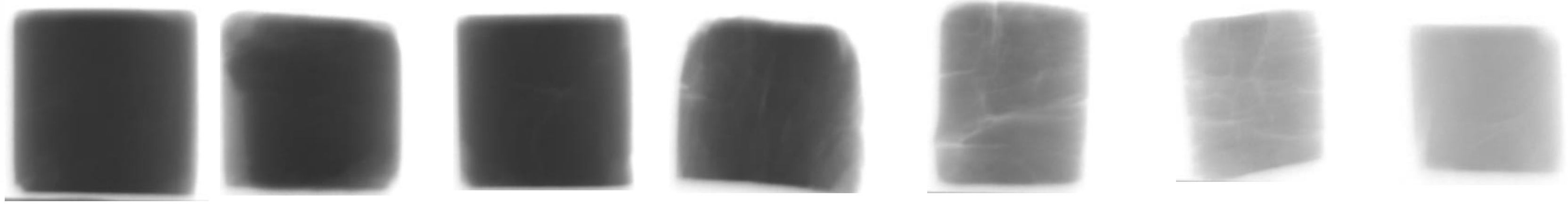


Macro pores and fissures affect mass and heat transfer in/out of particle

Microporosity/structure affect mass and heat transfer in/out of particle as well

Chemical composition affects gas product species and kinetic rates of reaction

Both physical and chemical properties of coal change as gasification occurs – the project uses advanced diagnostic tools to quantify changes



Raw 200 °C 300 °C 400 °C 600 °C 800 °C 1000 °C

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Sub-bituminous Coal Shown. Relative image sizes approximate.

Combination of Diagnostics to Capture Complete Science

Technique	On-Line/ Off-Line	Target Data	Notes on Project Timing
Proximate and Ultimate Analysis	Off-Line	Chemical composition	Ongoing (Began in Year 1)
GC-MS Pyroprobe*	**On-Line***	Hydrocarbon speciation vs. temp.	Ongoing: Year 1 results shown last year
Laser-Induced Breakdown Spectroscopy (LIBS)	Off-Line	Chemical composition by spatial location in coal sample	Small Year 2 activity - results not as promising as hoped
Nuclear Magnetic Resonance (NMR)	Off-Line	Chemical composition	Year 2 activity
B.E.T. with Porosity (Micrometrics)	Off-Line	Surface area and microporosity	Year 2 activity
SpaciMS/IR (Capillary-Based Spatio-Temporal Gas Speciation)	**On-Line**	Spatio-temporal characterization of gas species emitted vs. temp.	Progress delayed (COVID +) - will accelerate in Year 3
Neutron Attenuation and Imaging (ORNL-HFIR and NIST)	**On-Line**	Physical and chemical change of coal during pyrolysis/gasification	Focus in all project years - progressed from off-line to on-line in Year 1 thru 2
Neutron Inelastic Vibrational Spectroscopy (ORNL-SNS-VISION)	Off-Line	Non-destructive chemical composition (inside sample)	Year 2 - recent data obtained (data analysis ongoing)
Small Angle Neutron Scattering (SANS) [ORNL and NIST]	Off-Line	Non-destructive microstructure characterization	Year 2 planned experiments delayed to Q1 of Year 3 (COVID)

On-Line: dynamic, real-time *in situ* observation of pyrolysis/gasification
Off-Line: laboratory or in neutron beam not in real time, pre-pyrolyzed at different temperatures

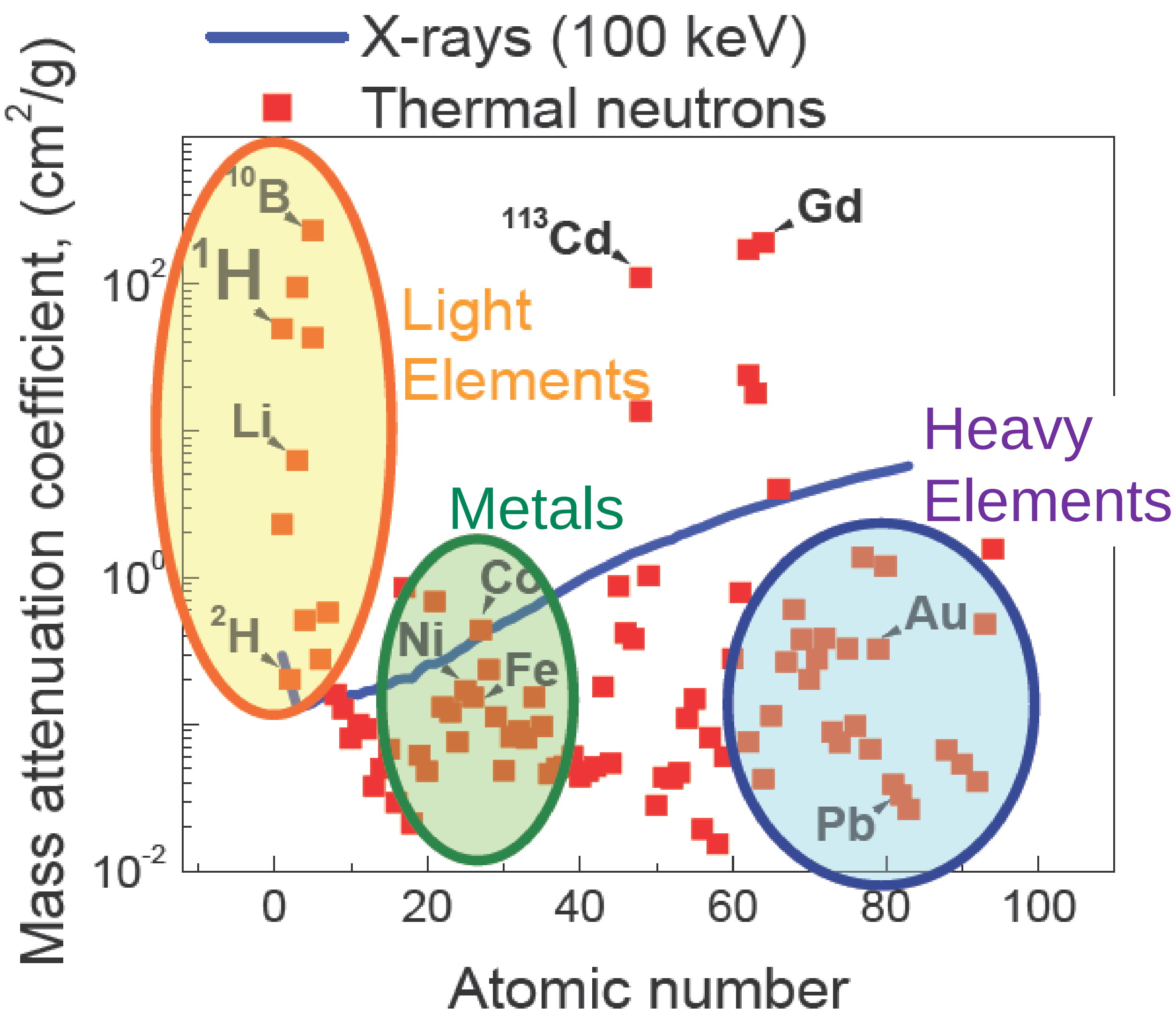
Project correlates data from more common techniques with advanced neutron techniques

*GC-MS=Gas Chromatography-Mass Spectrometry; pseudo On-Line technique allows on-line sampling of very small sample size (not spatial specific) then direct port of gas emitted to GC-MS for speciation

Neutron-Based Research

- Center for Neutron Research at the National Institute of Standards and Technology
- High Flux Isotope Reactor at Oak Ridge National Laboratory
- Spallation Neutron Source at Oak Ridge National Laboratory

Neutron-scattering measurements match our process well



Neutron interaction with light elements is why neutron imaging is a suitable diagnostic to view pyrolysis and gasification *in situ*. We have demonstrated utility and are refining technique.

Neutron attenuation for H >> attenuation for C

N. Kardjilov's presentation at IAN2006
http://neutrons.ornl.gov/workshops/ian2006/MO1/IAN2006oct_Kardjilov_02.pdf

Coal samples

Various samples of coal were acquired to determine suitability for neutron studies and for design of the experimental apparatus.

Sample	Rank	Source	Carbon [1] [wt %]	Moisture [2] [%]	Mass loss [3] [%]
A	Anthracite	Reading Coal Company (PA)	87–98	3	5
B	Bituminous	Blue Gem / Straight Creek (Pineville KY)	77–87	1	42
C	Bituminous	Pittsburgh #8	77–87	1	42
D	Sub-bituminous	Monarch PRB (Sheridan WY)	71–77	19	45
E	**Lignite**	Center Coal Mine (Center ND)	60–70	29	52
U	**Sub-bituminous**	Usibelli Coal Mine (Healy AK)	70 [4]	29 [4]	

[1] From USGS dry, mineral-content-free basis.
[2] Based on weights as-received and after desiccation.
[3] Based on weights after desiccation and pyrolysis in argon at 1000 °C.
[4] Usibelli Coal Mine.

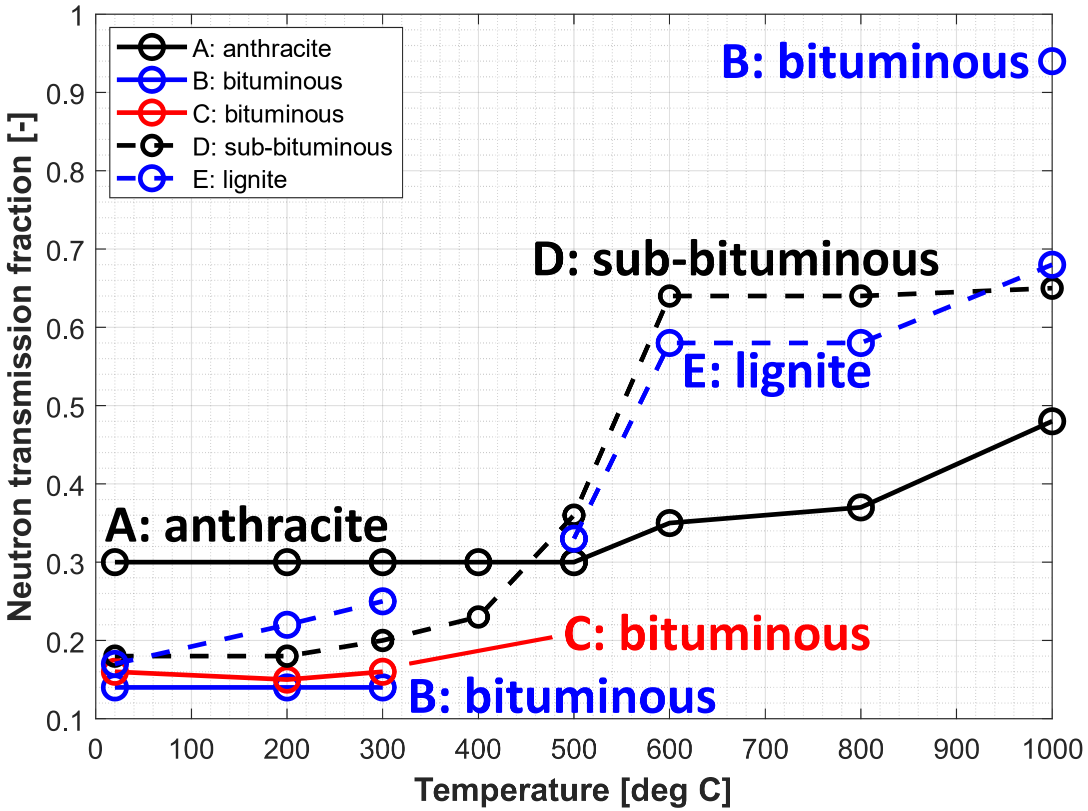
Current (Year 2) focus

Usibelli coal was obtained in April and added to ORNL studies.

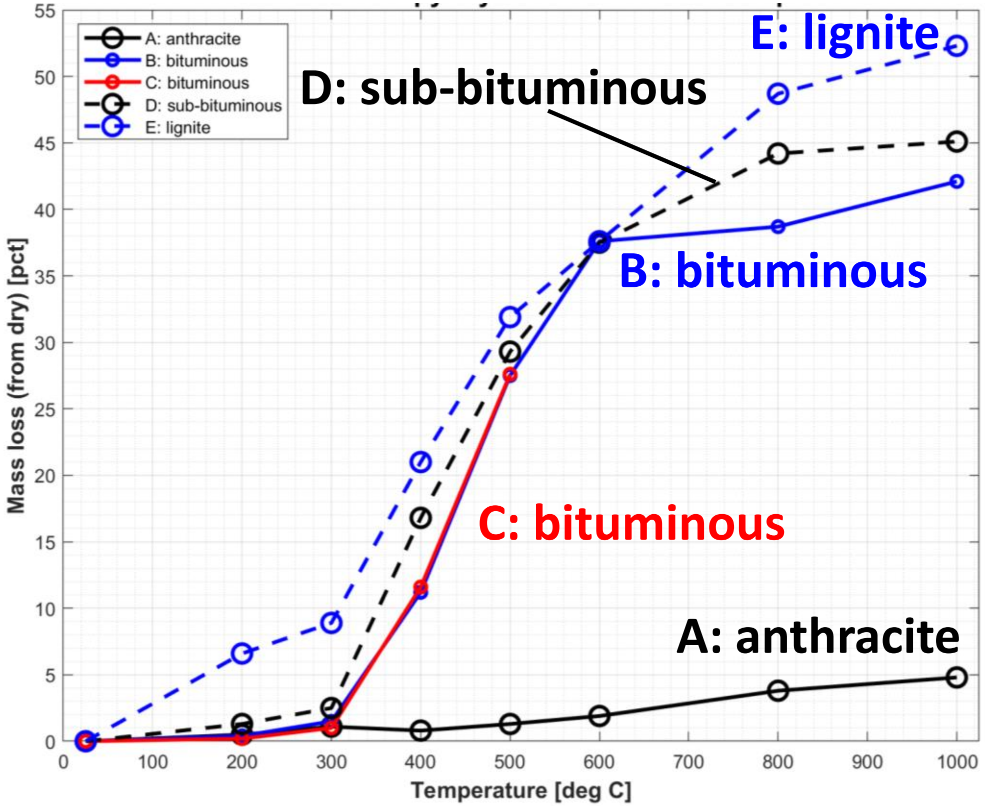
Mass loss correlates with neutron attenuation, which varies with degree of pyrolysis.

Neutron transmission increases with degree of pyrolysis

Neutron transmission / ~cm



Mass loss



Neutron interactions follow rough trends with mass loss, but there is a complex relation dependent on the pyrolysis chemistry.

Analytical chemistry characterization enables correlation of chemistry and neutron attenuation data

These data provide guidance for gasifier design and experiments in the neutron beam.

Summary of neutron experiments

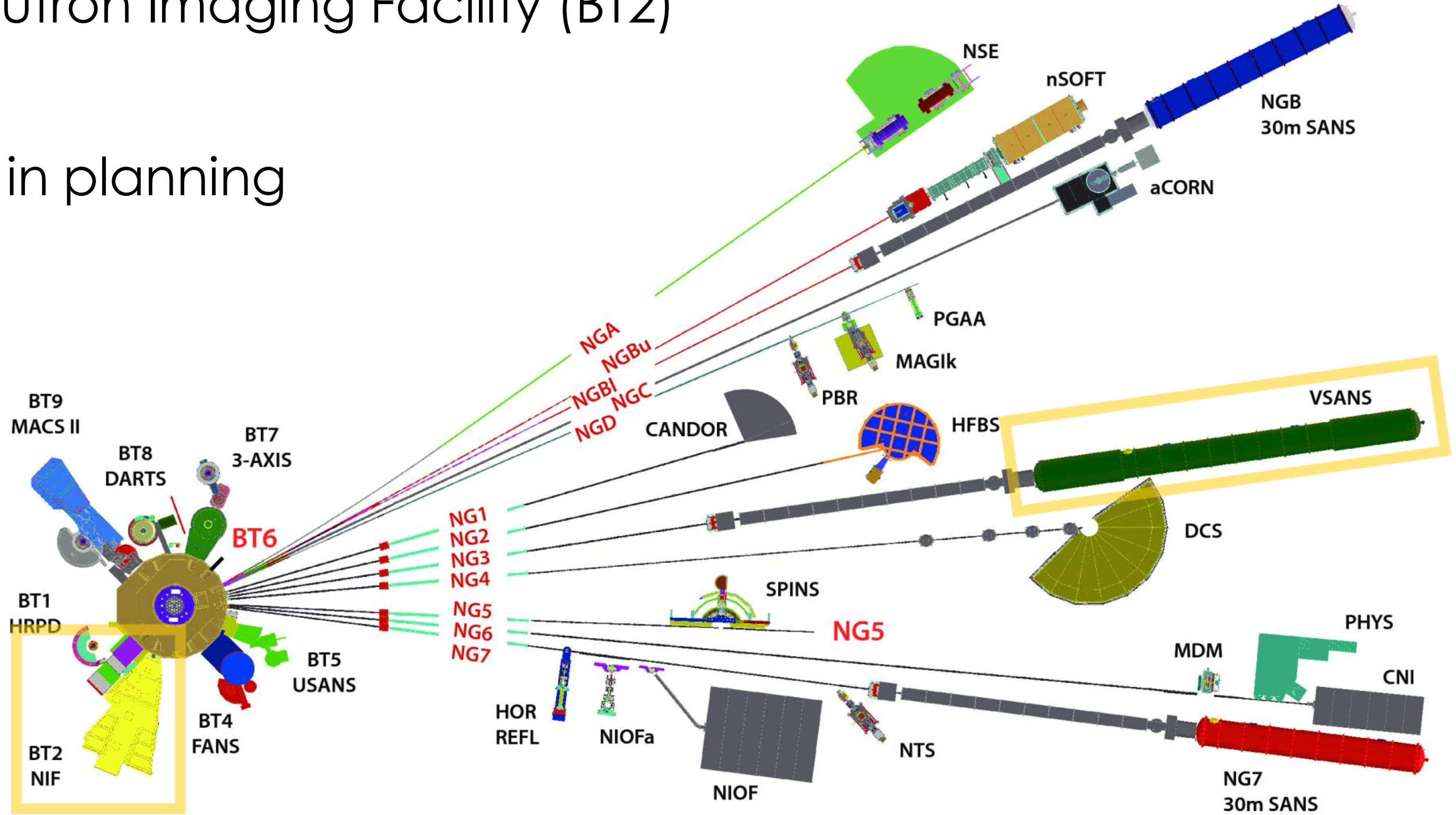
Dates	Facility	Beamline	Samples
February 2019	NIST CNR	BT2 NIF	**Coal** (anthracite, bituminous(2), sub-bituminous, lignite), pre-pyrolyzed
August 2019	NIST CNR	BT2 NIF	Dynamic *in situ* pyrolysis of **poplar** – 2 solid cylinders, 2 beds of solid rods; CTs (reduced scope because of site delay)
November 2019	ORNL HFIR	CG-1D	Dynamic *in situ* pyrolysis of 2 beds of **lignite**
July 2020	ORNL SNS	VISION	Vibrational spectroscopy of **lignite** and **Usibelli**, pre-pyrolyzed
2020a (awarded)	NIST CNR	BT2 NIF	Dynamic *in situ* pyrolysis of **coal** (anticipated: FY2021Q2 – COVID-19 restrictions)
2020a (awarded)	NIST CNR	vSANS	**Coal**, pre-pyrolyzed (anticipated: FY2021Q1 – COVID-19 restrictions)
2020b (awarded)	ORNL HFIR	CG-1D	Dynamic *in situ* **gasification** of **coal** (anticipated: FY2021Q2 – COVID-19 restrictions)

We have demonstrated the utility of neutron imaging and are now refining and calibrating the methodology.

NIST Center for Neutron Research (NCNR) (Gaithersburg MD)

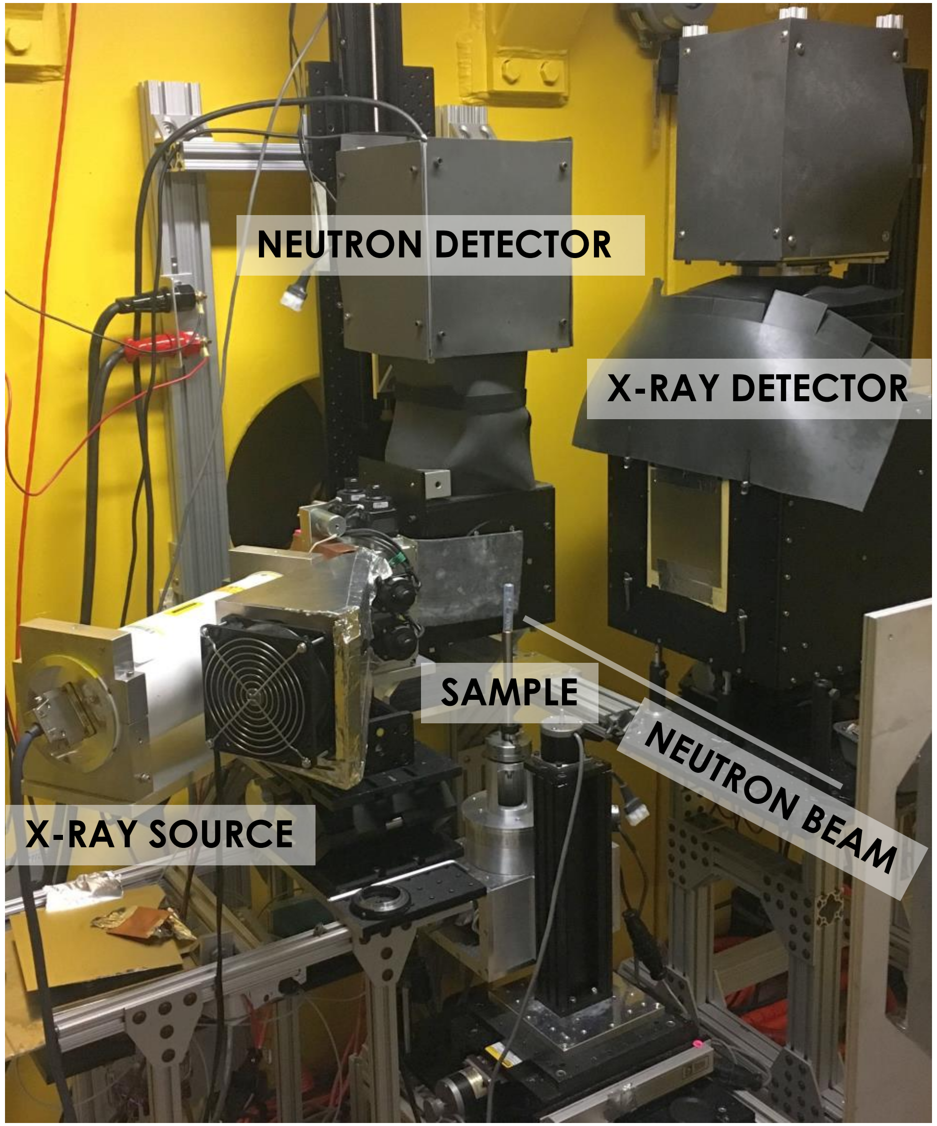
- NeXT – simultaneous neutron and X-ray tomography available at the Neutron Imaging Facility (BT2)

- vSANS experiments in planning

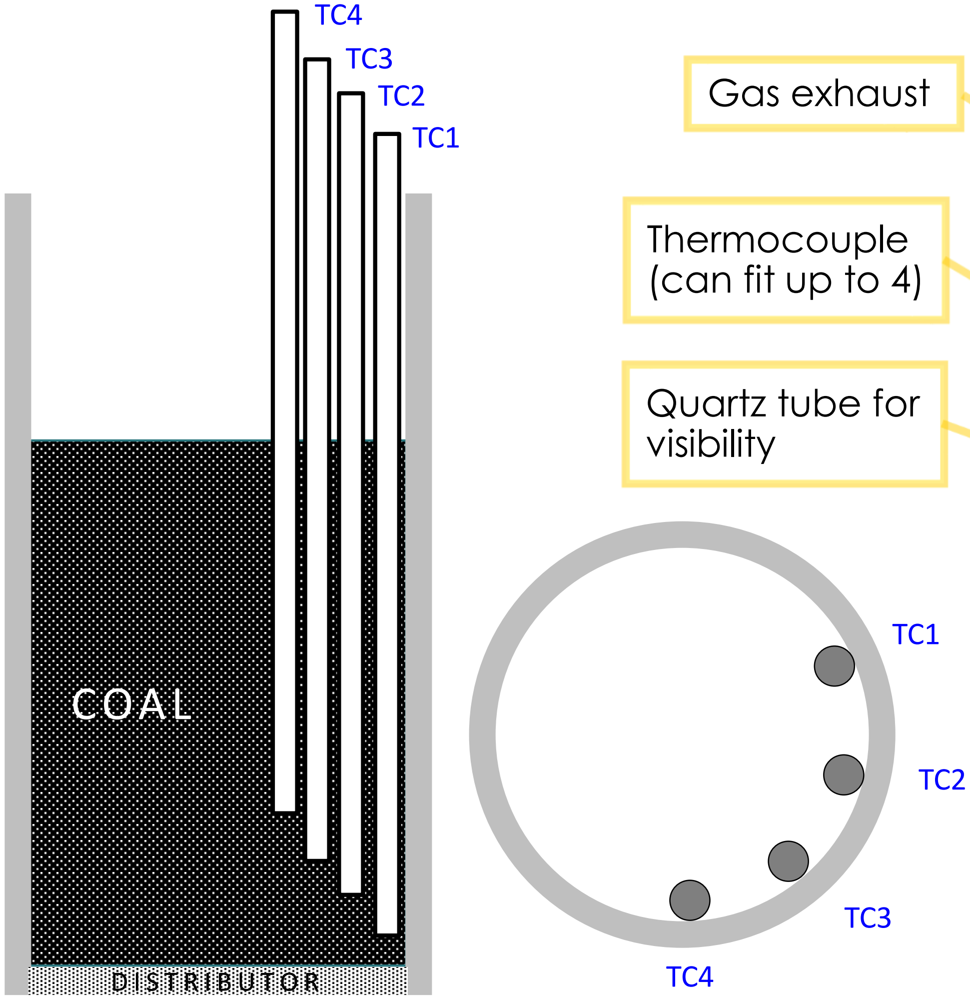


Overview of NCNR experiments

- February 2019 – **to gauge neutron response**
  - Samples A–E, pre-pyrolyzed at 200, 300, 400, 500, 600, 800, 1000 °C
  - Imaging
    - Radiography – 2D maps of transmission through samples
    - Tomography – neutron and X-ray CT for 3D maps of sample sets B and D
- August 2019 – **to dynamically detect pyrolysis**
  - Poplar cylinders (lignite was postponed)
  - Dynamic radiography at slow heating rate to view drying & pyrolysis fronts

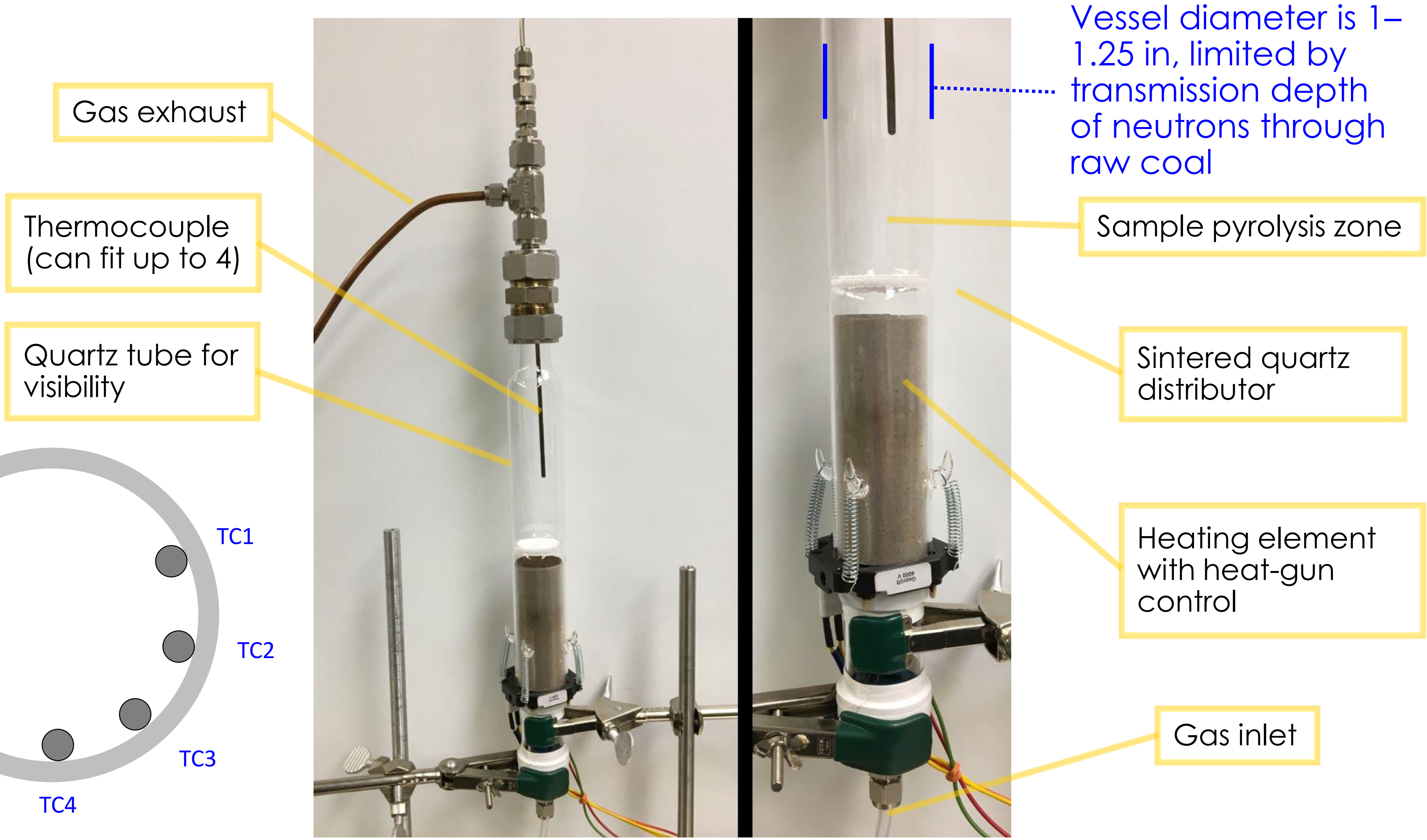


A portable pyrolyzer is used for both neutron & laboratory work



SIDE VIEW

TOP VIEW

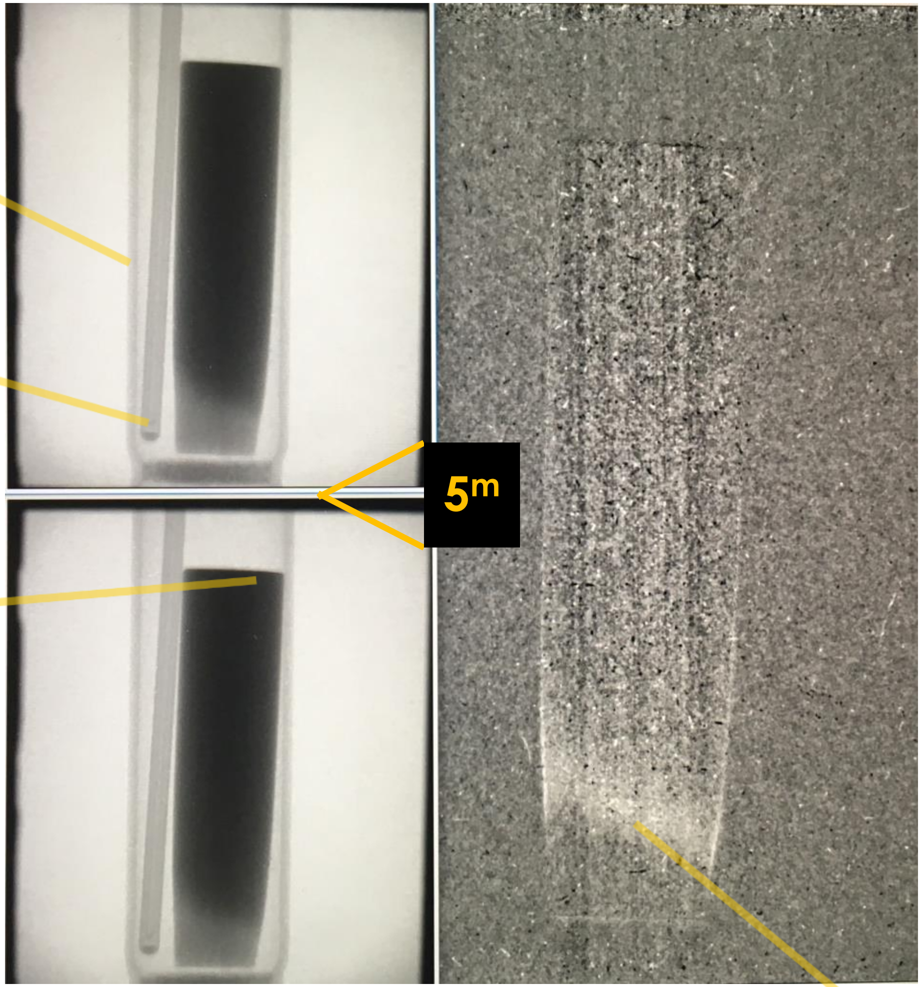


Pyrolysis of poplar dowel shows clear pyrolysis front

Quartz tube wall

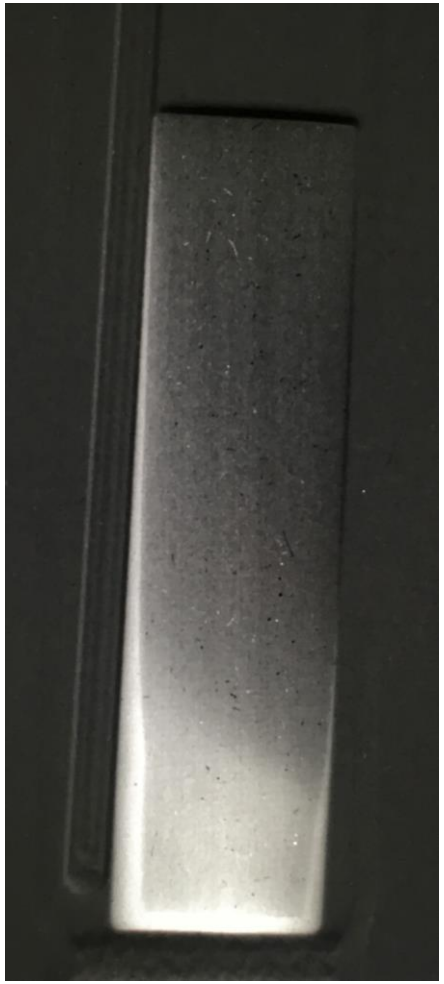
Thermocouple

Sample pinned against tube wall by TC

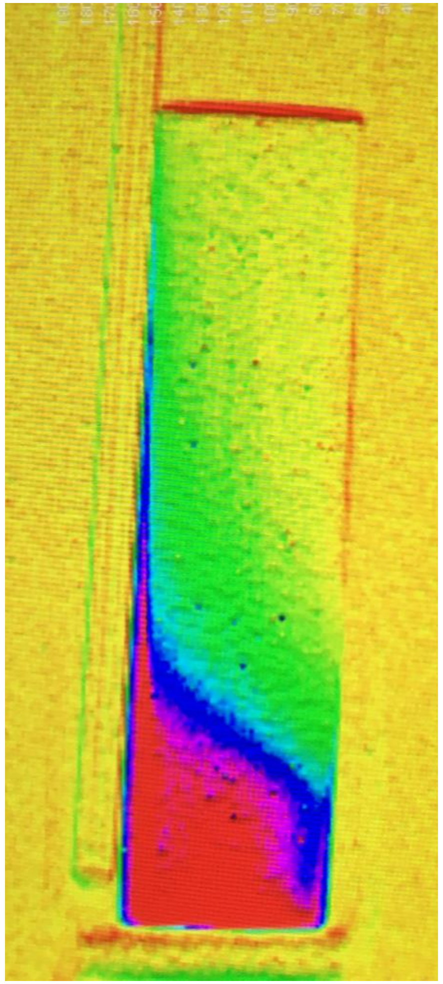


Lagged-difference normalization showing pyrolysis front

Pyrolysis front at angle, reflecting sample tilt



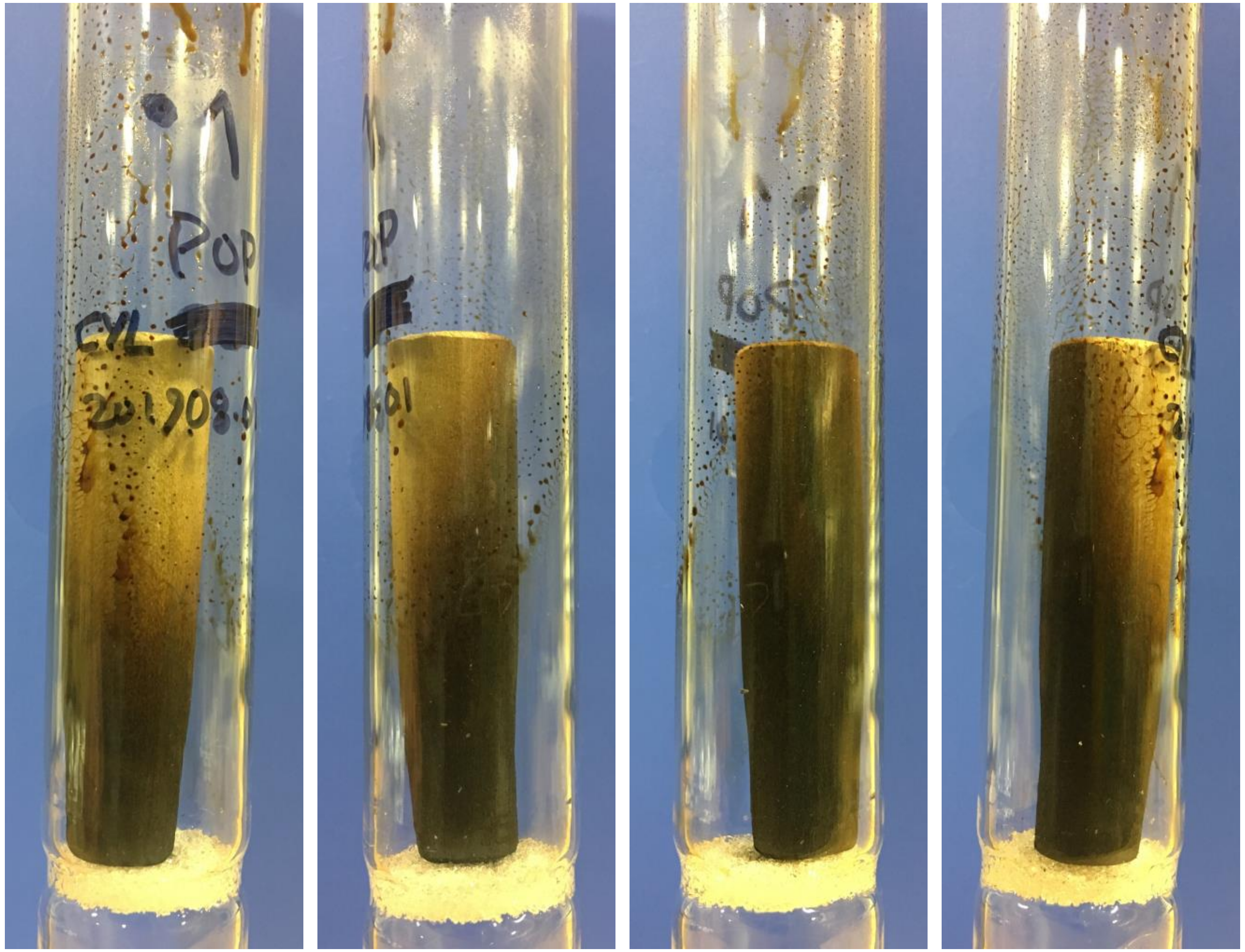
Lagged-difference normalization showing before & after differences



False-color rendering

D=12, H=50 mm

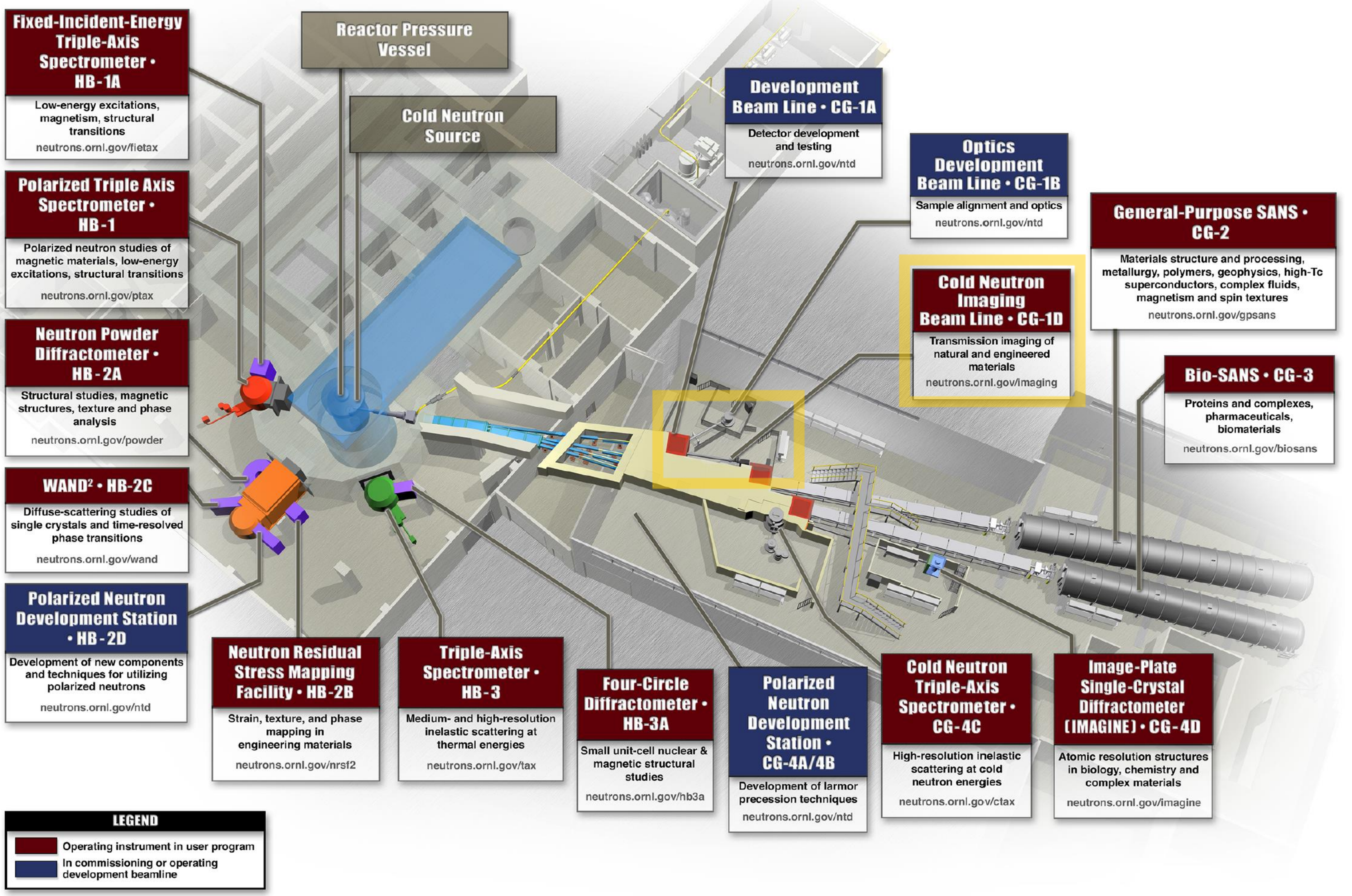
Poplar dowel shows asymmetric pyrolysis seen in neutron images



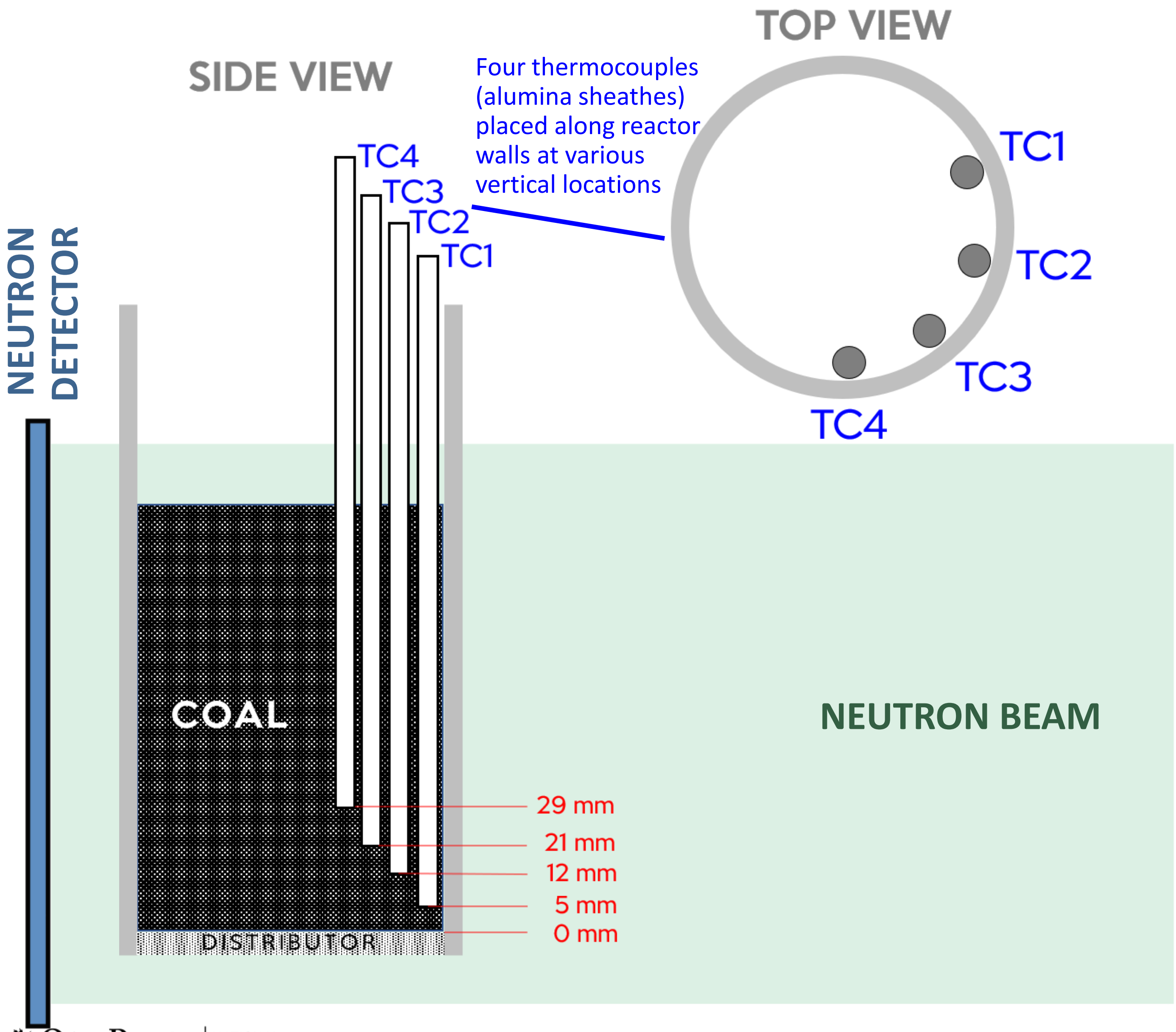
After – 4 rotations

High Flux Isotope Reactor (Oak Ridge National Laboratory)

- Highest flux reactor-based source of neutrons for research in the US
- Imaging Beamline (CG-1D)



HFIR – *in situ* real-time imaging of coal pyrolysis

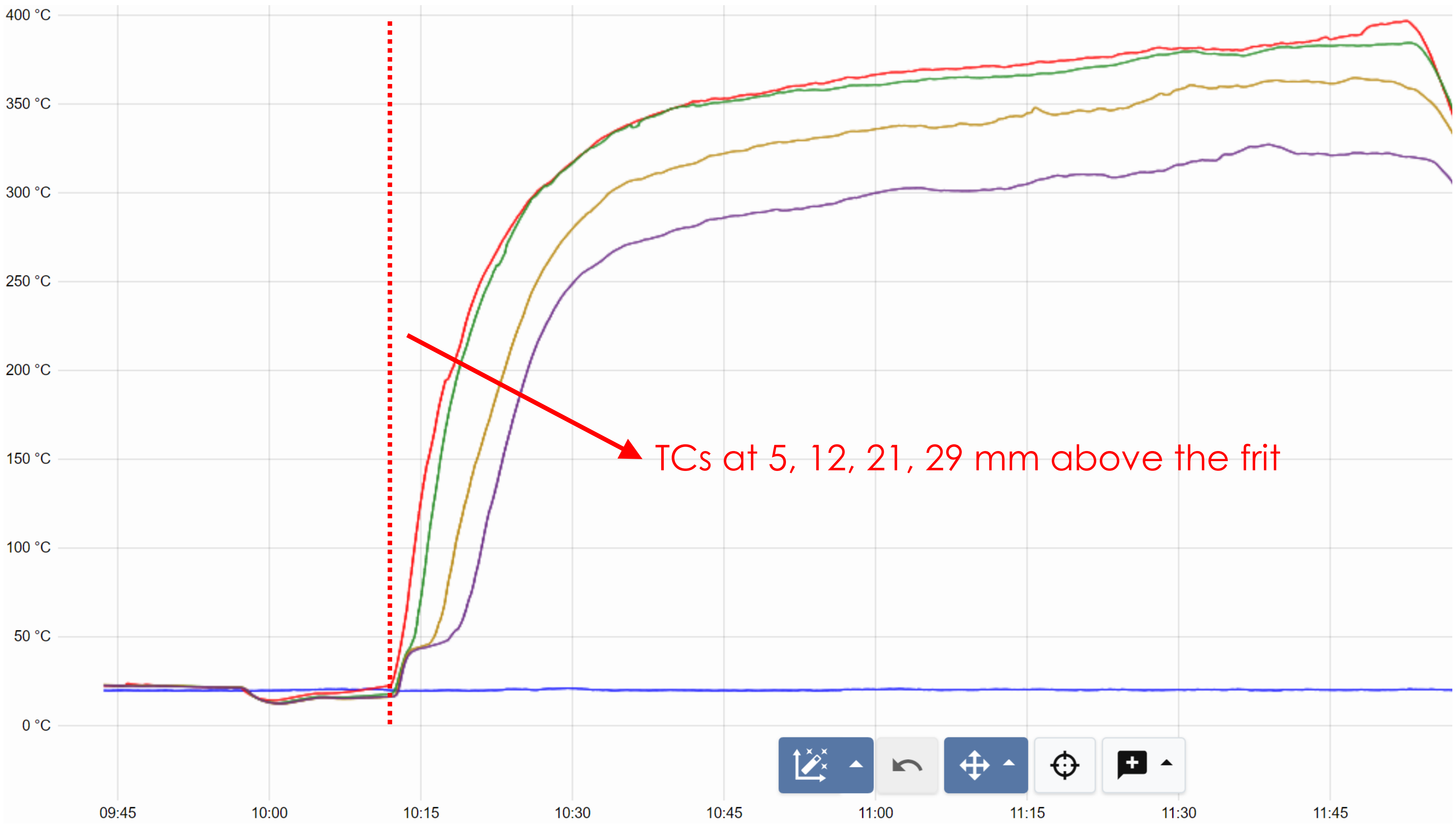


- Nonintrusive measurements for model validation
  - 2D map of gasification progress – transmitted neutrons projected onto detector screen
- Lignite
  - Sieved to 1000 – 2360 µm (8×18)
  - Low sphericity
- Type K exposed-junction thermocouples placed along reactor walls at various heights to estimate axial temperature profiles over time
- N_2 inert sweep gas
- Tube wrapped in Al foil for containment and to reduce radiative losses

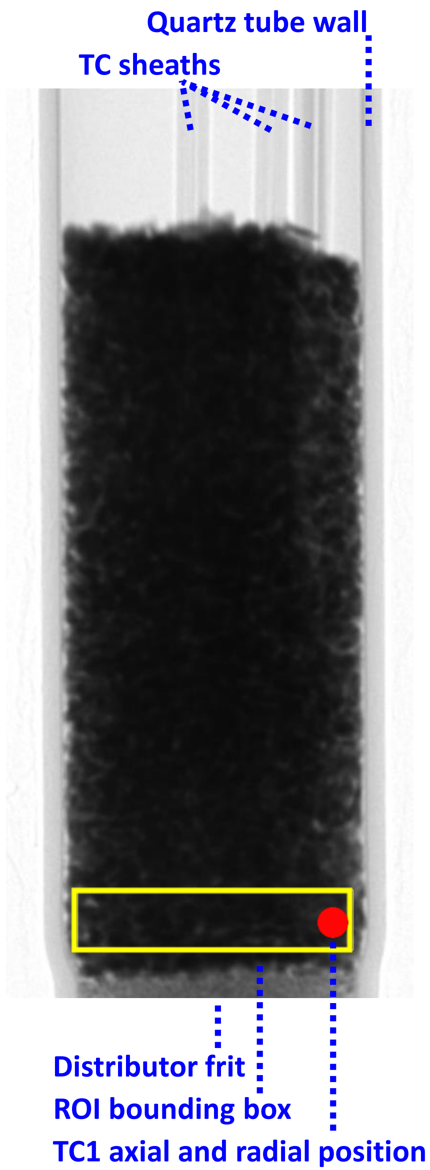
HFIR – lignite bed – transmission radiographs

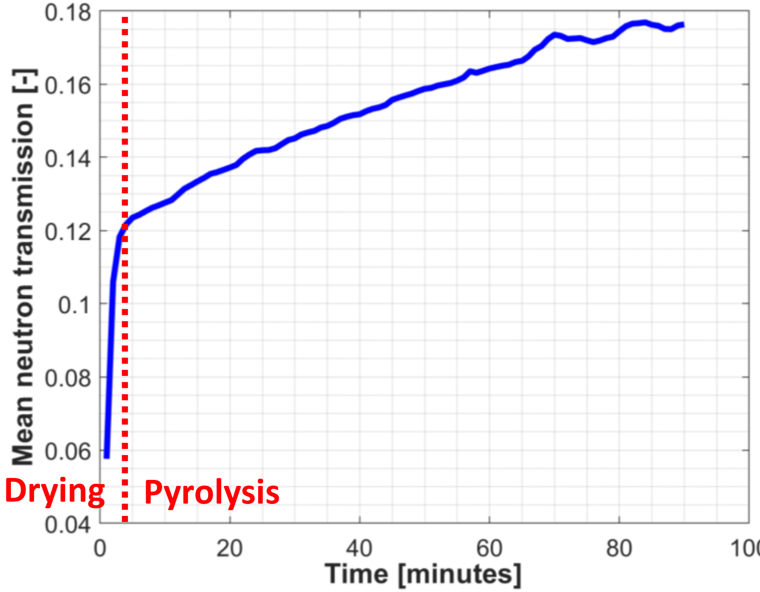
- Movie shows the neutrons transmitted through the coal bed over time, along with a 5-minute difference map
- Reaction rates, based on heat input, slowed down to see changes using 1-minute neutron exposures – can speed up as needed
- Experiment terminated due to time
- Takeaways:
  - Progressive pyrolysis is seen during the experiment – proof of principle
  - Bed settling will need to be accounted for or a continuous feed system implemented

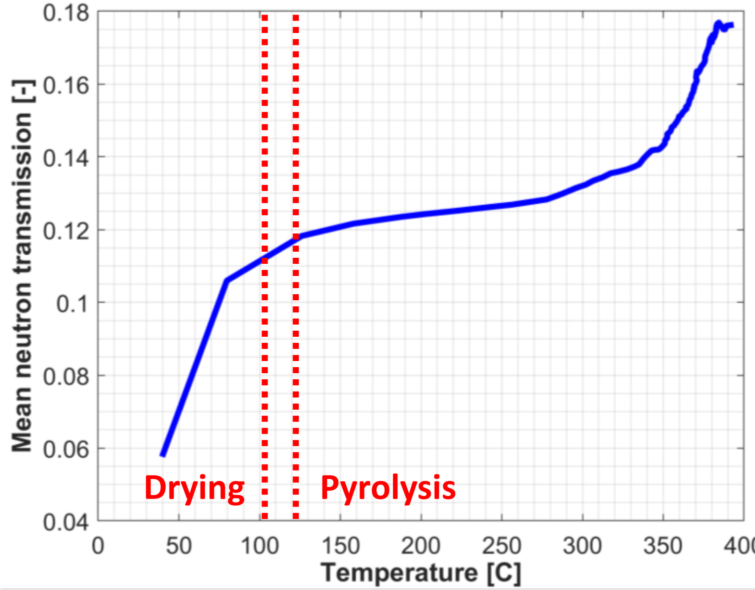
HFIR – lignite bed – temperature measurements



HFIR neutron transmission shows drying & pyrolysis stages



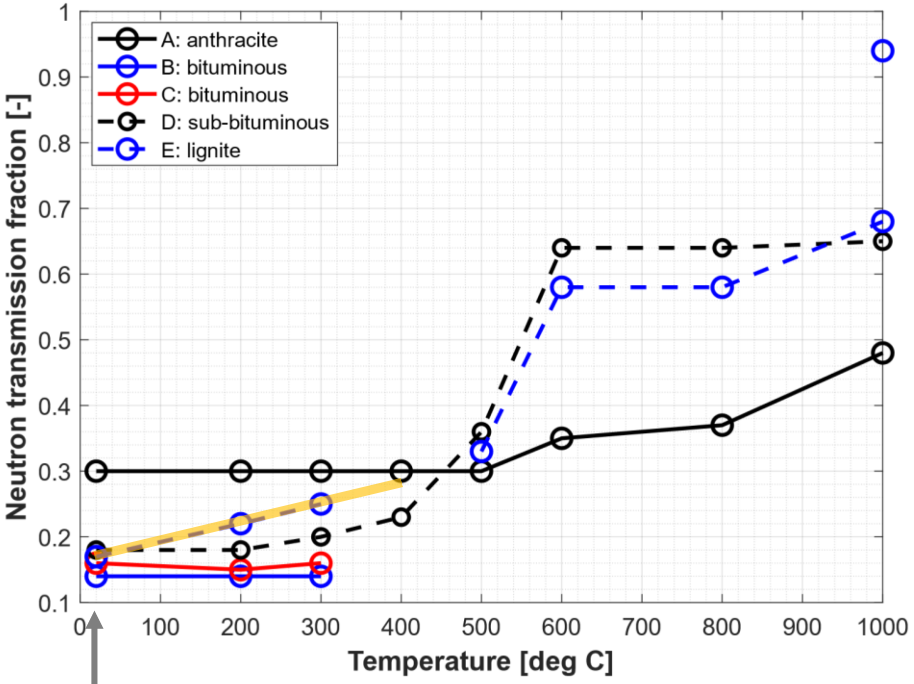




Path-length corrections in progress

Compare

Compare with neutron transmission changes in 20–400 °C range

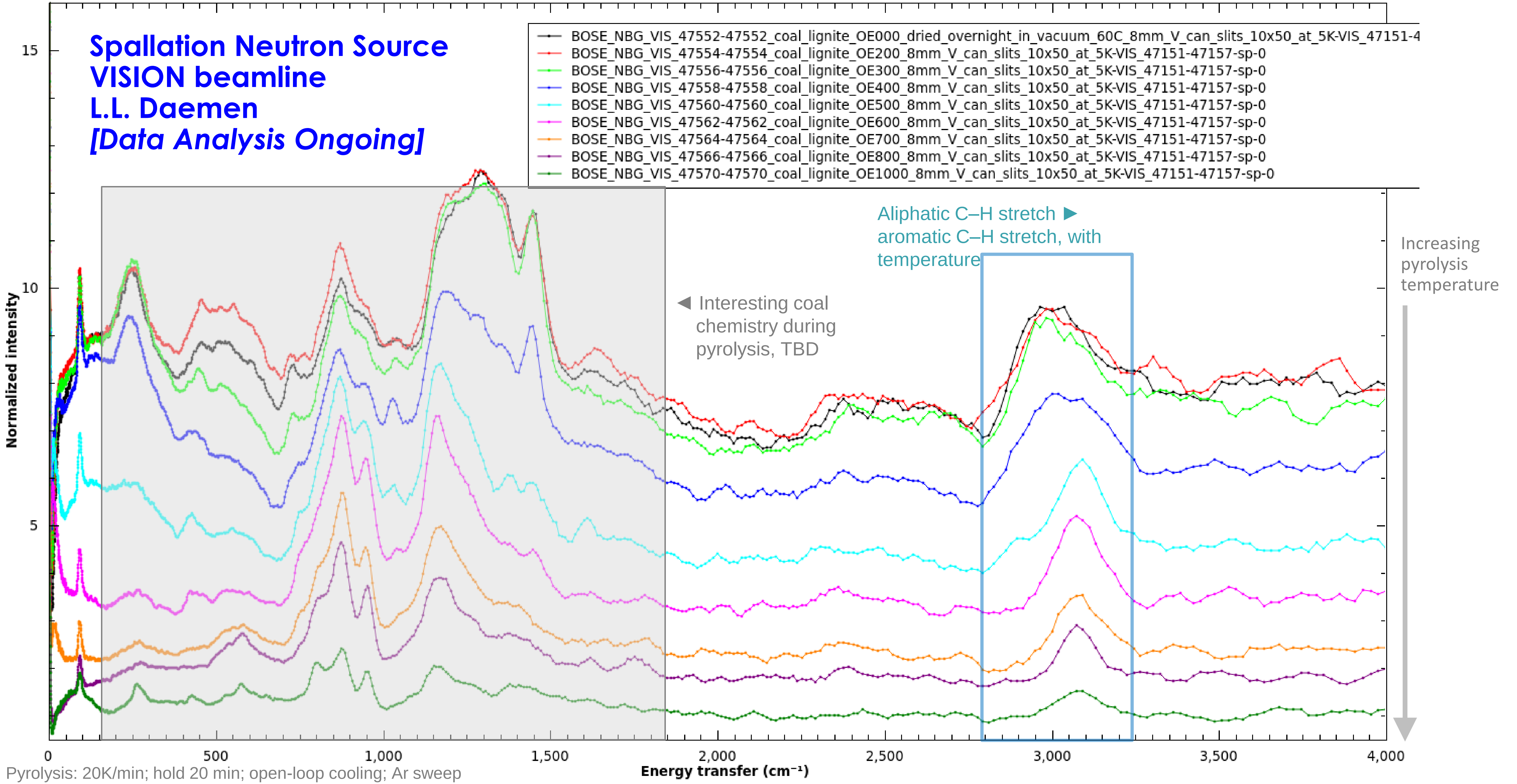


Note: room temperature data on this plot from post-dried samples

Recent and Emerging Coal Characterization with Neutron Techniques

- Vibrational spectroscopy (chemistry)
- Porosity and Microstructure

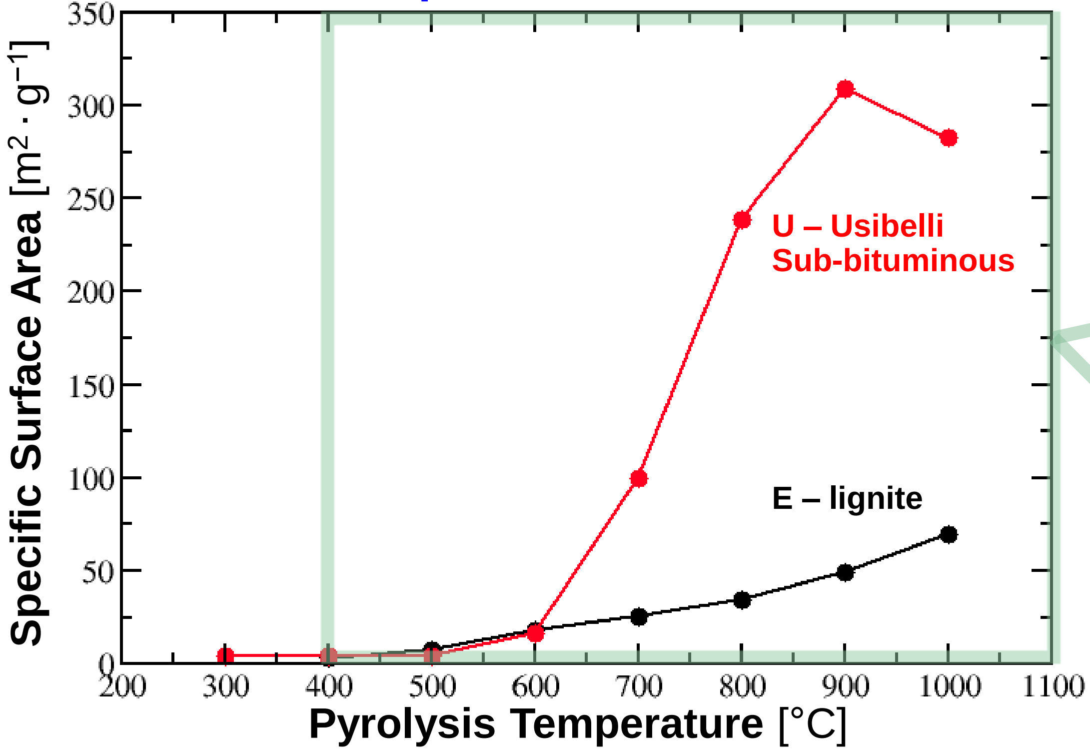
Neutron vibrational spectrographs show how lignite molecules degrade with pyrolysis



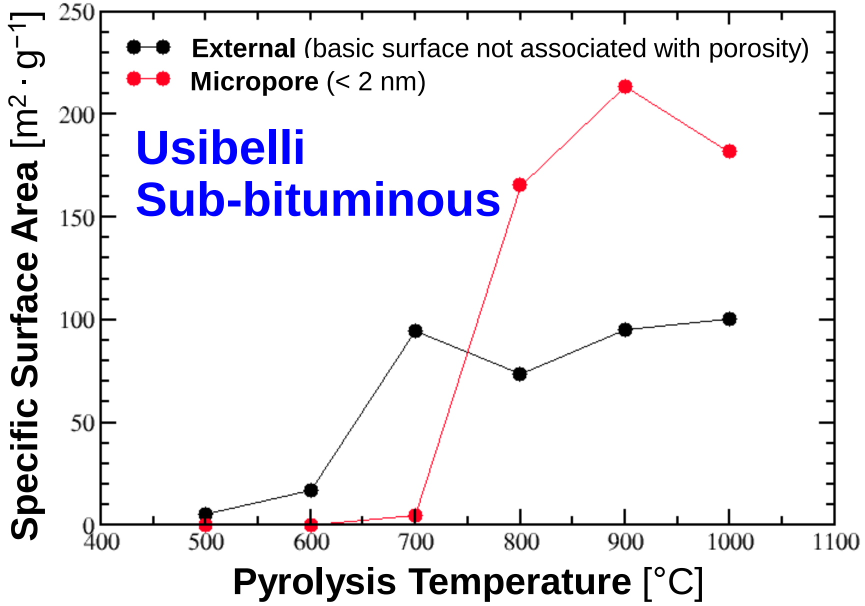
Pyrolysis: 20K/min; hold 20 min; open-loop cooling; Ar sweep

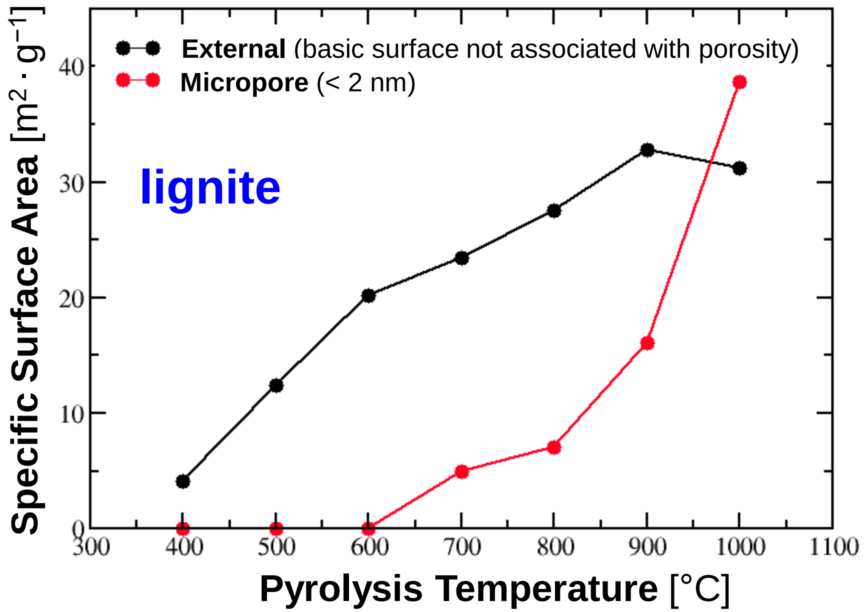
Coal porosity changes significantly with pyrolysis temperature

Total specific surface areas



Decomposed specific surface areas





- **Off-Line B.E.T. data shown**
- **Neutron-based experiments planned for next quarter**
  - **A complete mapping with Small Angle Neutron Scattering (SANS) will improve knowledge of coal structure under pyrolysis.**

BET from Micromeritics Gemini VII
t-plot analysis based on Harkins-Jura equation
Pyrolysis: 20K/min; hold 20 min; open-loop cooling; Ar sweep

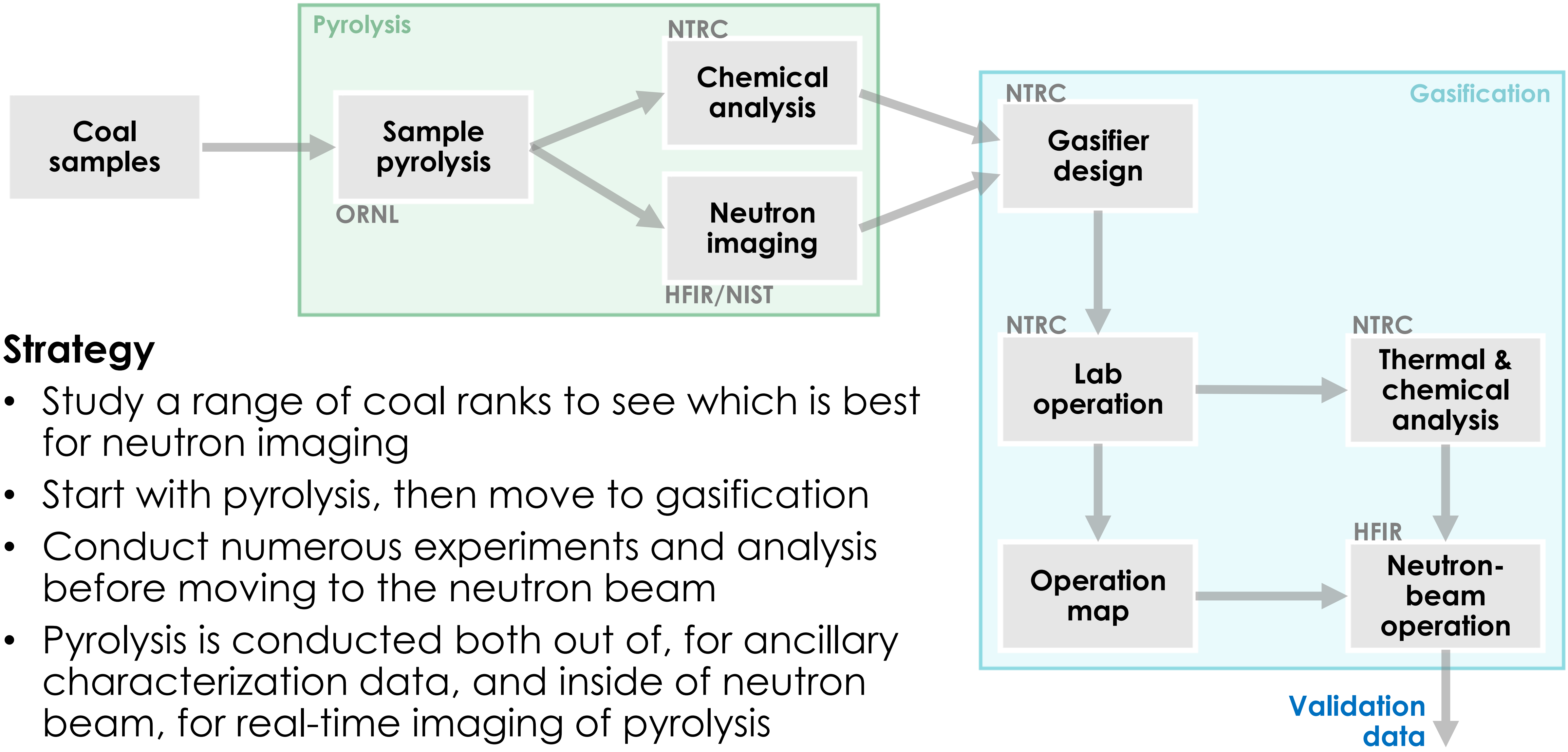
Summary

- Neutrons offer ability to see into reactor and observe gasification process *in situ*
  - Complex relationship of neutron attenuation and mass loss
    - Dedicated experiments using multiple analytical chemistry techniques under controlled conditions enable mapping neutron attenuation data to chemical changes in the coal
  - Preliminary comparisons between neutron-based results and lab techniques made
    - Will continue to compare/contrast/correlate to provide greater understanding (and to enable identification of critical characteristics for modeling)

- Plans moving forward:
  - Work is progressing from pyrolysis to gasification
  - Continue *in situ* neutron studies (lots of progress on technique, get more data)
  - Investigate SANS technique for porosity characterization (next Q)
  - Add gaseous emission data

Backup Slides

This project employs an incremental approach



Strategy

- Study a range of coal ranks to see which is best for neutron imaging
- Start with pyrolysis, then move to gasification
- Conduct numerous experiments and analysis before moving to the neutron beam
- Pyrolysis is conducted both out of, for ancillary characterization data, and inside of neutron beam, for real-time imaging of pyrolysis