Biochar for Sustainable Resource Recovery and Remediation

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EPSRC

Pioneering research and skills

Environmental and Remediation

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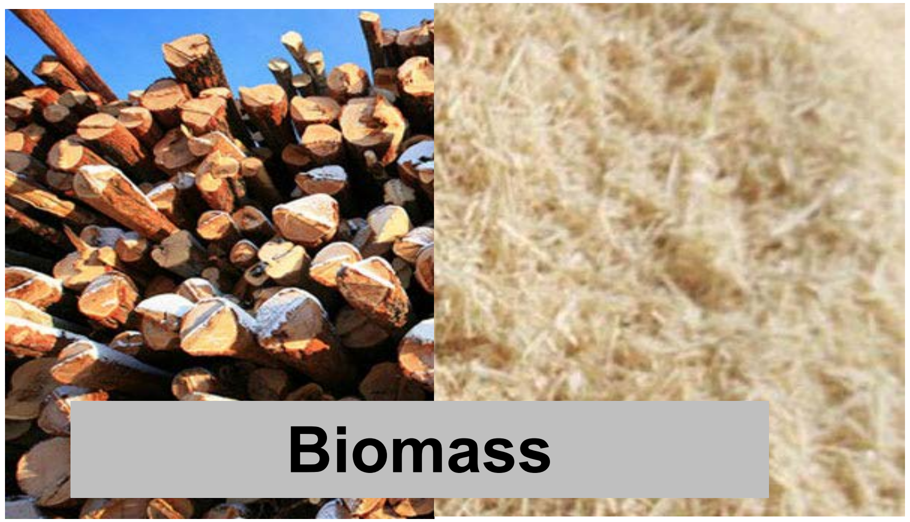
GCRF

Global Challenges Research Fund

Waste for contaminant immobilization and resource recovery?

Sewage Sludge/Urban Waste

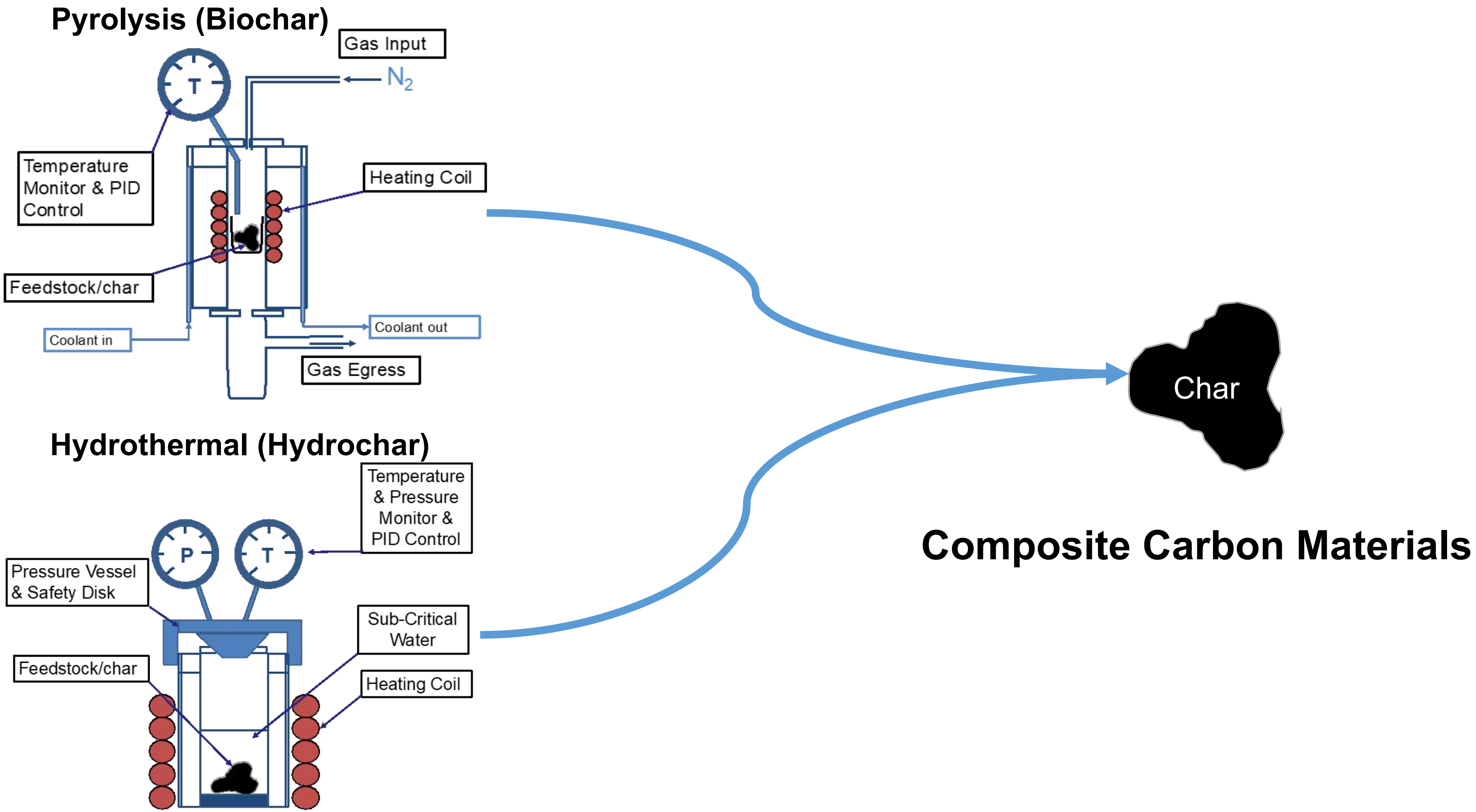
Agricultural Waste



Biomass

Plastics

Technologies for Feedstock Conversion



Composite Carbon Materials – Sustainable Applications

Energy Production:
- Pyrolysis & Gassification
- Advanced Combustion

Waste Management:
- Sustainable waste disposal
- Bioenergy from wastes

Climate Change Mitigation:
- Soil Carbon Sequestration
- Bioenergy production

Agriculture & Horticulture:
- Soil Improvement
- Land Remediation
- Livestock Feed

Sorbents & Remediation:
- Land Remediation
- Toxic cleanup
- Recovery of precious material

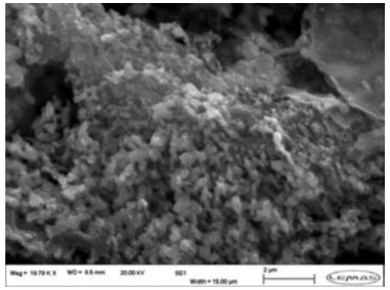
Manufacture & Other uses:
- Fuel Cells
- Catalysis
- Building Materials
- CO2 sequestration etc etc…

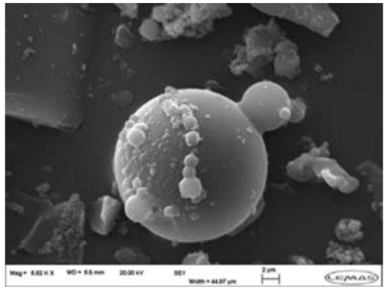
Understanding fundamental chemical properties of chars

What is the Carbon chemistry of chars?

Biochar

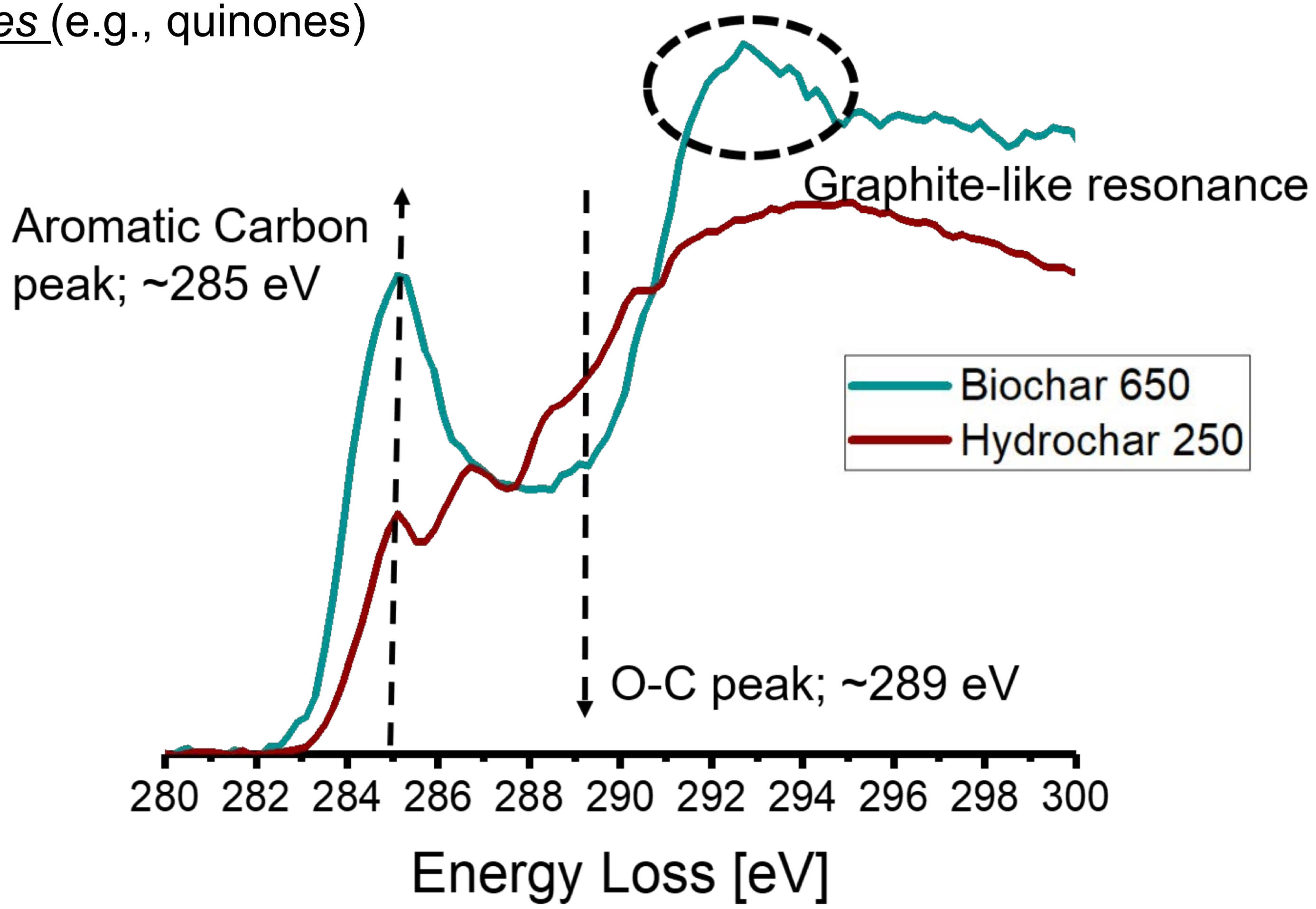
- ❑ Mostly aromatic carbon, including *electron shuttles* (e.g., quinones)
- ❑ Surface vs. bulk chemistry may be very different.



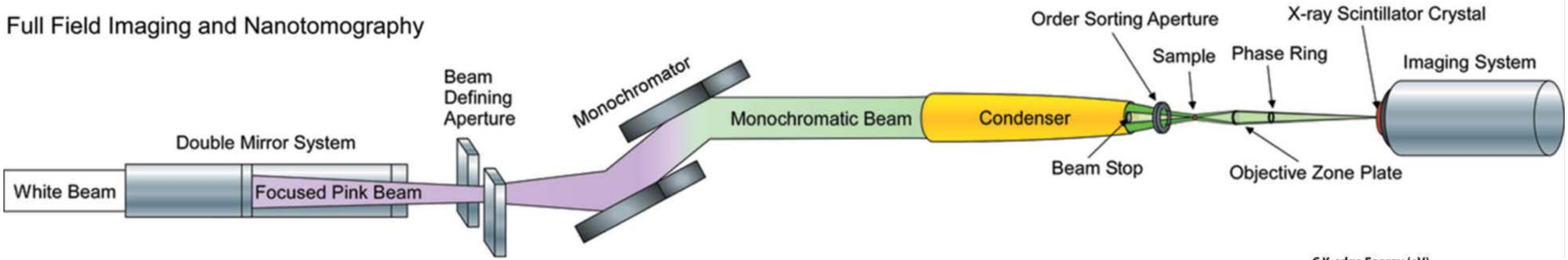


Hydrochar

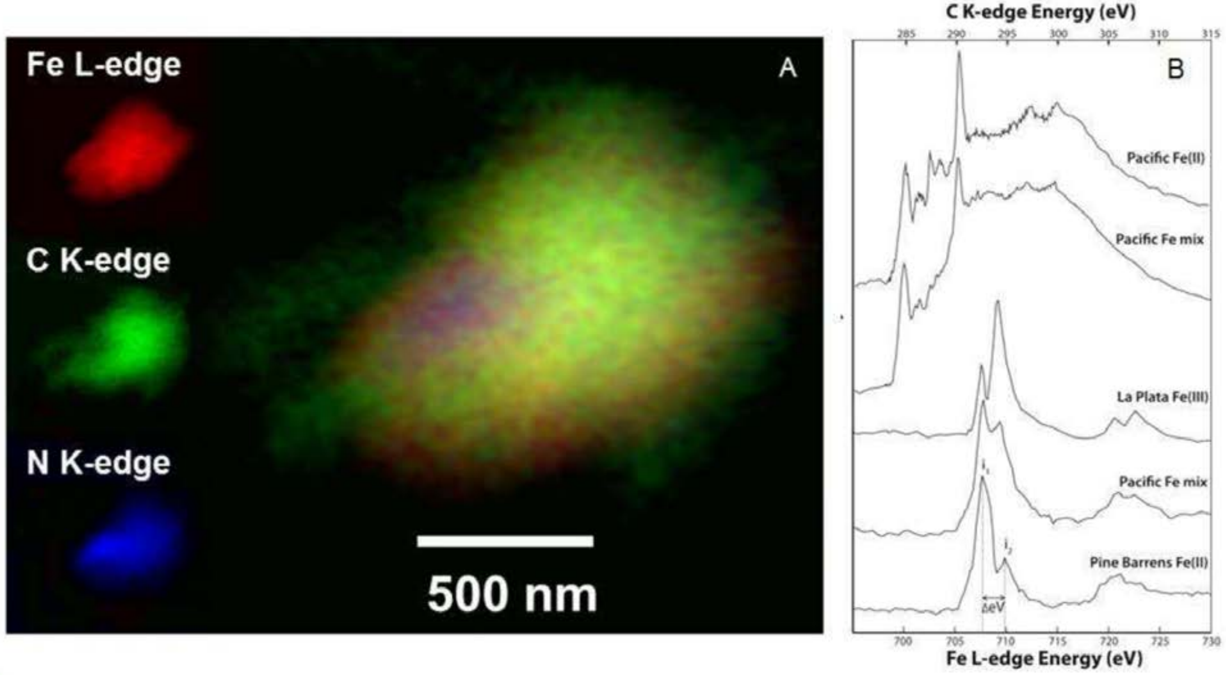
- ❑ High Molecular Mass
- ❑ Complex Oils on Surface



Surface Carbon Chemistry

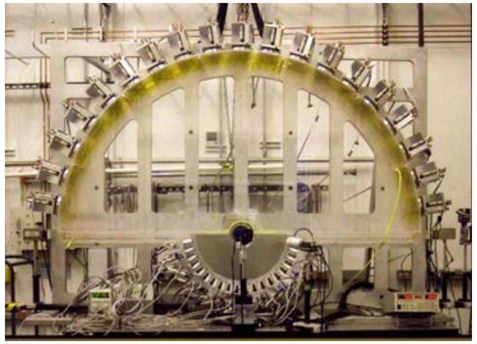


~ 30 - 40 nm spatial resolution

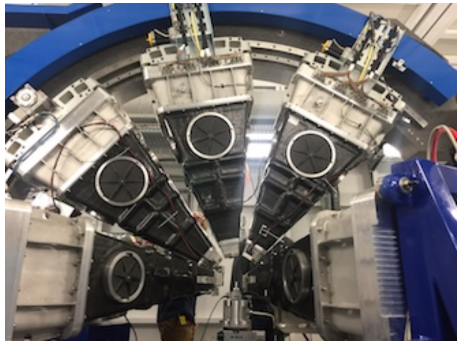


Bulk Carbon Chemistry

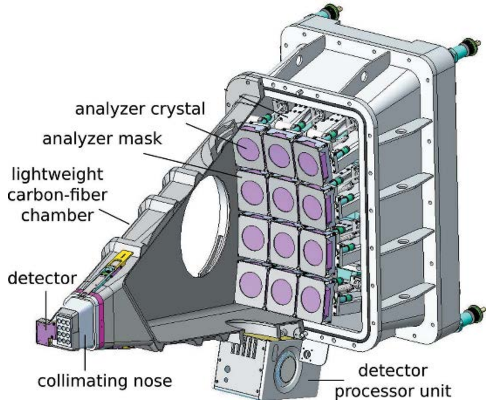
X-ray Raman scattering technique embodies all the advantages of hard X-rays and yields information typically obtained by soft x-ray (NEXAFS)

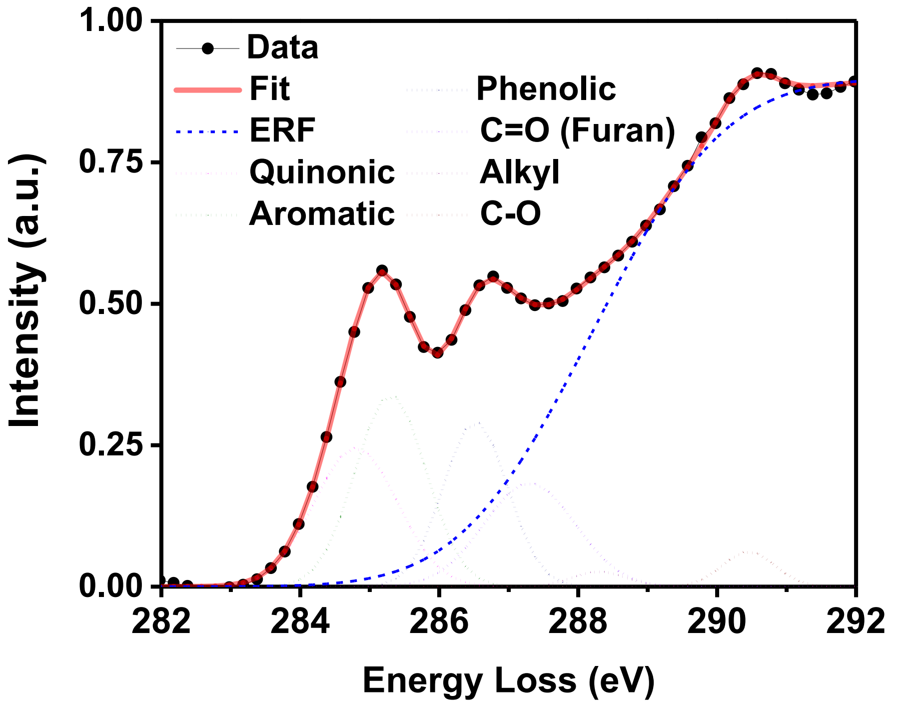


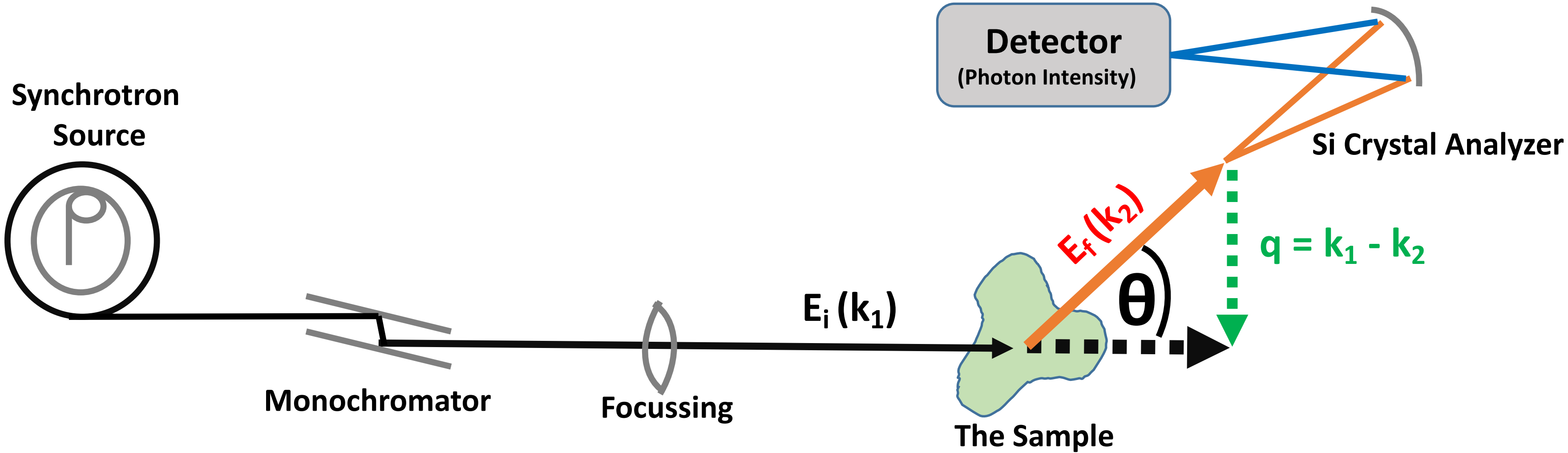
APS in Chicago



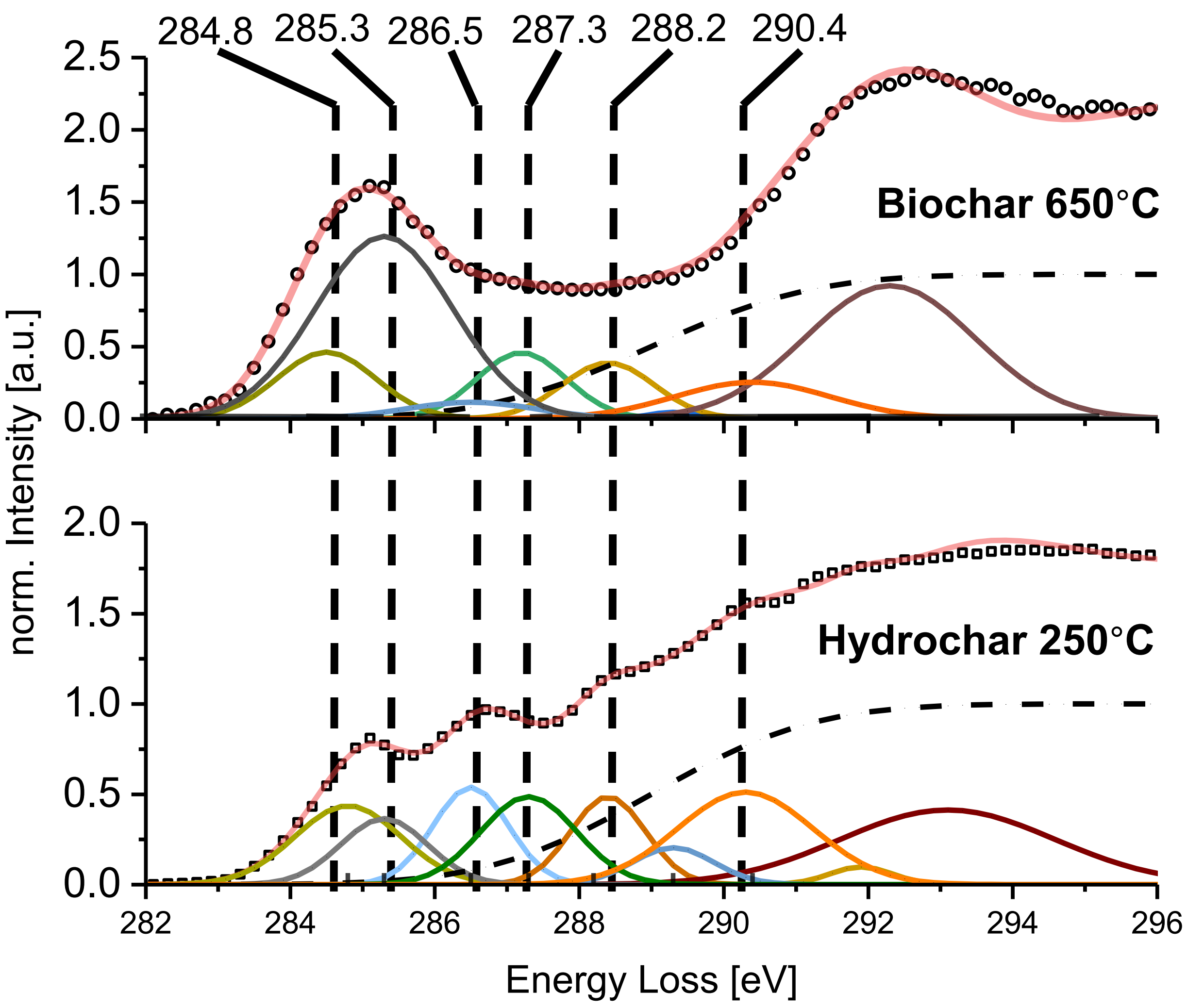
ESRF in Grenoble



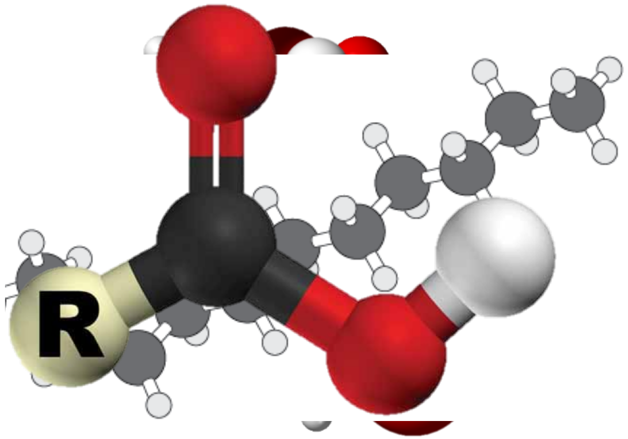




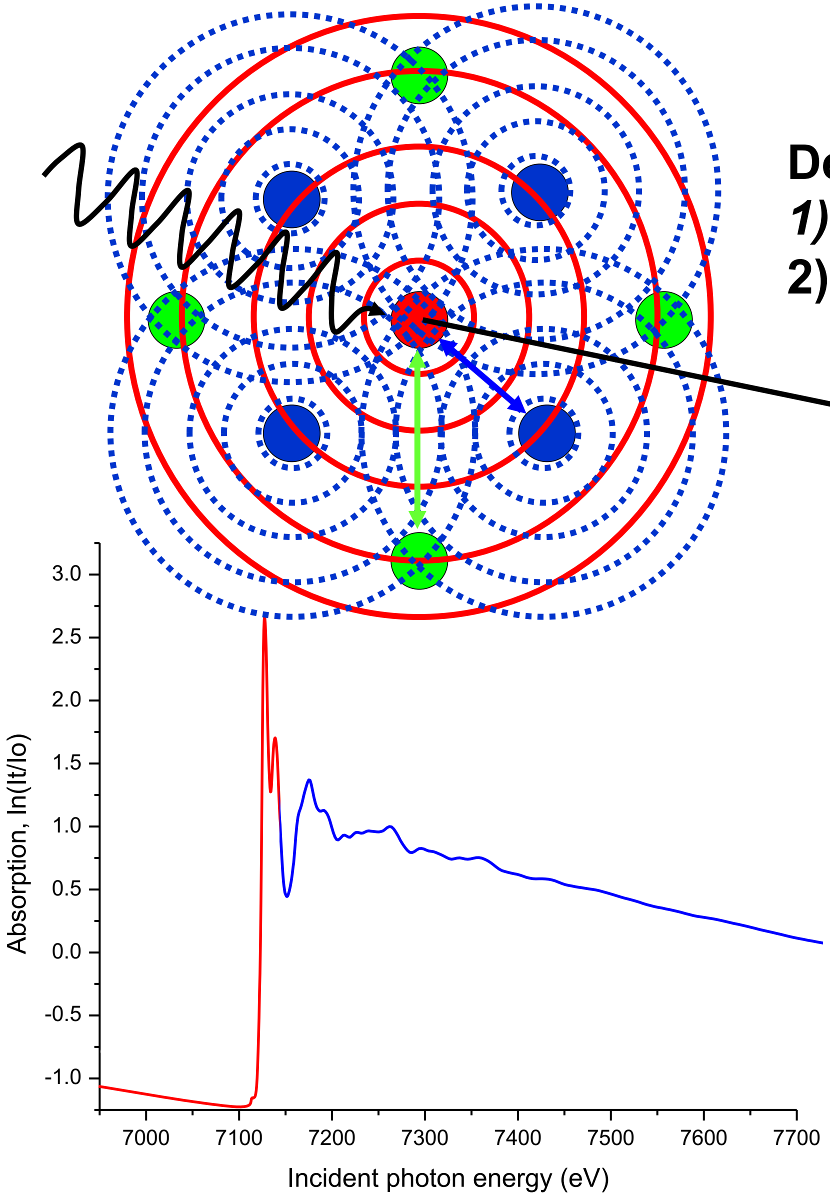
Comparing Biochar and Hydrochar Carbon Chemistry



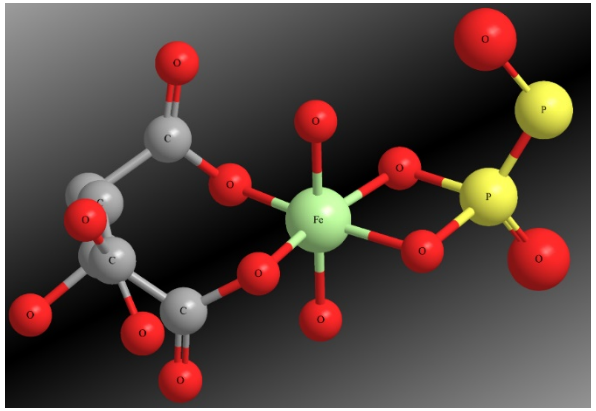
Energy in eV	Biochar Peak area	Hydrochar Peak area
284.8	0.79	0.81
285.3	1.72	0.55
286.5	0.26	0.70
287.3	0.71	0.81
288.2	0.62	0.63
289.3	0.04	0.29
290.4	0.68	1.20



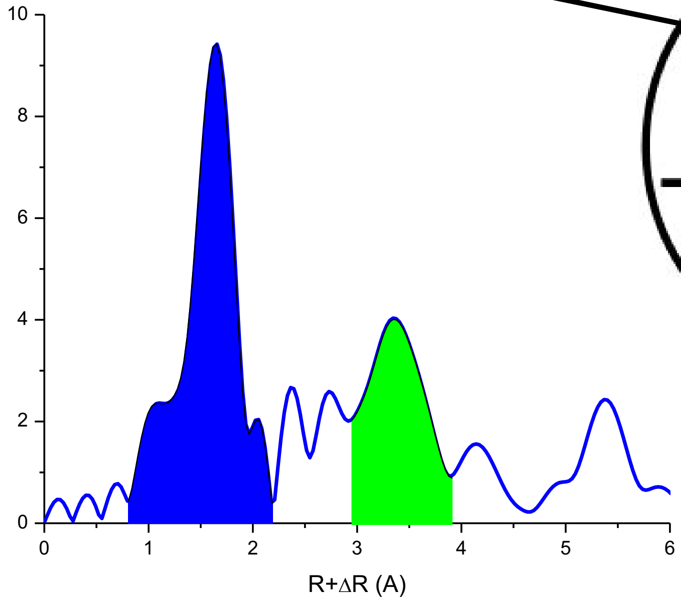
X-ray Absorption Spectroscopy for Fe and S Chemistry

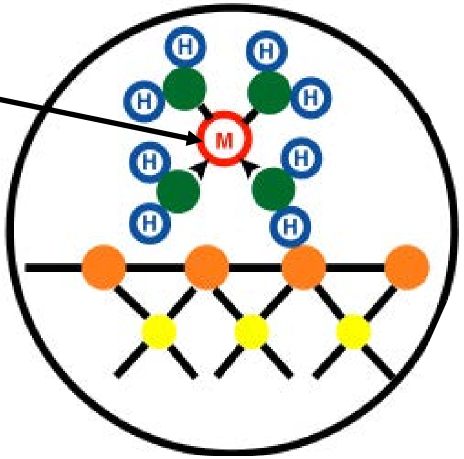


Determines:
1) ***effective*** **oxidation state**
2) detailed coordination environment



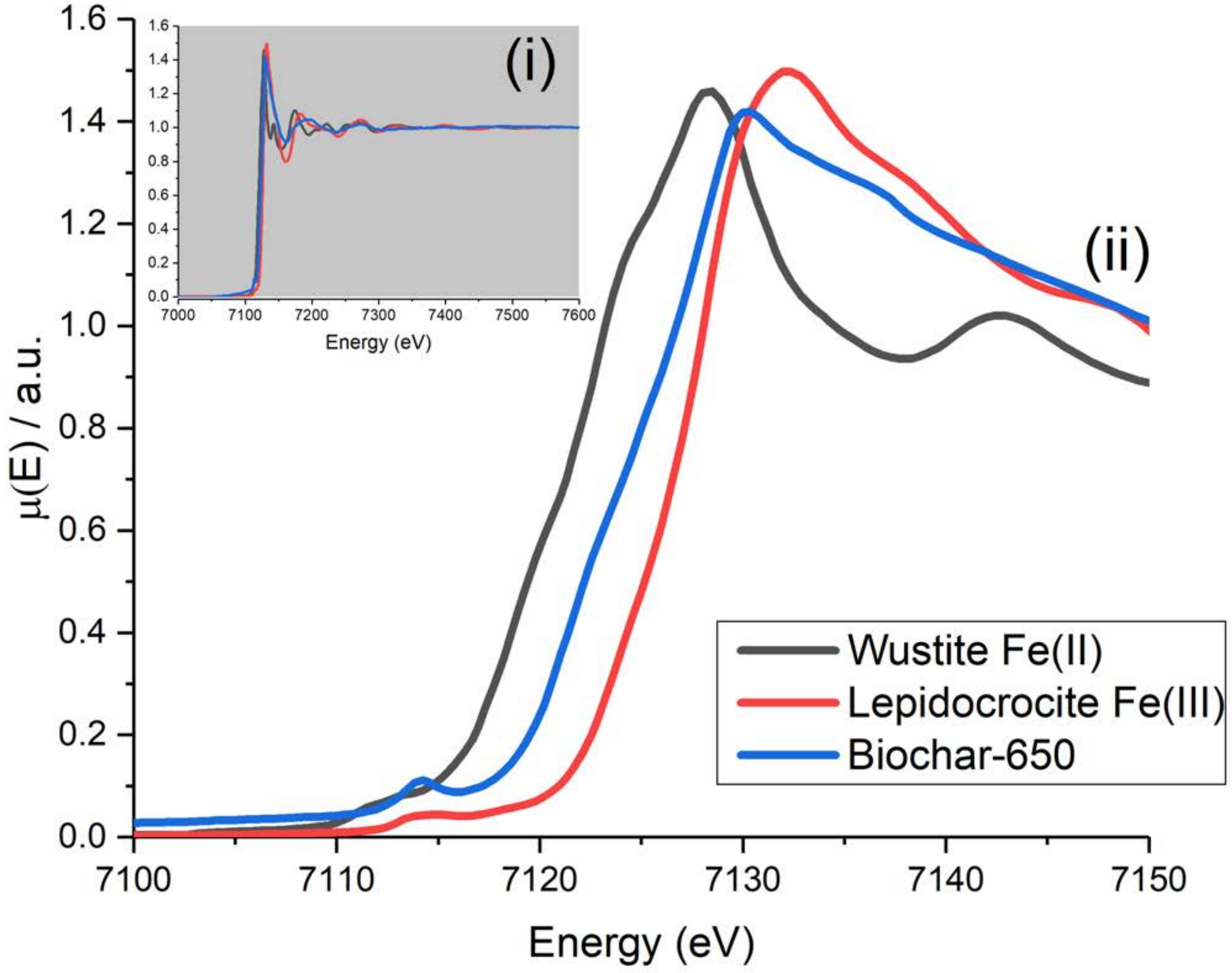
FTR





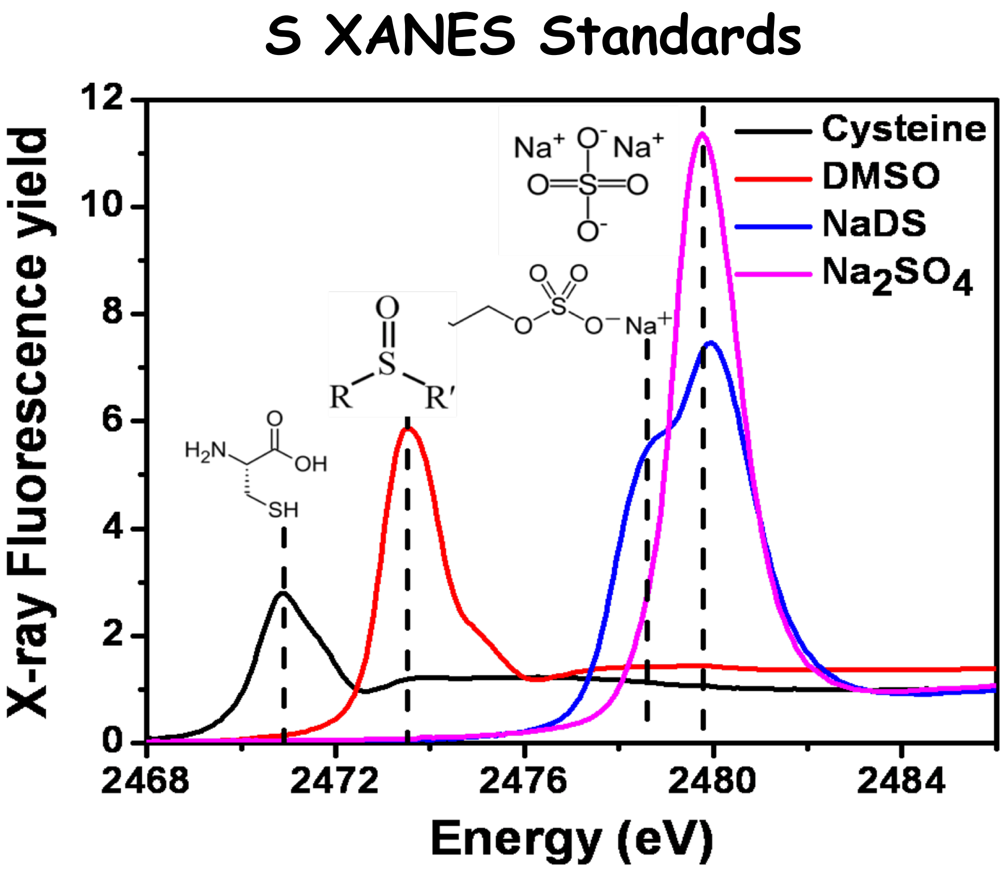
Iron Chemistry of Biochar

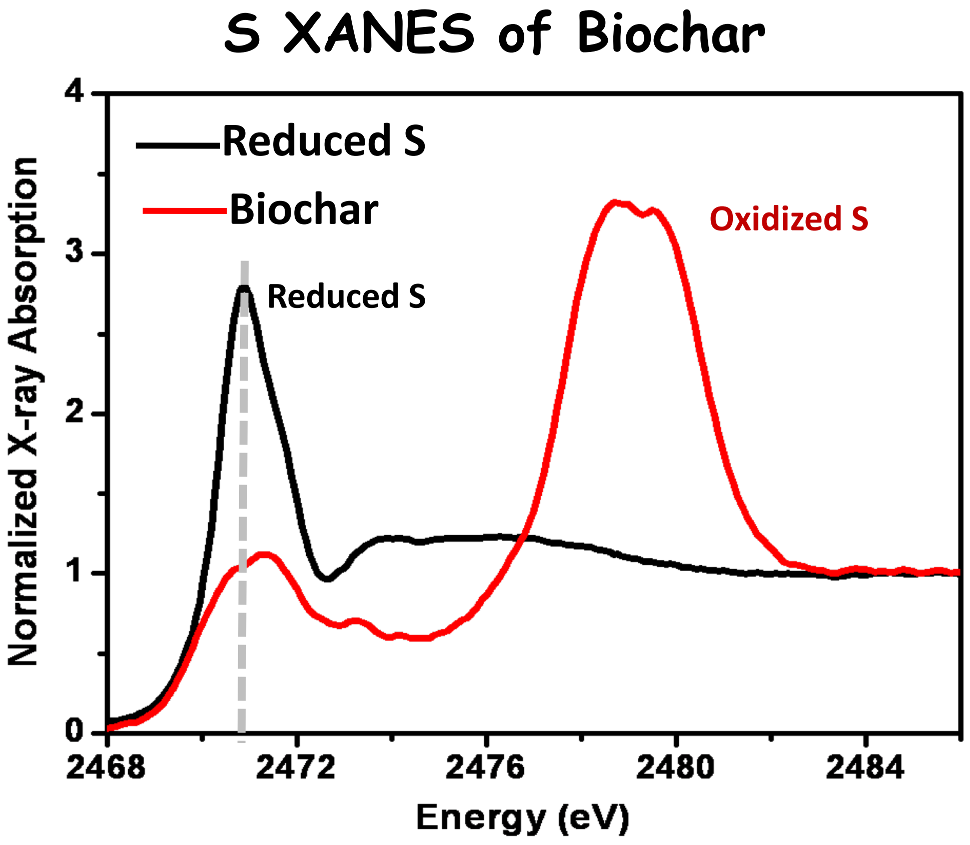
- Biochar has mixed Fe(II/III) species.
- Mixed Fe(II/III) oxides are strong reductant. (e.g., Magnetite)
- Biochar can reduce and immobilize many contaminants or recover resources.



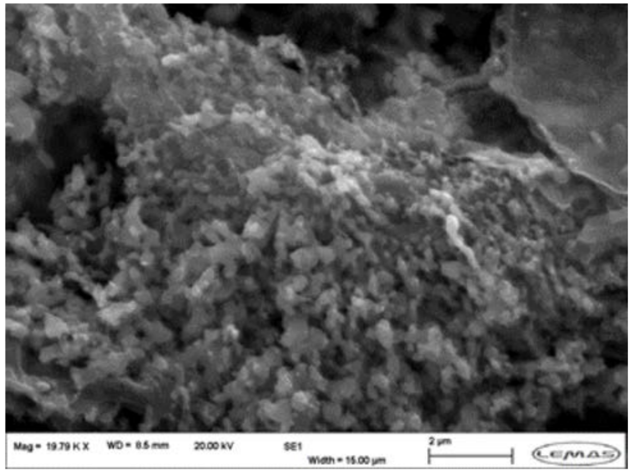
Sulfur Chemistry of Biochar

S moieties on Biochars include sulfhydryl groups.





Inherent Redox Properties of Biochar



- ❑ Electron shuttling capabilities.
- ❑ Mixed Fe(II/III) oxides i.e., reductants
- ❑ Sulfhydryl groups i.e., reductant/oxidant and complexing agent
- ❑ Most contaminants (heavy metals) could be easily reduced to less harmful forms (i.e., Cr, U, Hg).

How can we enhance chemical properties of Biochar?

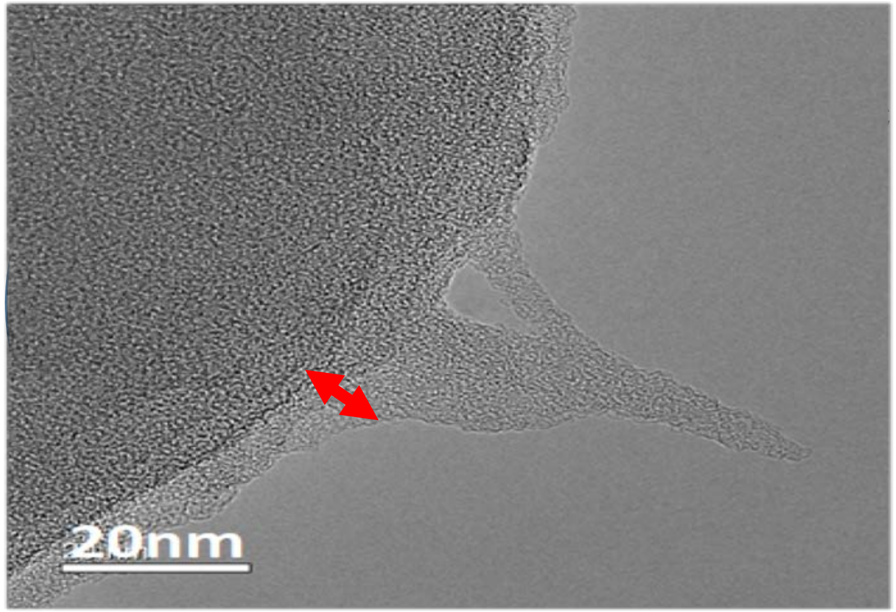
What are the drivers of Biochar Chemistry?

Can we modify surface complexation properties of chars?

- **Synthesis Condition**
  - Aromaticity
  - Functionality
  - Stability

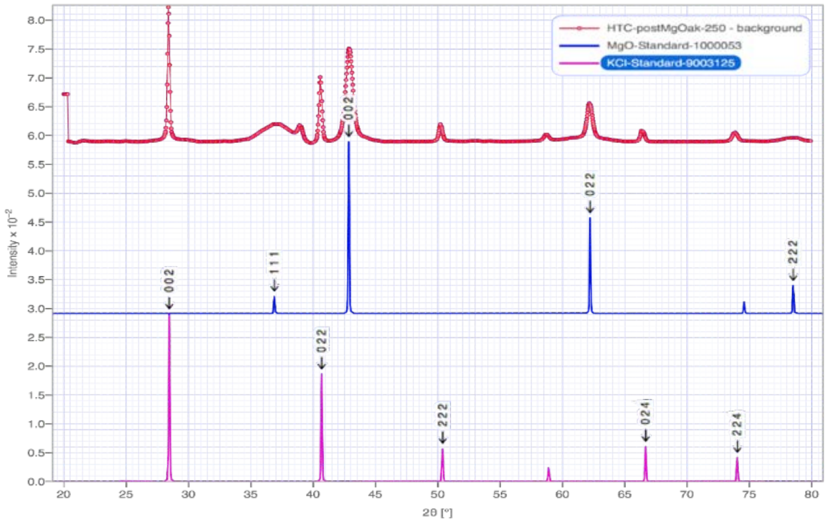
- **Starting Material**
  - Porosity
  - Morphology
  - Inorganic Chemistry

The Shell Model



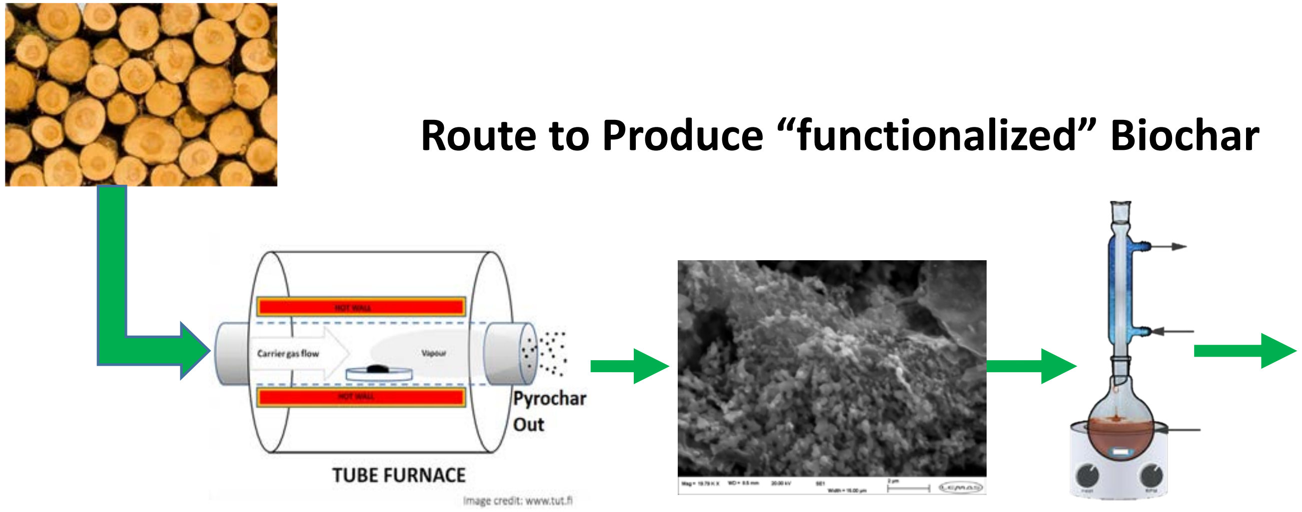
Functionalized Engineered Biochar from Our Group

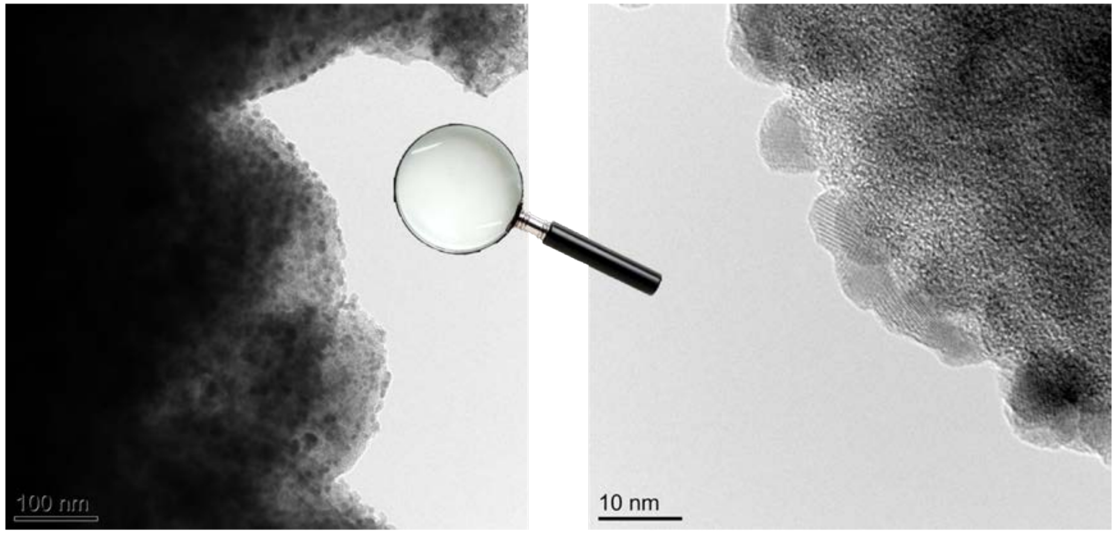
- *We impregnate biochar surface with minerals (e.g., MgO/MnO_2) and functionalize them with ligands (e.g., thiols, amines).*



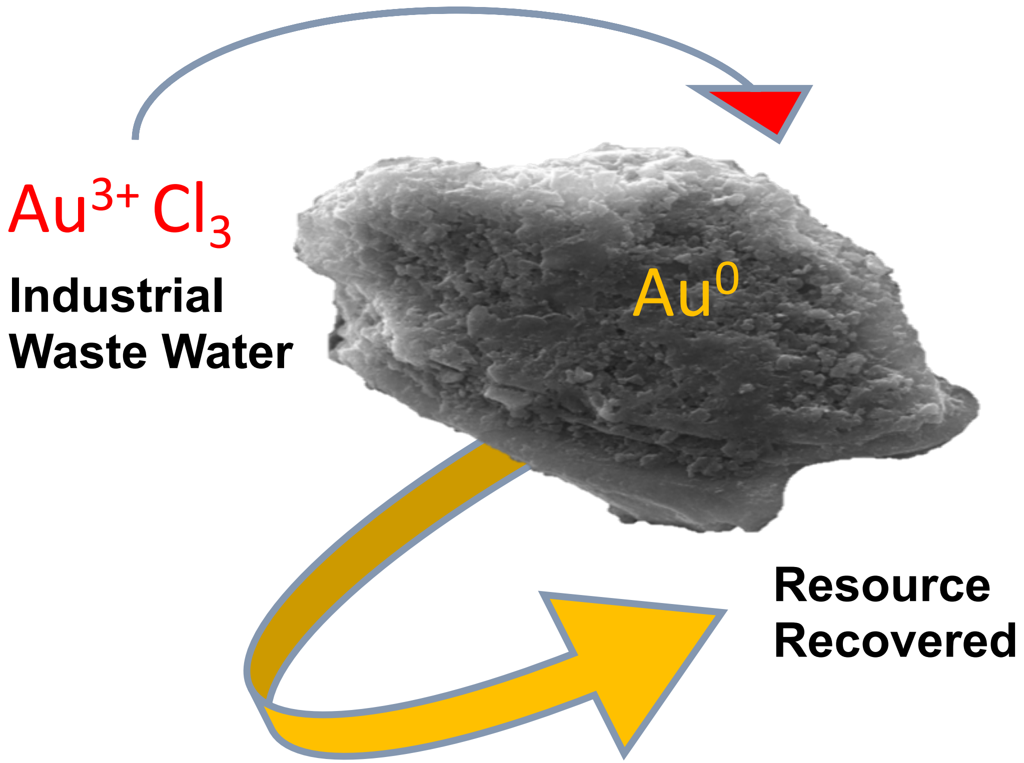
MgO nanoparticulate on surface confirmed by XRD and TEM.

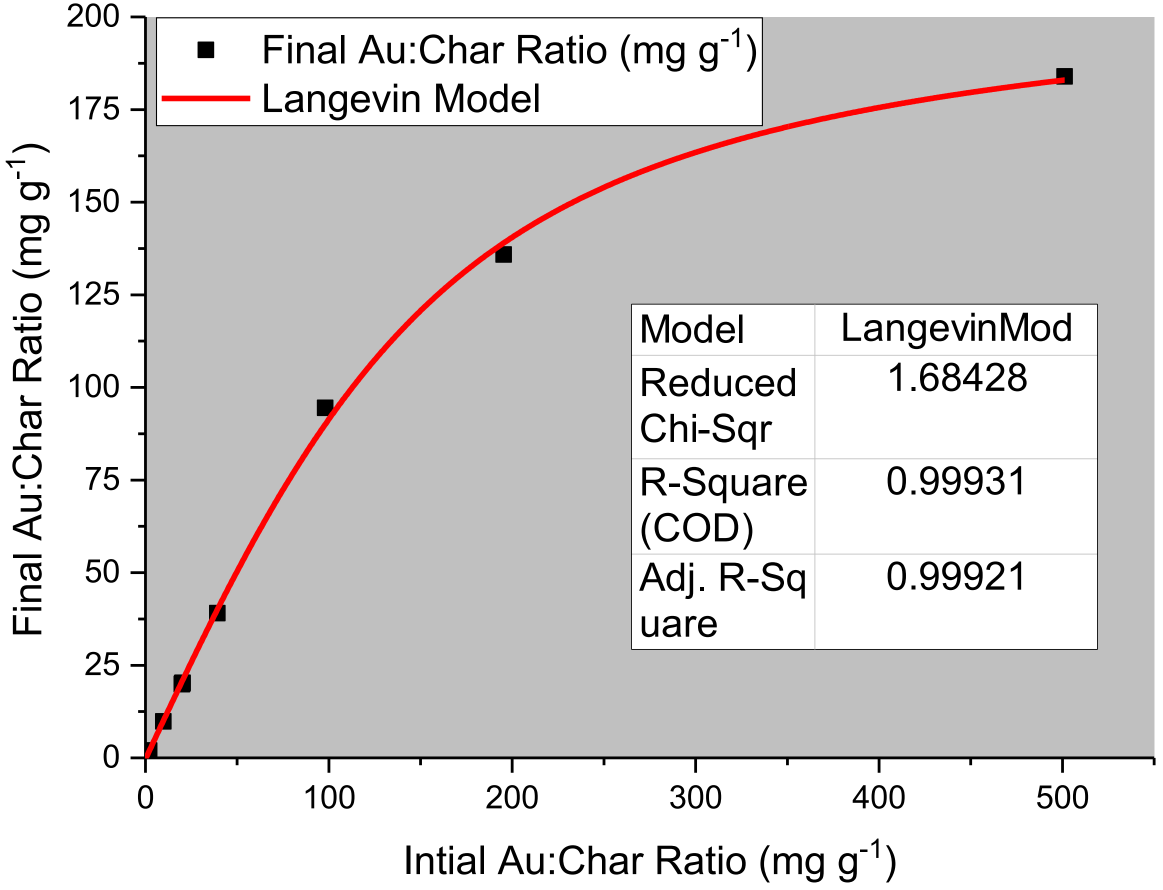
Route to Produce "functionalized" Biochar



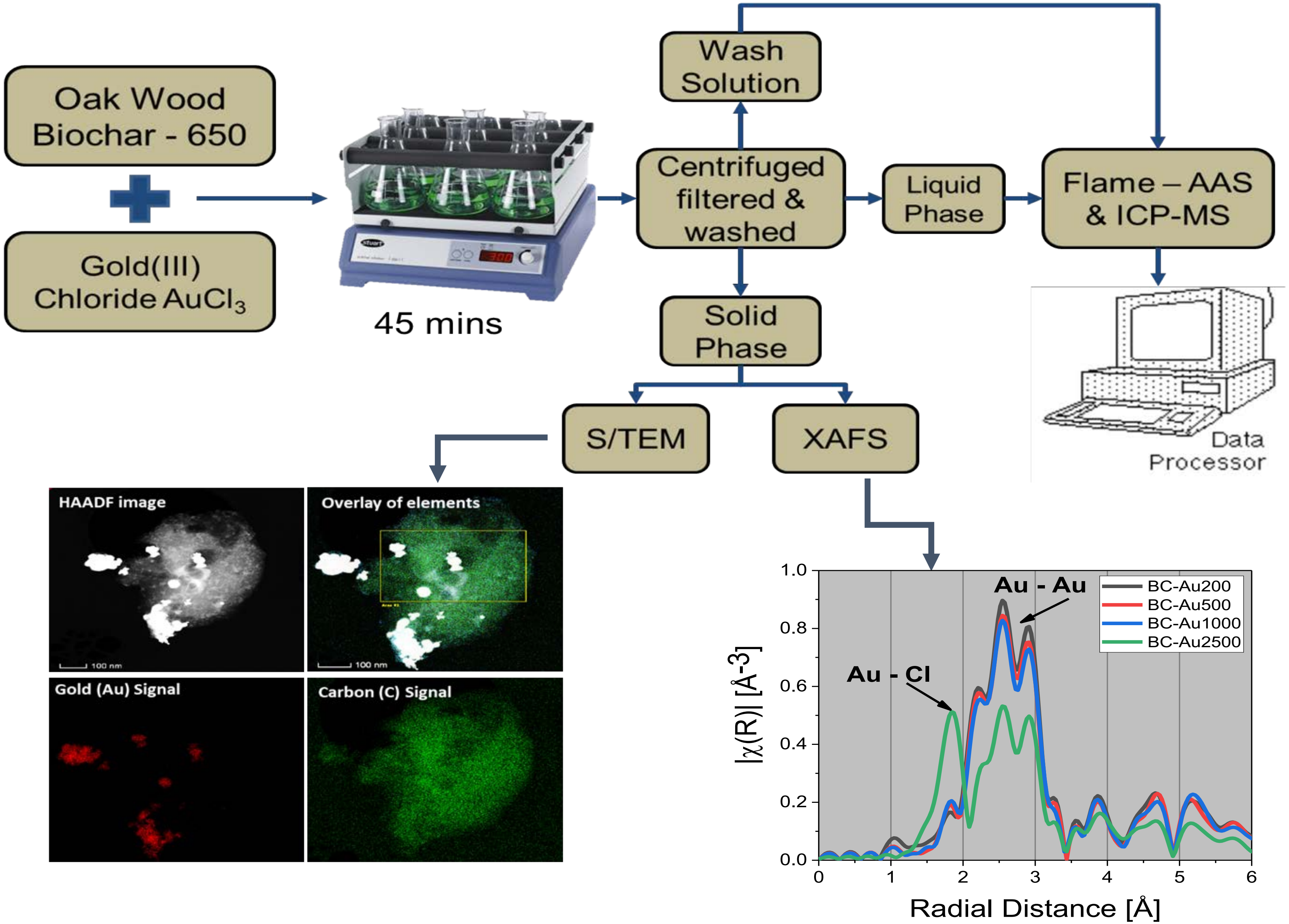


Recovery of Gold from Industrial Waste Water?



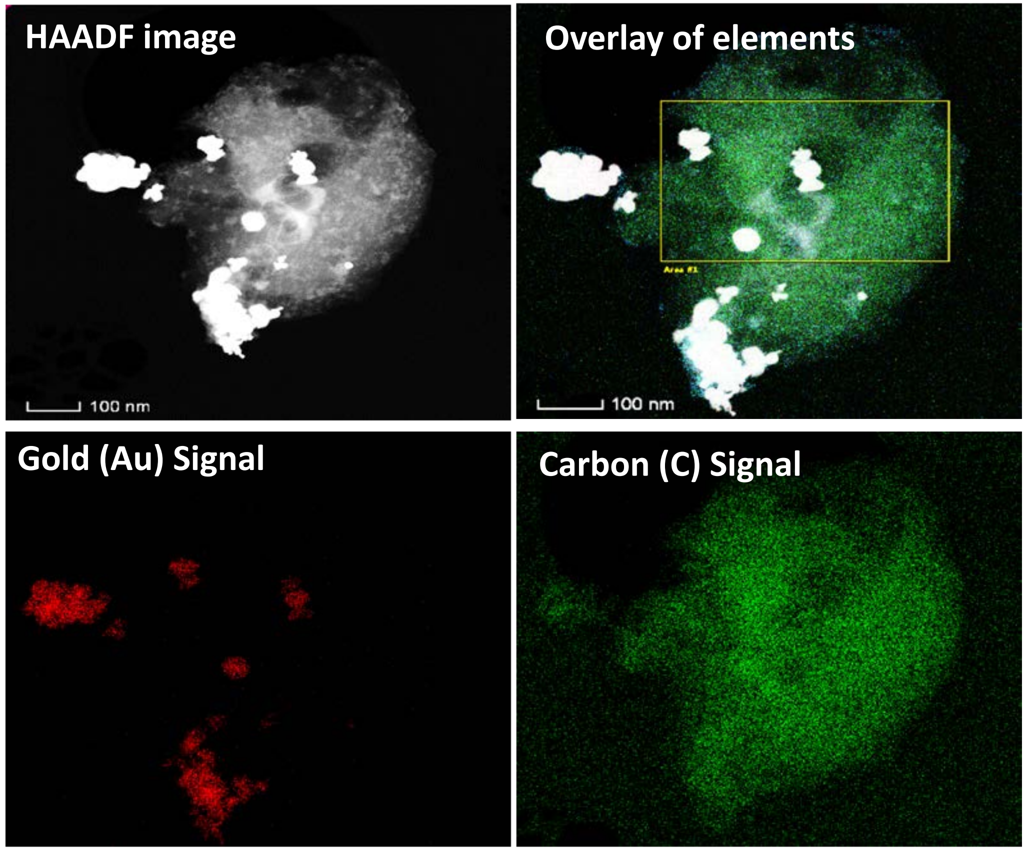


Experimental Set-up for Metal Uptake & Analyses



TEM Characterization of Au on Biochar

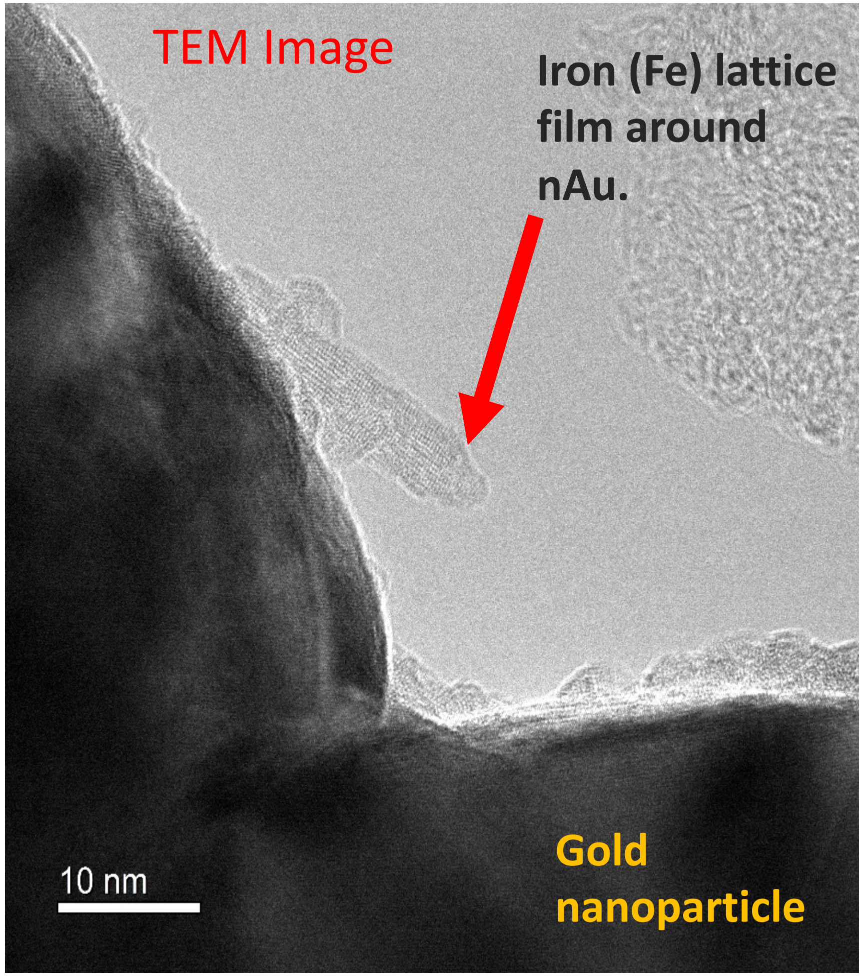
- ❑ TEM confirmed the presence of Au NP.
- ❑ Au was distributed both on the surface and within the biochar.
- ❑ Average visible Au NP size was around ~10nm.
- ❑ Interestingly, many of the Au NP were located next to Fe oxides in the biochar.



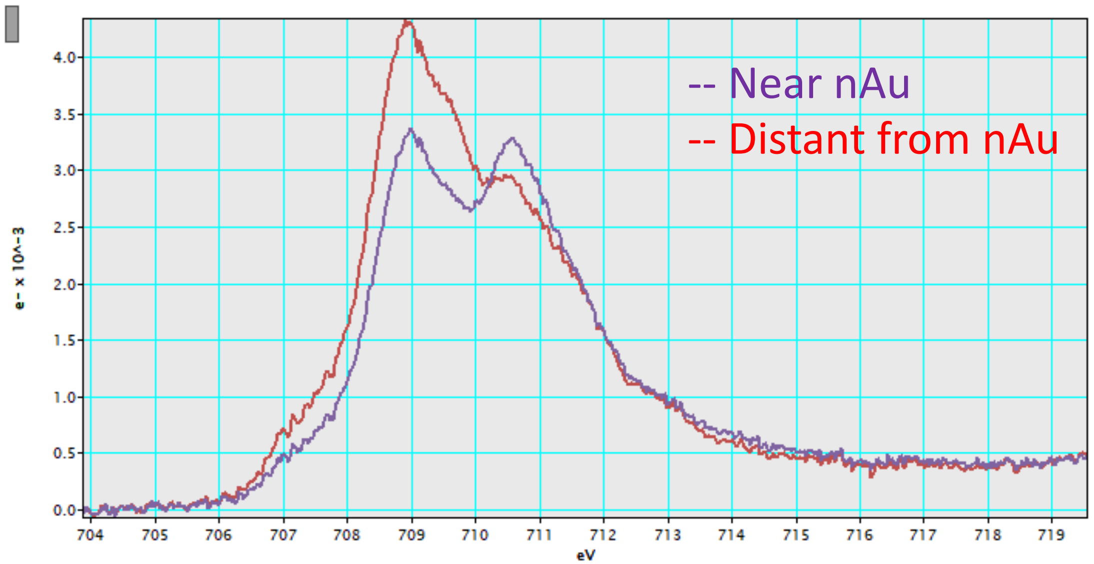
STEM EDX imaging of a porous char particle after adsorption of gold onto the surface. Gold can be seen as a red colour, whilst carbon can be seen in green.

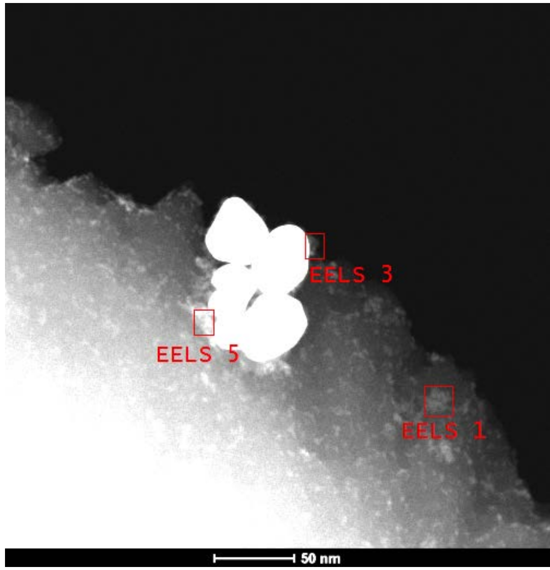
Fe ELNES using TEM

- A film of Fe Oxide surrounds Au nanoparticle.
- Fitting ELNES data showed a change in redox state for Iron oxide.



$Au(III) + 3Fe^{2+} \rightarrow Au(0) + 3Fe^{3+}$

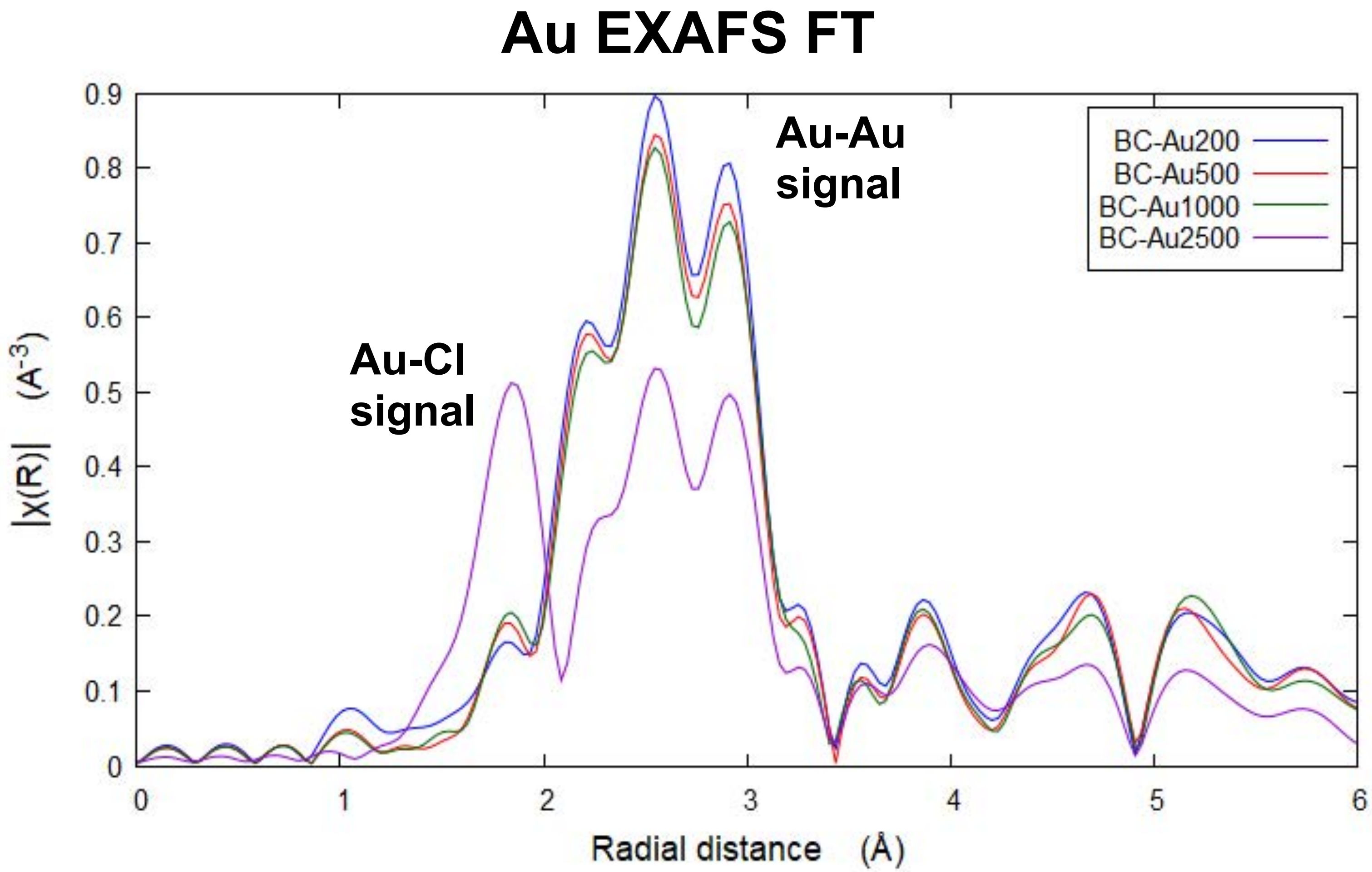




Position	Hedenbergite (Fe2+)	Haematite (Fe3+)
Distant	44%	52%
Adjacent	67%	38%

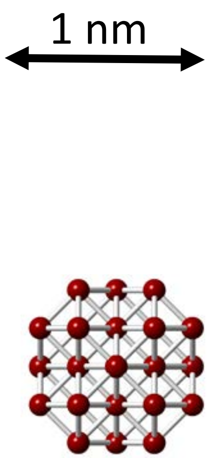
Au EXAFS on Biochar

- ❑ Au EXAFS confirmed Au NP.
- ❑ Three different mechanisms (Fe, C, S) responsible for Au redox transformations.
- ❑ EXAFS average NPAu size 3-4 nm; smaller than observed by TEM.
- ❑ ~20 weight% capacity of Biochar to recover Au as NP.

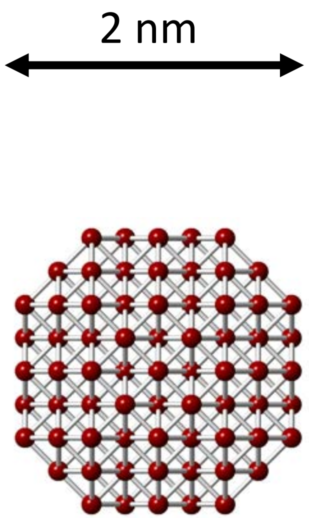


Sensitivity for CN vs. Particle Size

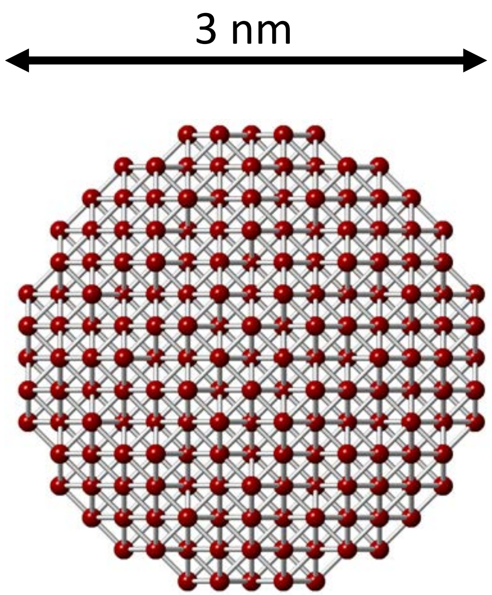
Au edge EXAFS



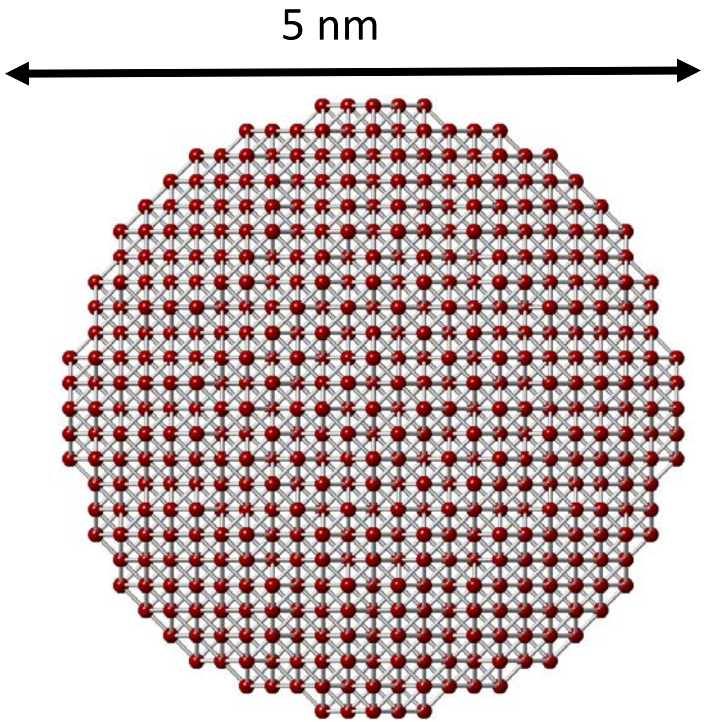
Au	Calculated
Au1	6.81



Au	Calculated	Observed
Au1	9.26	10.2



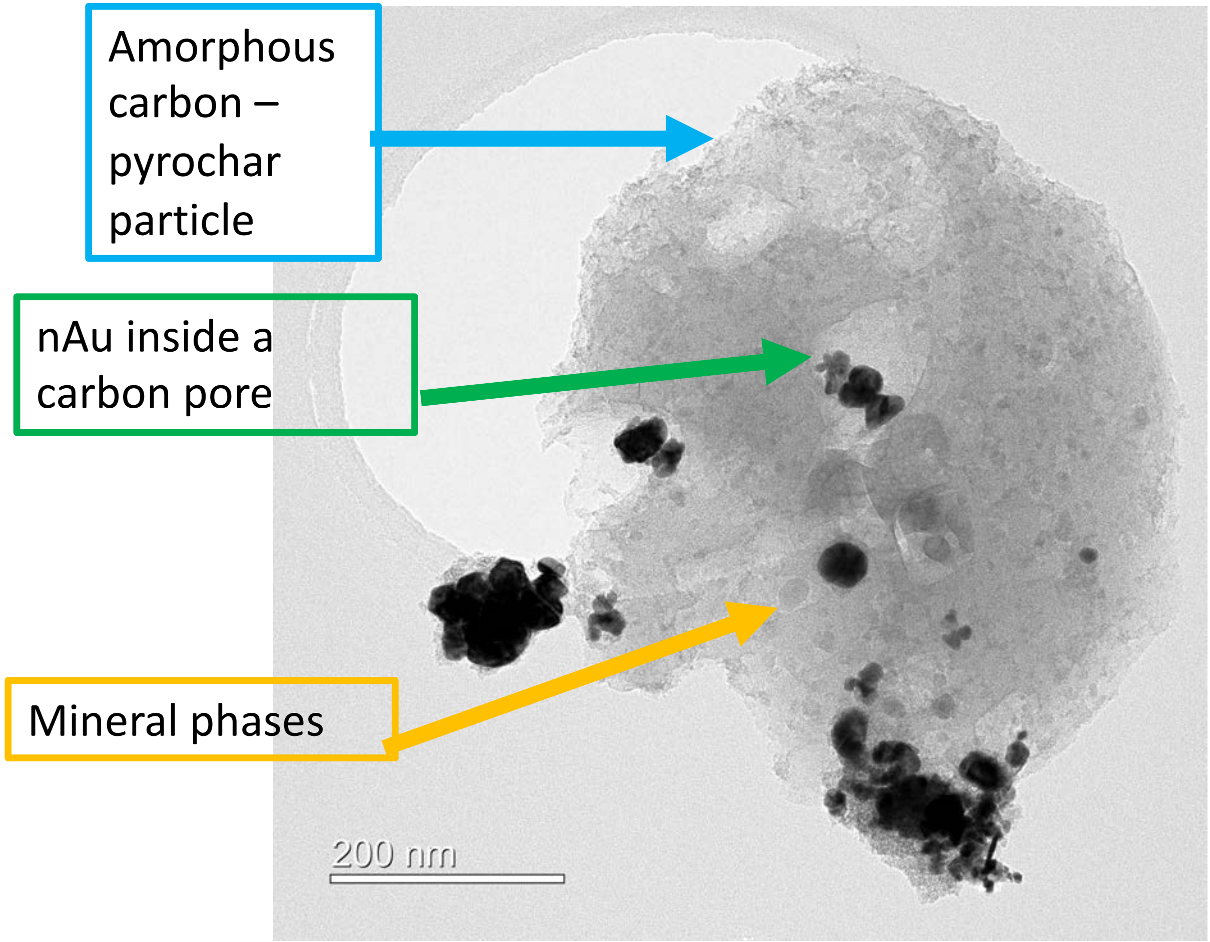
Au	Calculated
Au1	10.2



Au	Calculated
Au1	11.0

Mechanisms Responsible for Au Transformations

- ❑ Evidence for the reduction by mixed Fe(II/III) Oxides
- ❑ Electron shuttling by Carbon moieties on in the biochar (e.g. Quinone)
- ❑ Intermediate speciation such as Au(I)S??



Summary

- Biochar and Hydrochar can be created from biogenic waste (e.g., Urban and Agricultural Waste)

- Biochar have inbuilt reductive and electron shuttling capabilities.

- In addition, they could be engineered for enhanced uptake of specific contaminants and resources, and transform them as desired.

- Applications include water treatment, waste management, and resource recovery (e.g., recovery of Au from industrial waste water).

- If converted to real time use, this could be first step towards truly circular economy and sustainable society.

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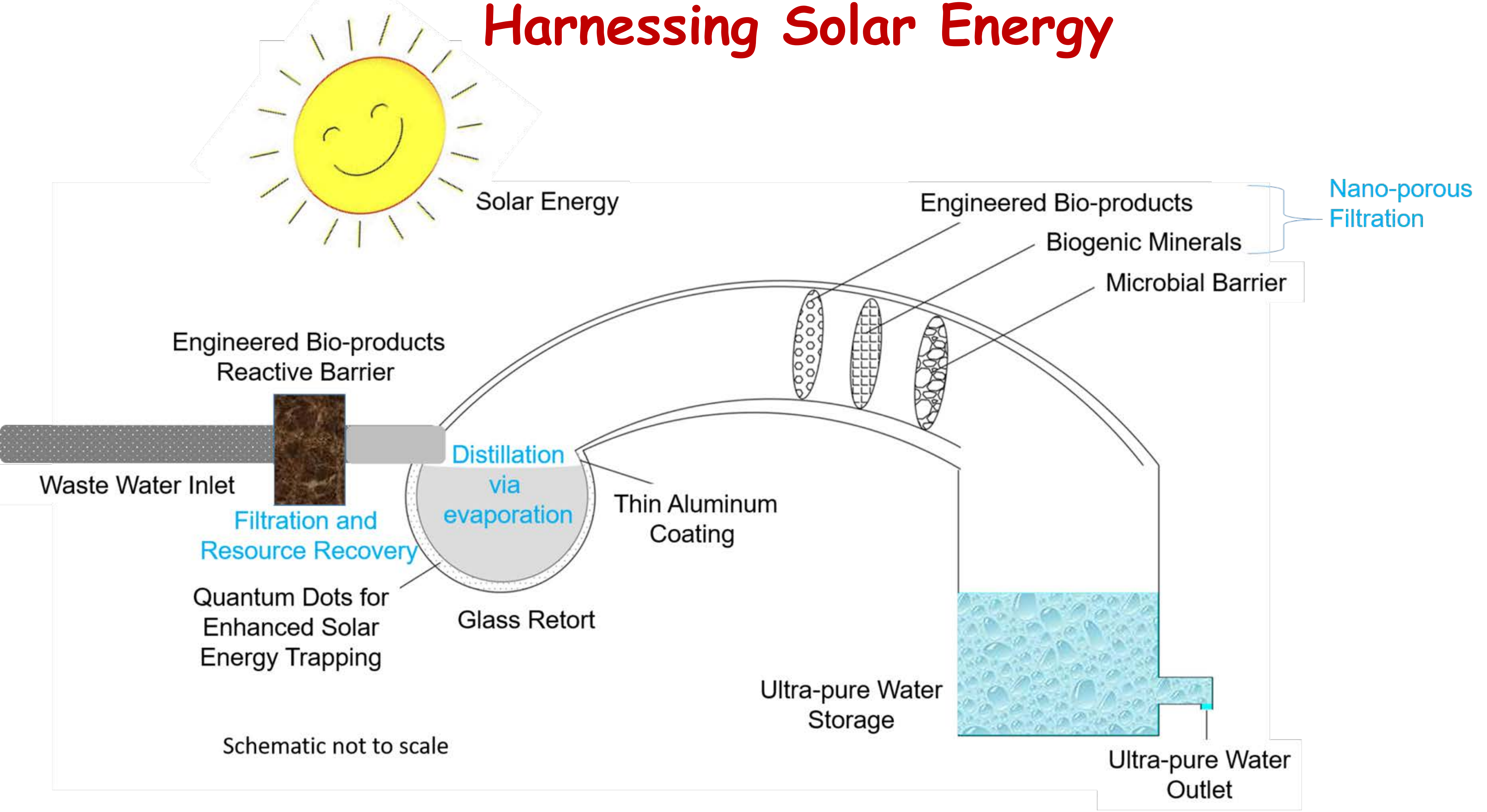
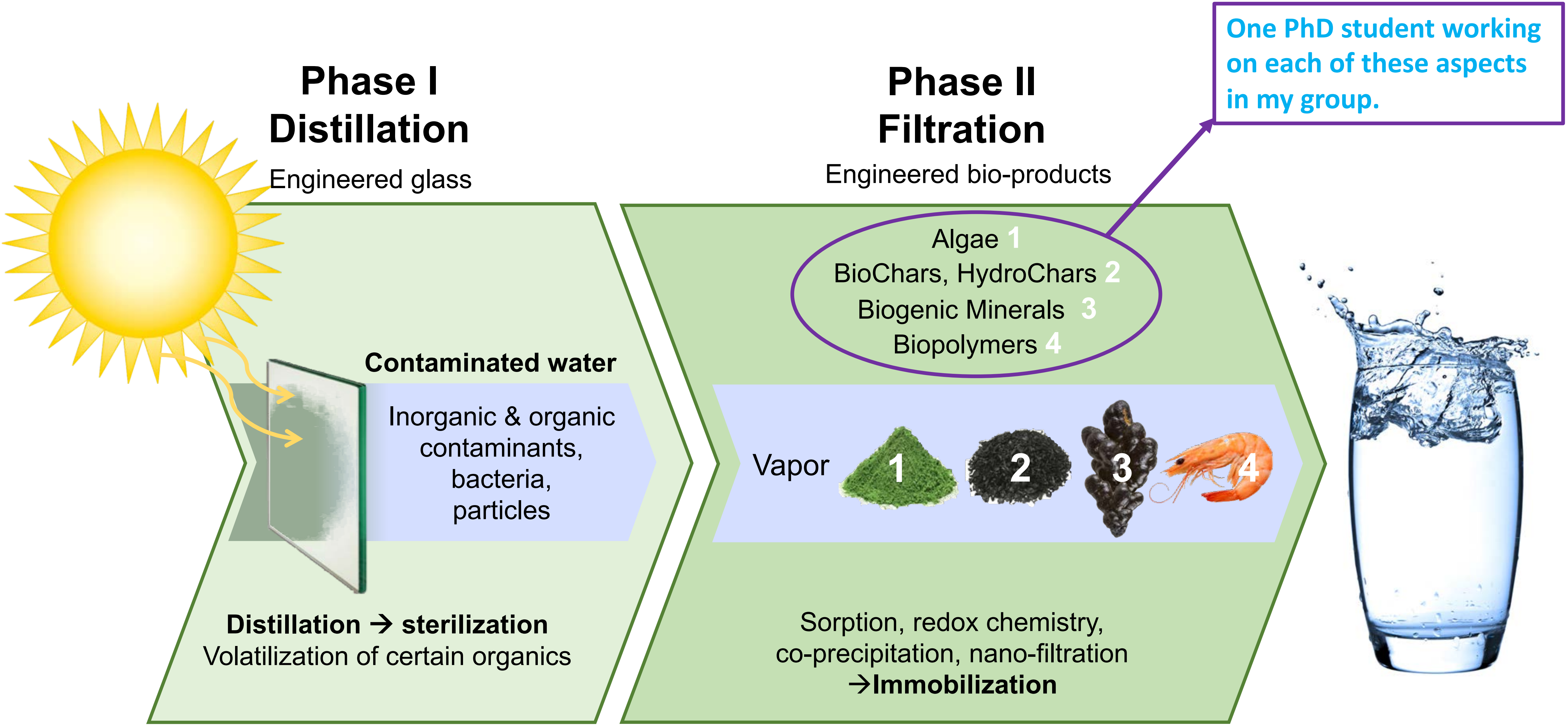
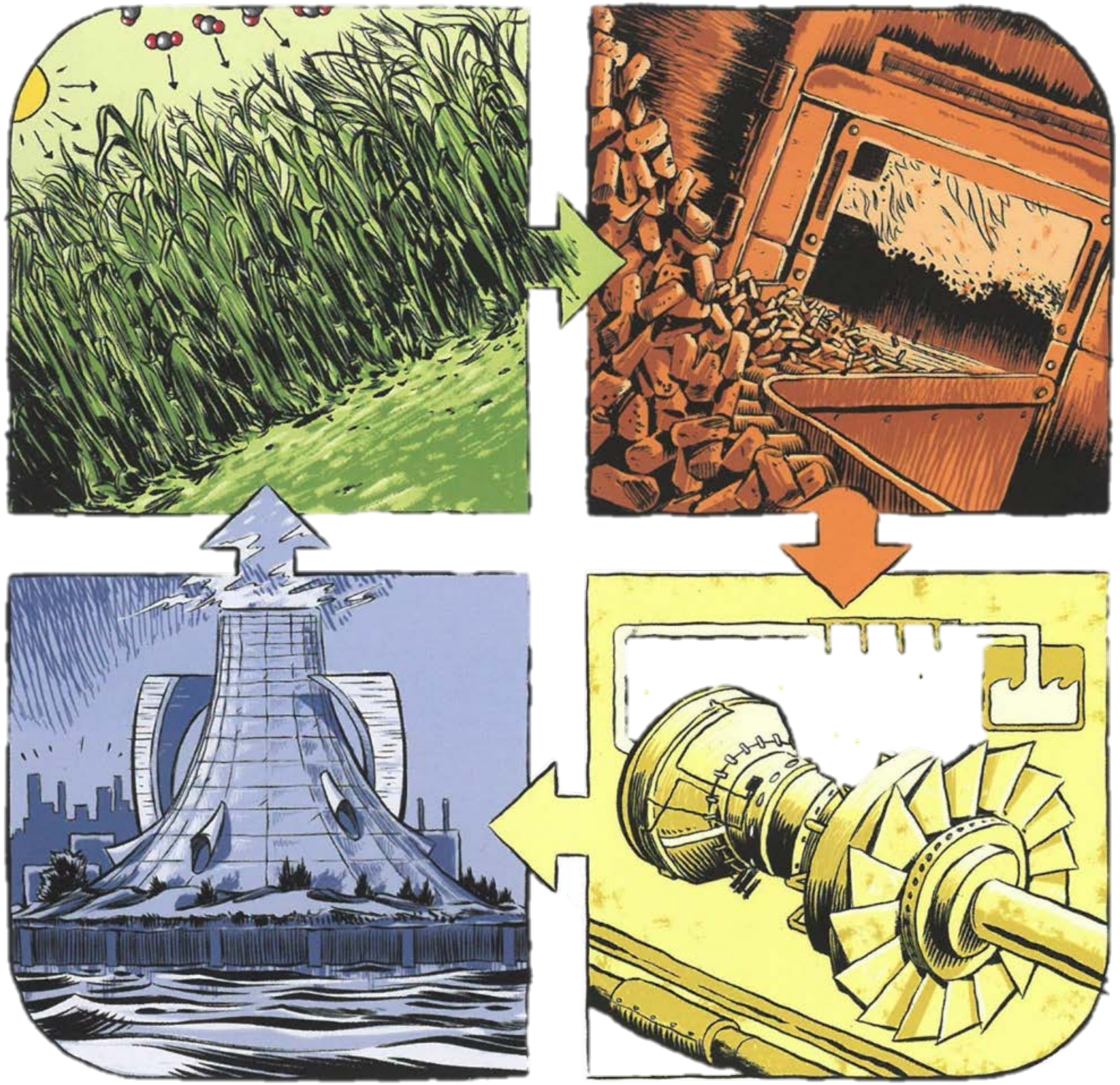
Conceptual Design of Distillation and Nano-filtration Harnessing Solar Energy



Conceptual Design….continued



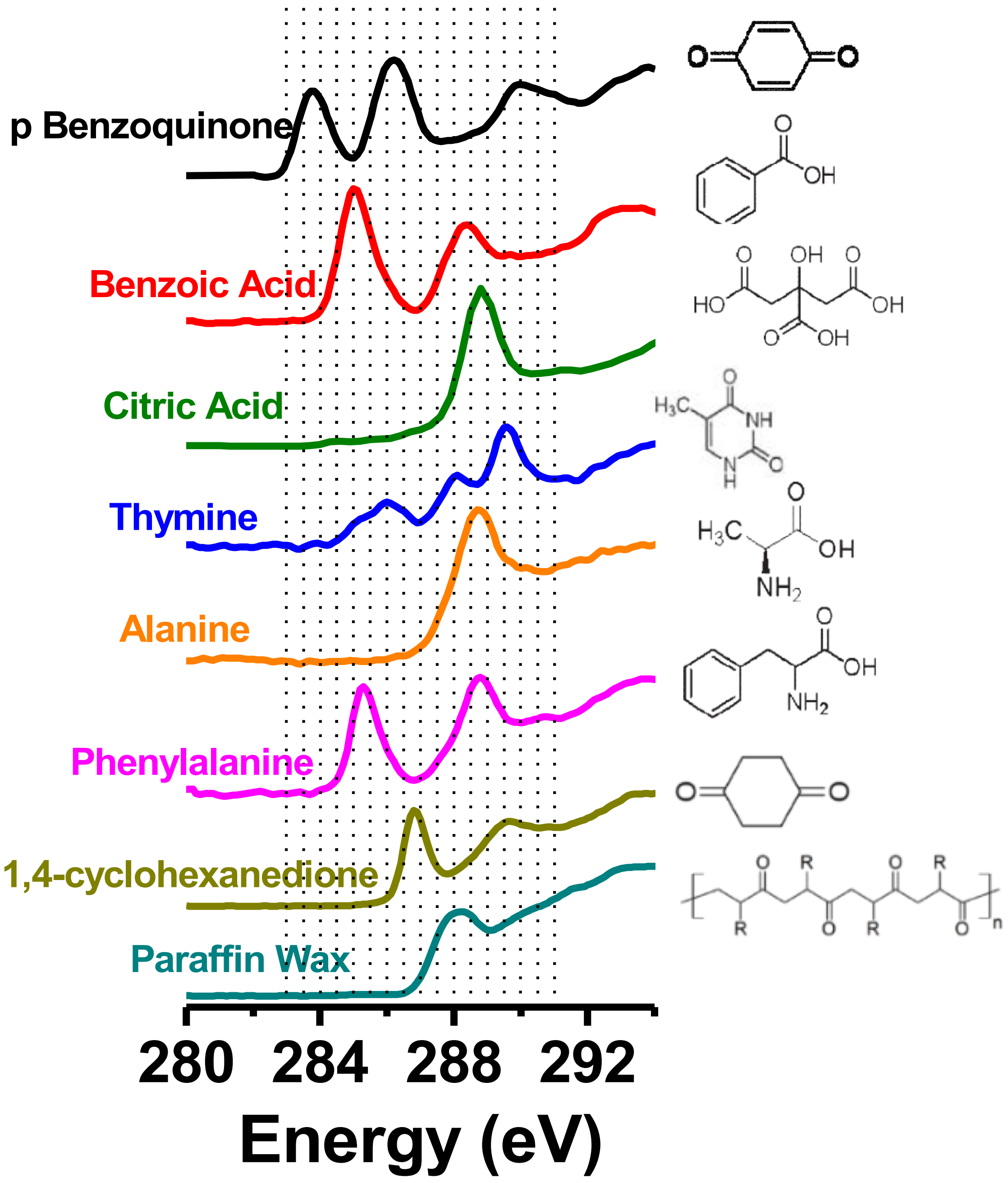
What do we do with biogenic waste?



© Corban Wilkin, Bioenergy a Graphic Introduction

- ❑ Biogenic waste from various sources
- ❑ Landfill -> GHGs
- ❑ Generally combusted for EfW -> no products
- ❑ Can we develop functional material out of it?

Carbon ChemistryX-ray Raman Standards with Soft X-ray



X-ray Raman and C NEXAFS compared

Standard	Peak energy this study	Peak energy published
p-Benzoquinone	283.8	284.52
		285.08
	286.2	286.22
		288.21
	289.8	289.82
Benzoic Acid	285.0	285.01
	288.3	288.35
		289.42
Citric Acid	288.7	288.72
Thymine	285.1	285.13
	286.0	286.02
		286.84
	288.1	288.01
	289.6	289.47
Alanine	288.7	288.72
Phenylalanine	285.3	285.29
	288.8	288.75