Biochar:
More than meets the eye

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USDA
United States Department of Agriculture
Agricultural Research Service

USBI
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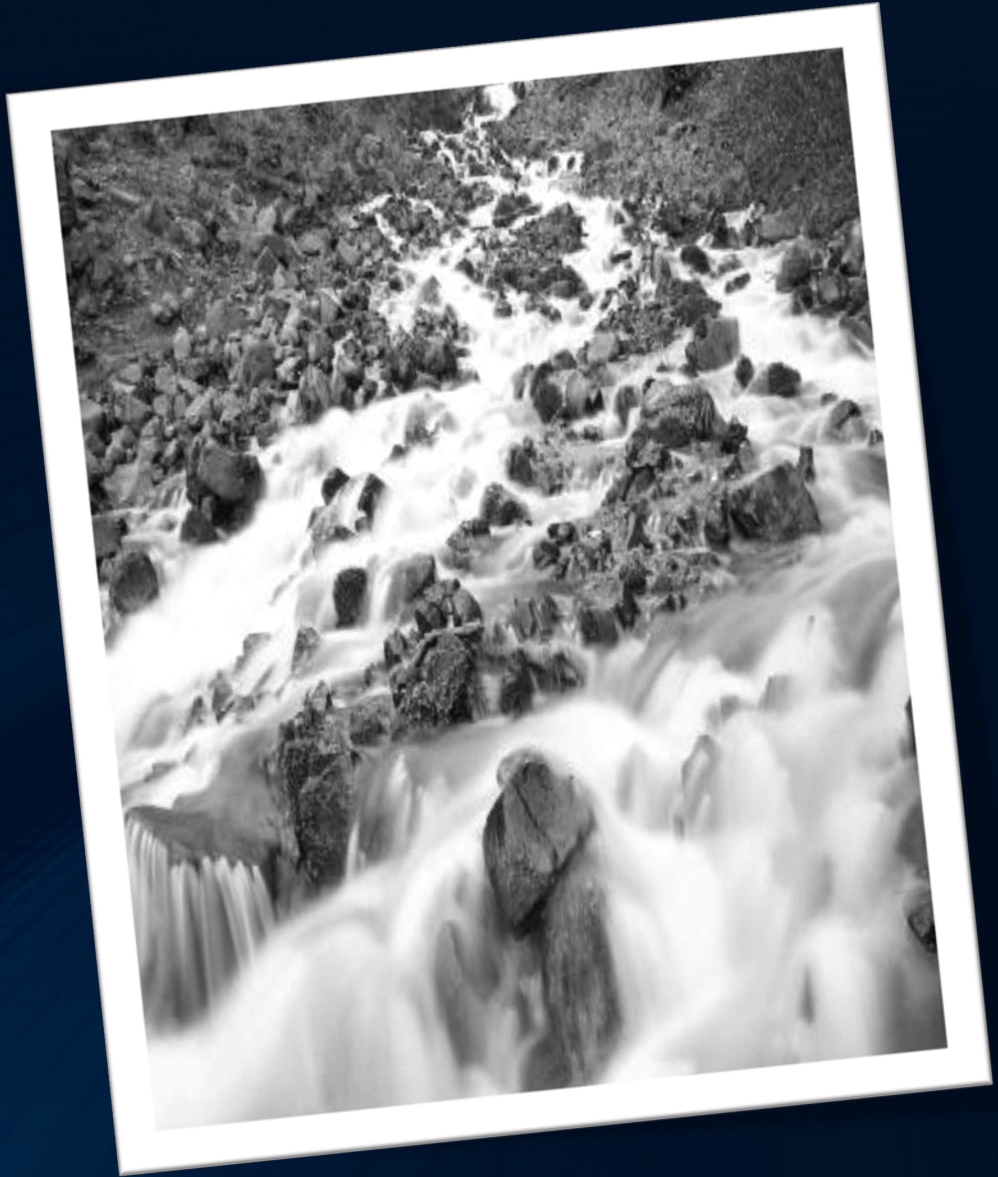
Water

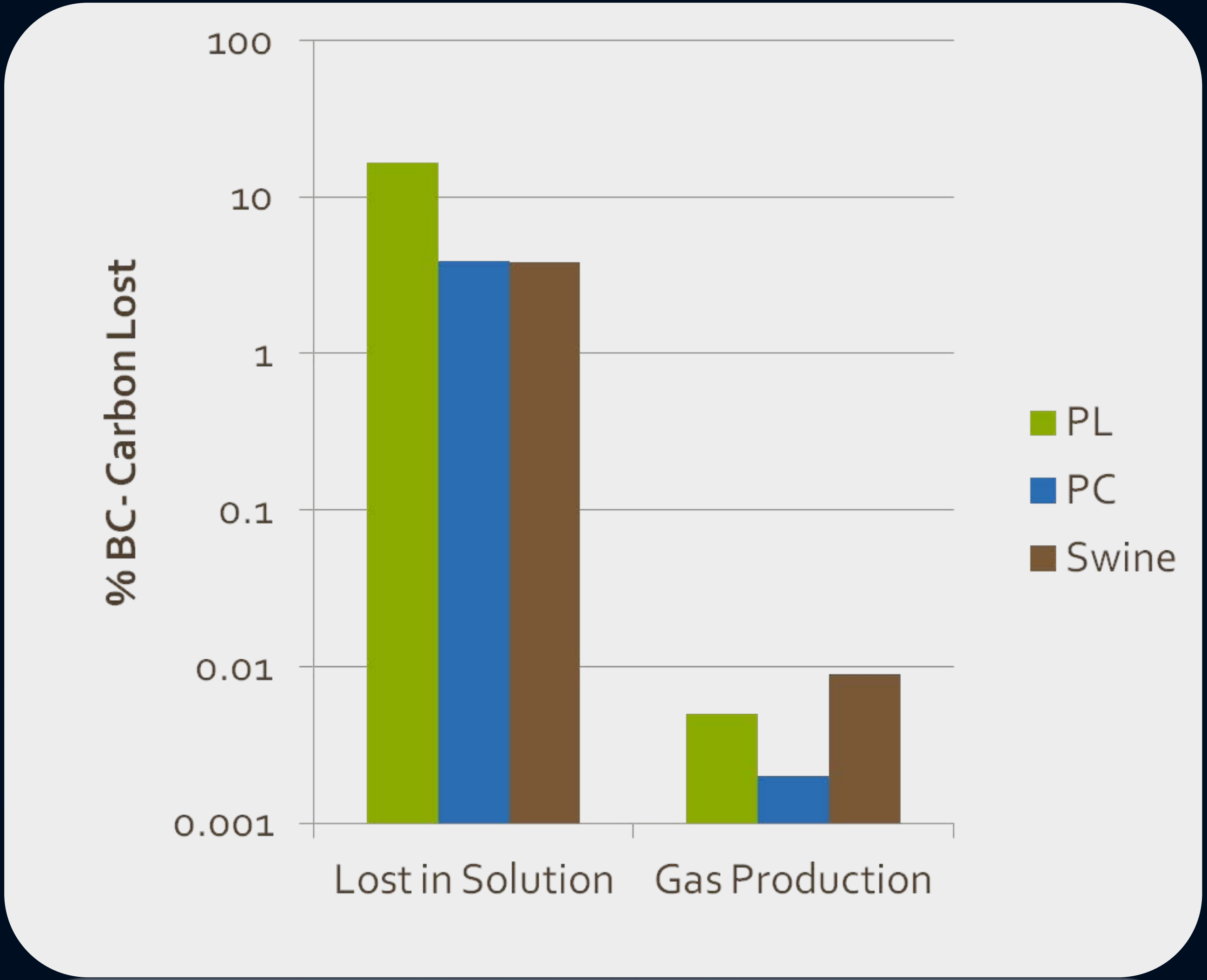
"Water is the driving force of all nature."

- Leonardo da Vinci

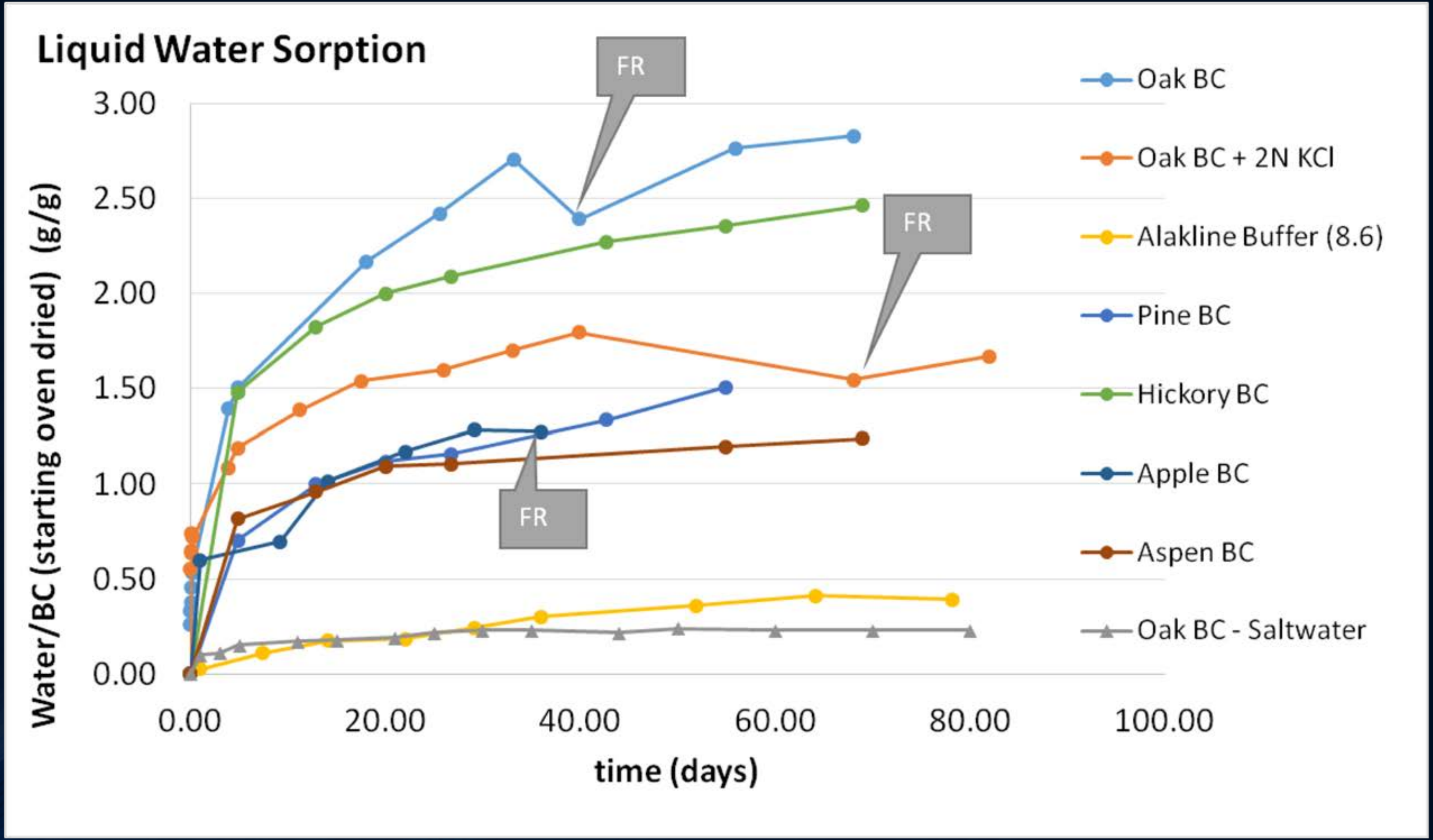


Physical Breakdown

Physical breakdown of the biochar accounts for **<u>3 orders</u>** of magnitude higher losses of C than microbial degradation for the initial 24 hour period

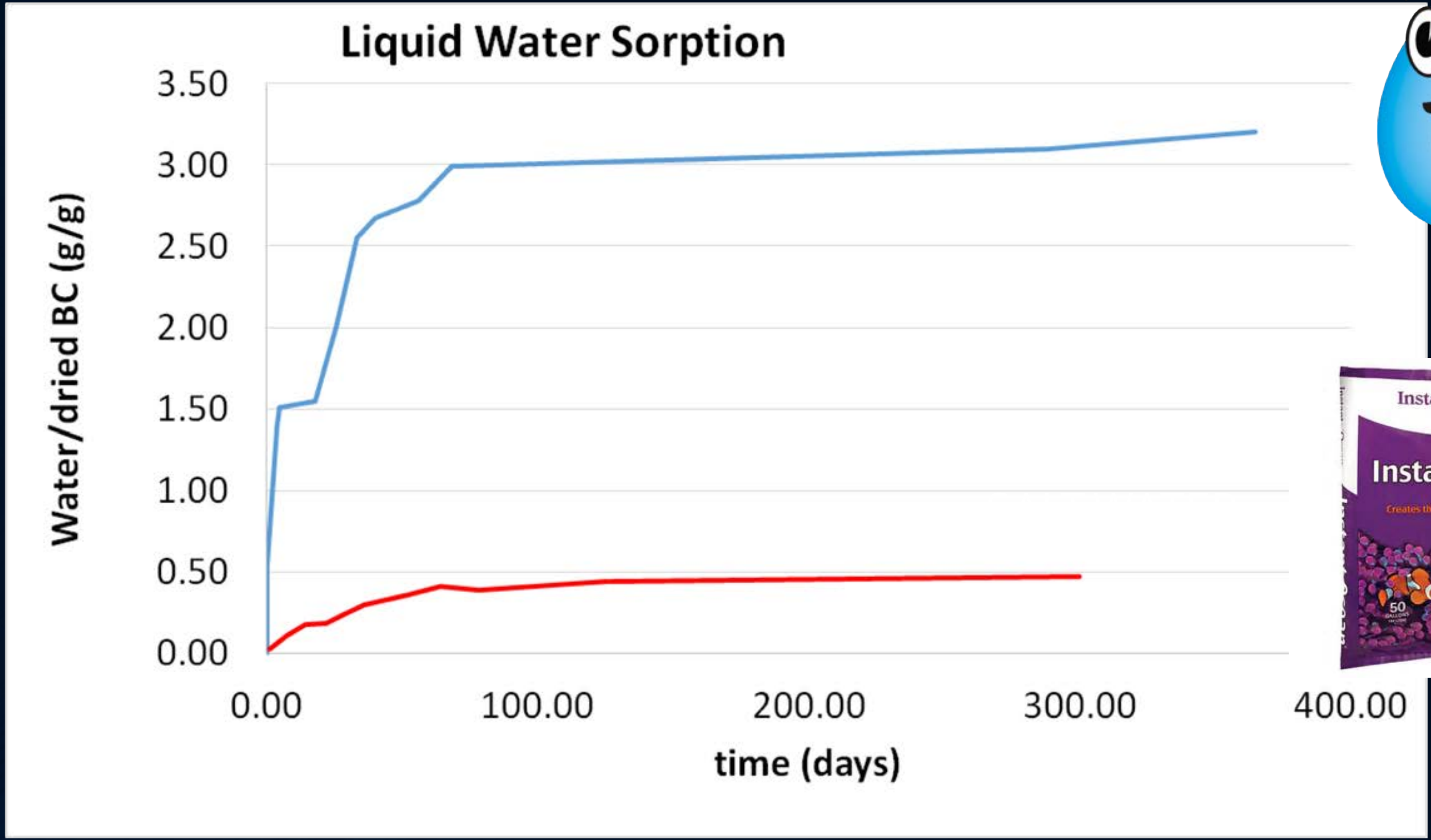


Liquid Water Uptake

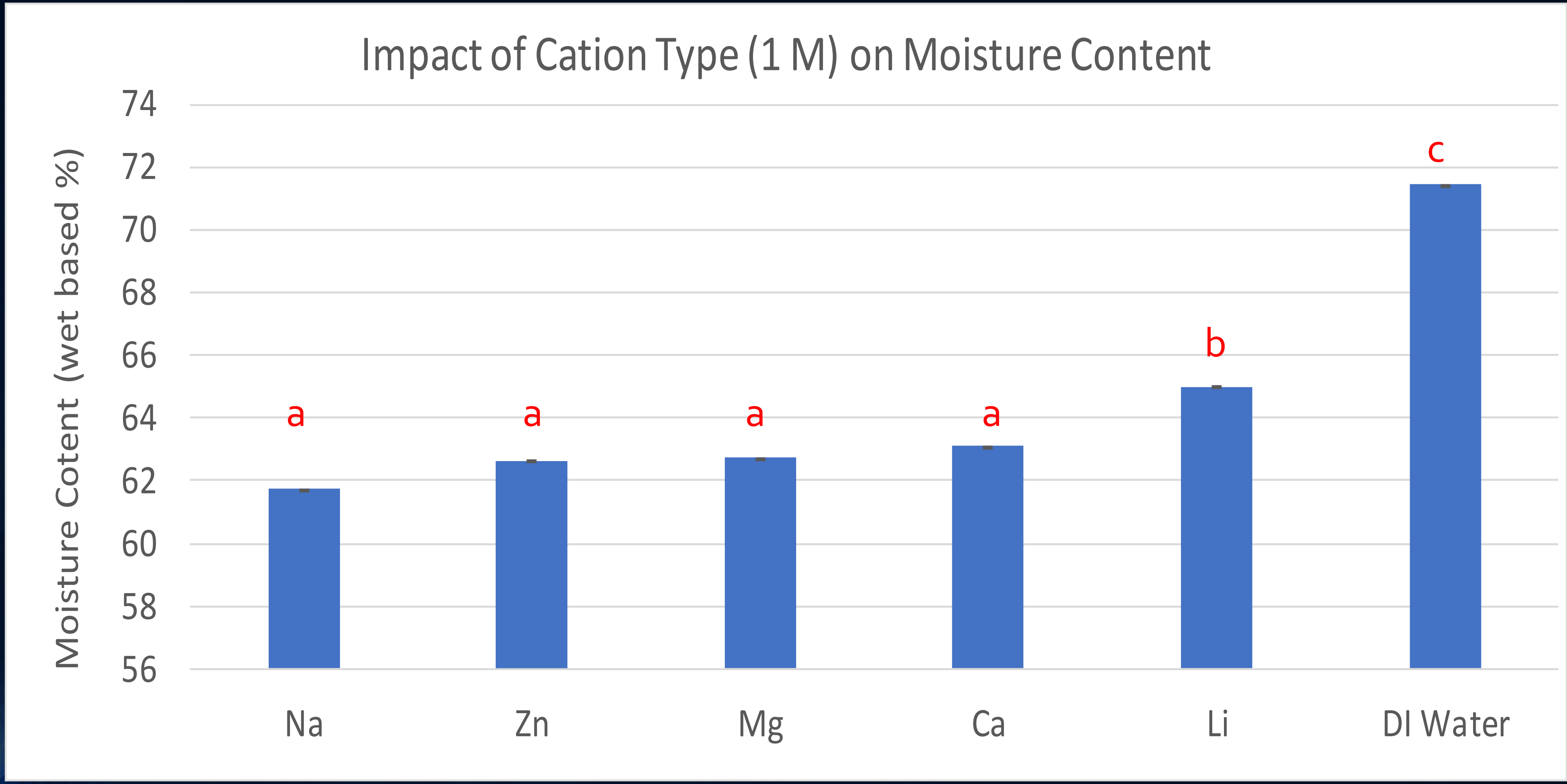


Salts

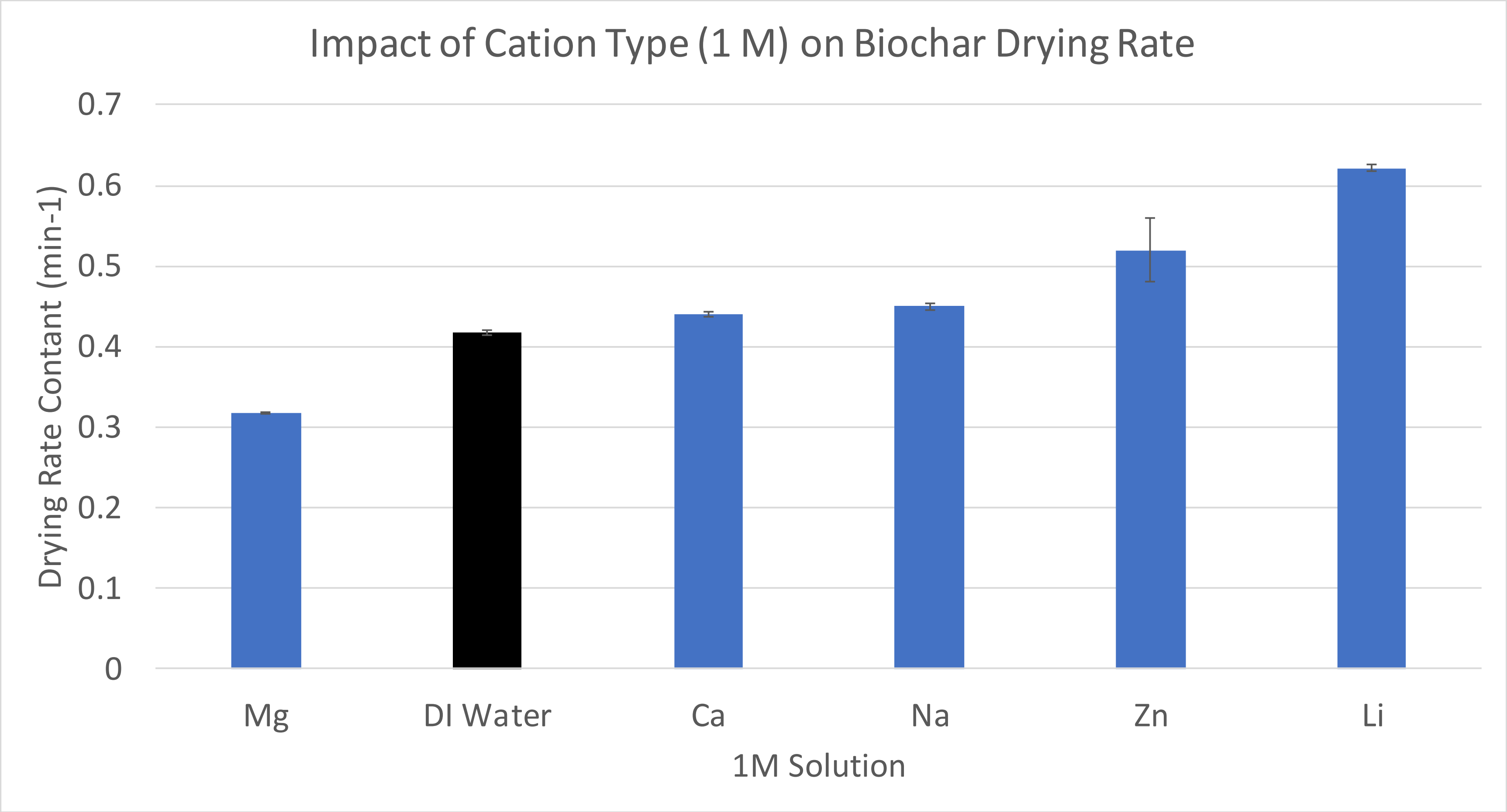
Seawater – Adds more diffusional character to water uptake



No clear impact of cation type ?

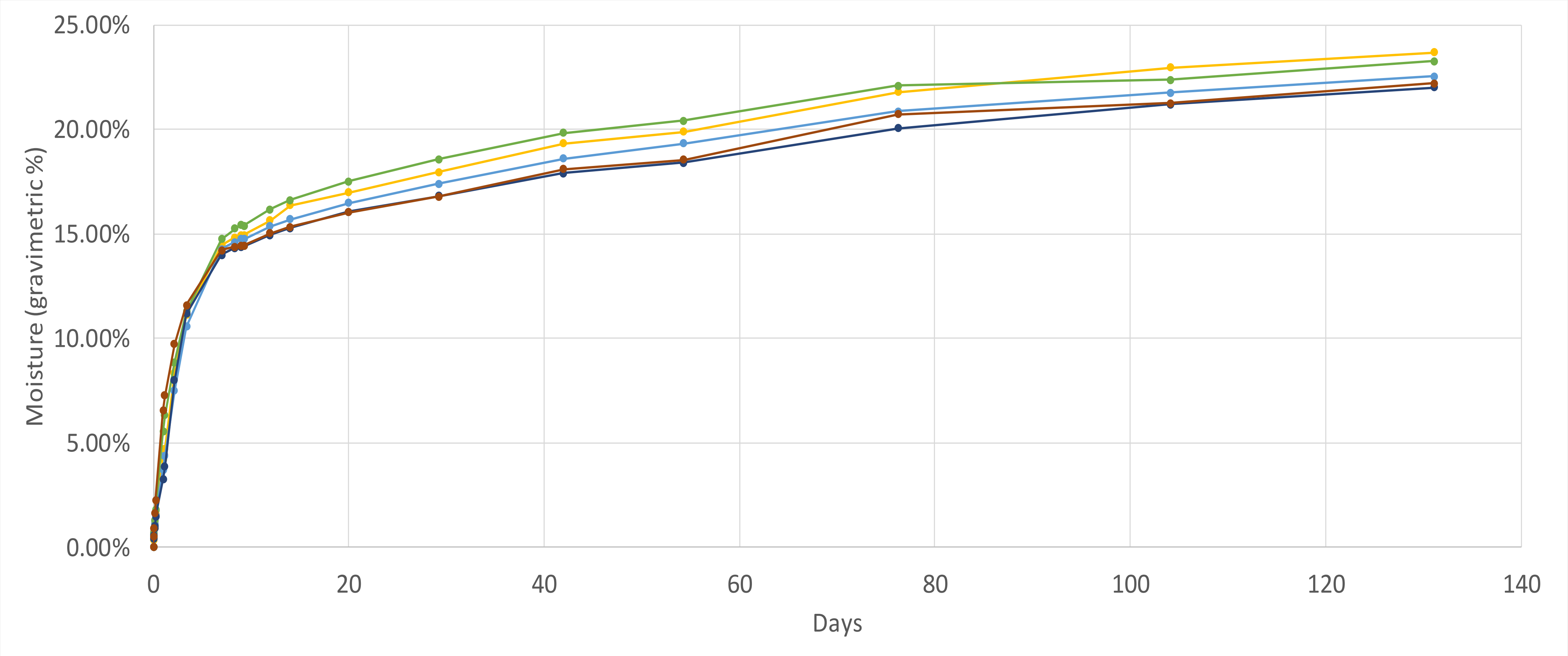


However, larger cation impact on drying rates

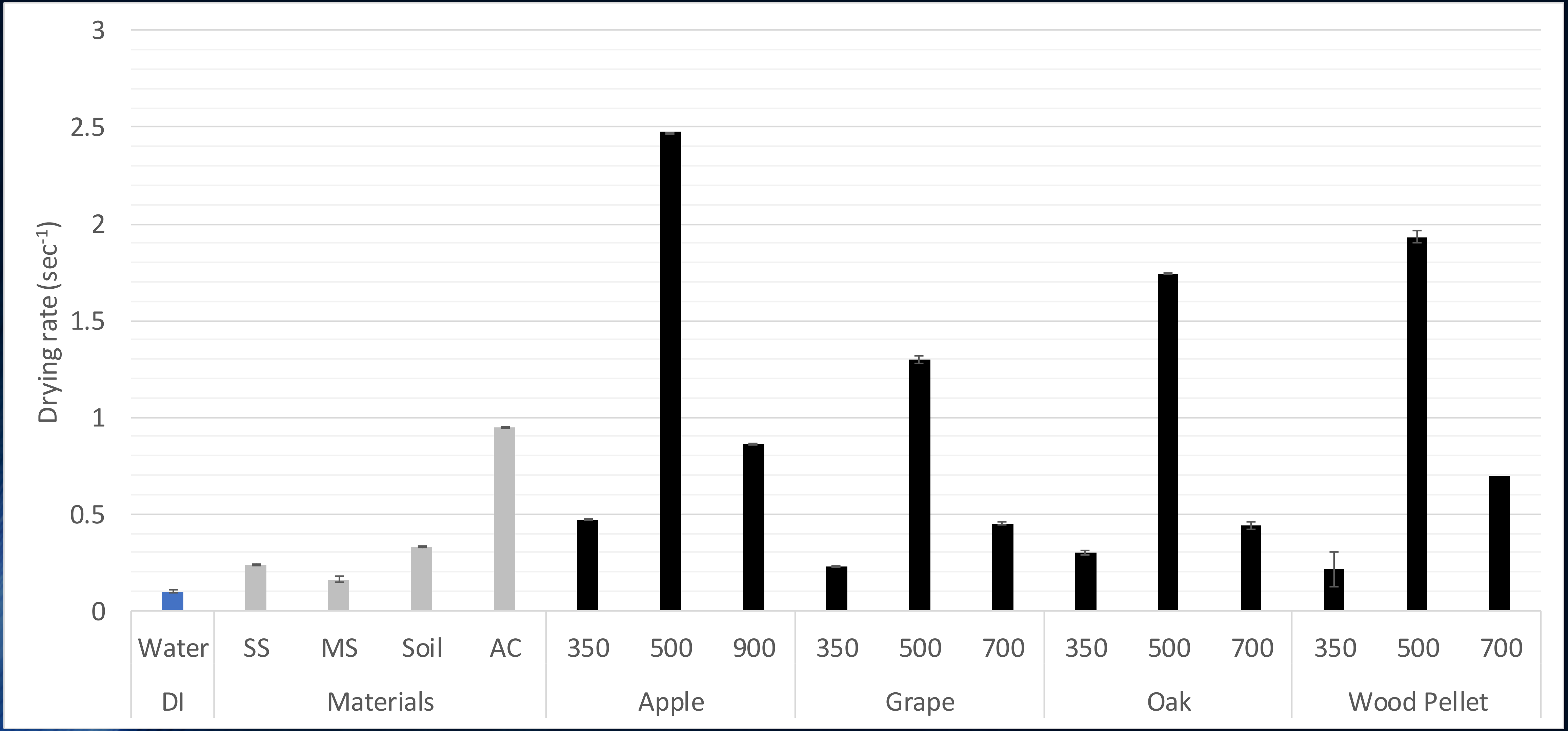


Water Vapor Sorption

Coconut BC – 575 ^{o}C biochar



Biochar – Drying Rate Kinetics



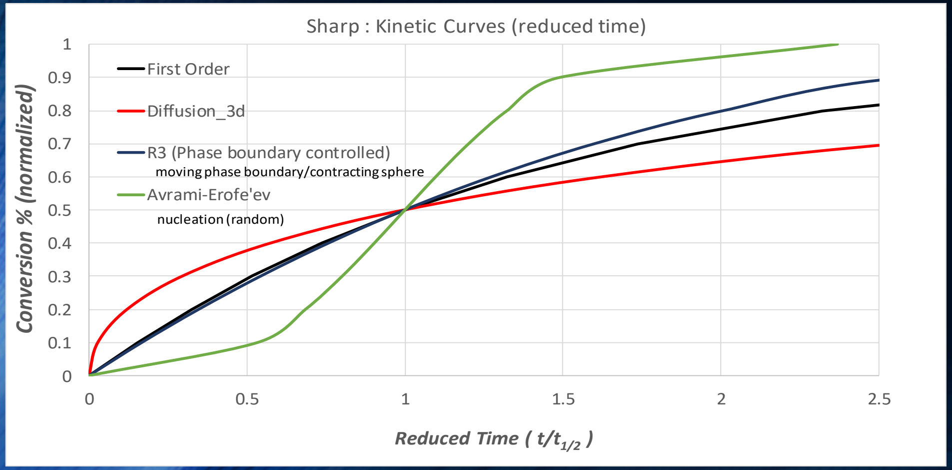
Sharp Reduced Time Curves: Rate Limiting Kinetic Mechanisms

$\frac{t}{t_{0.333}}$

Kinetic expression that describes any process by:

$$G(\alpha) = \mathrm{A}\left(\frac{t}{t_{0.333}}\right)$$

G(α) = theoretical kinetic expression
A is a constant
t is the time
$t_{0.333}$ is the time to the one-third completion

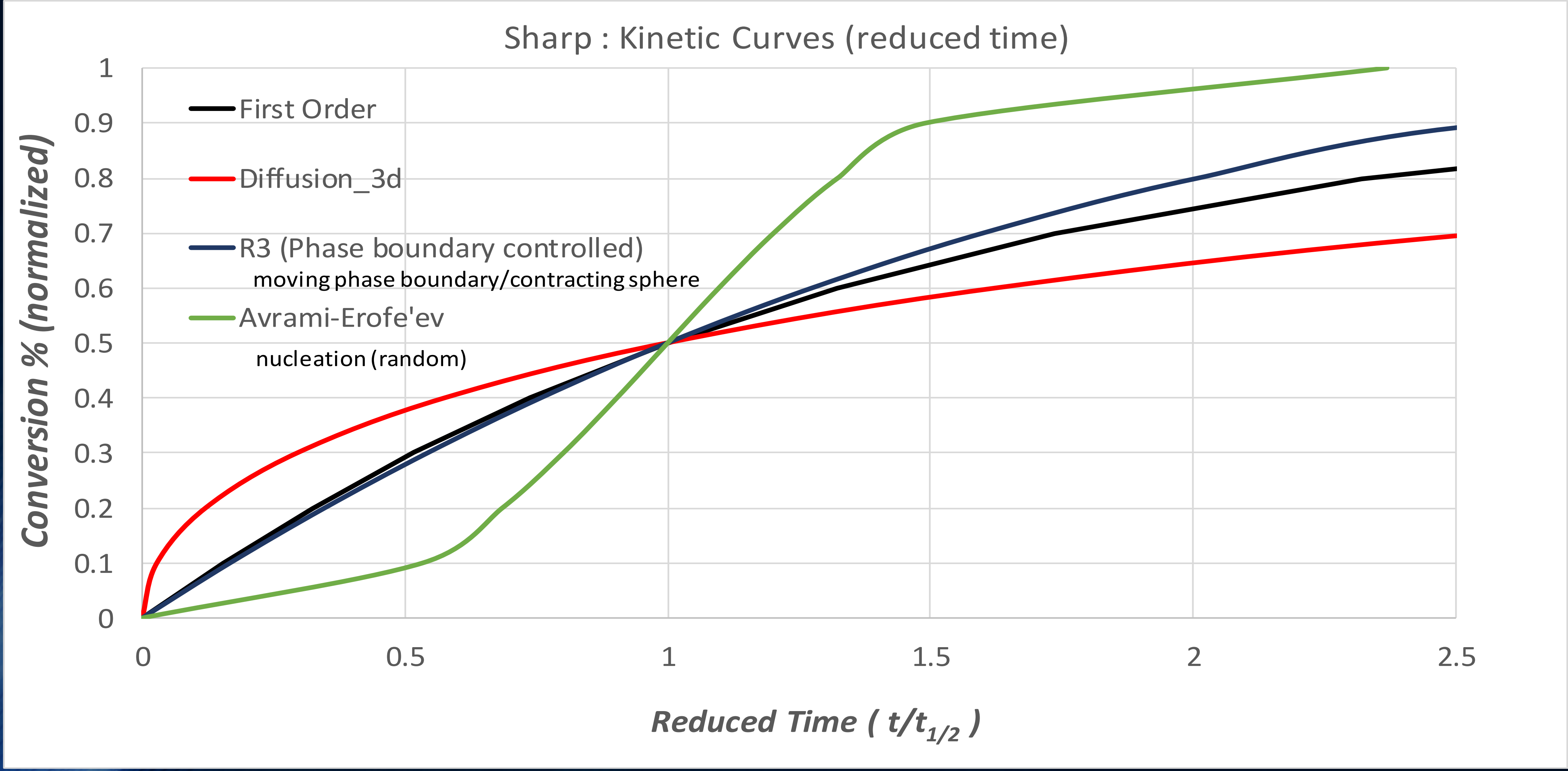


Summary of theoretical kinetic relationships [G(α)] and value of constant (A) for a time ratio occurring at 33.33% completion.

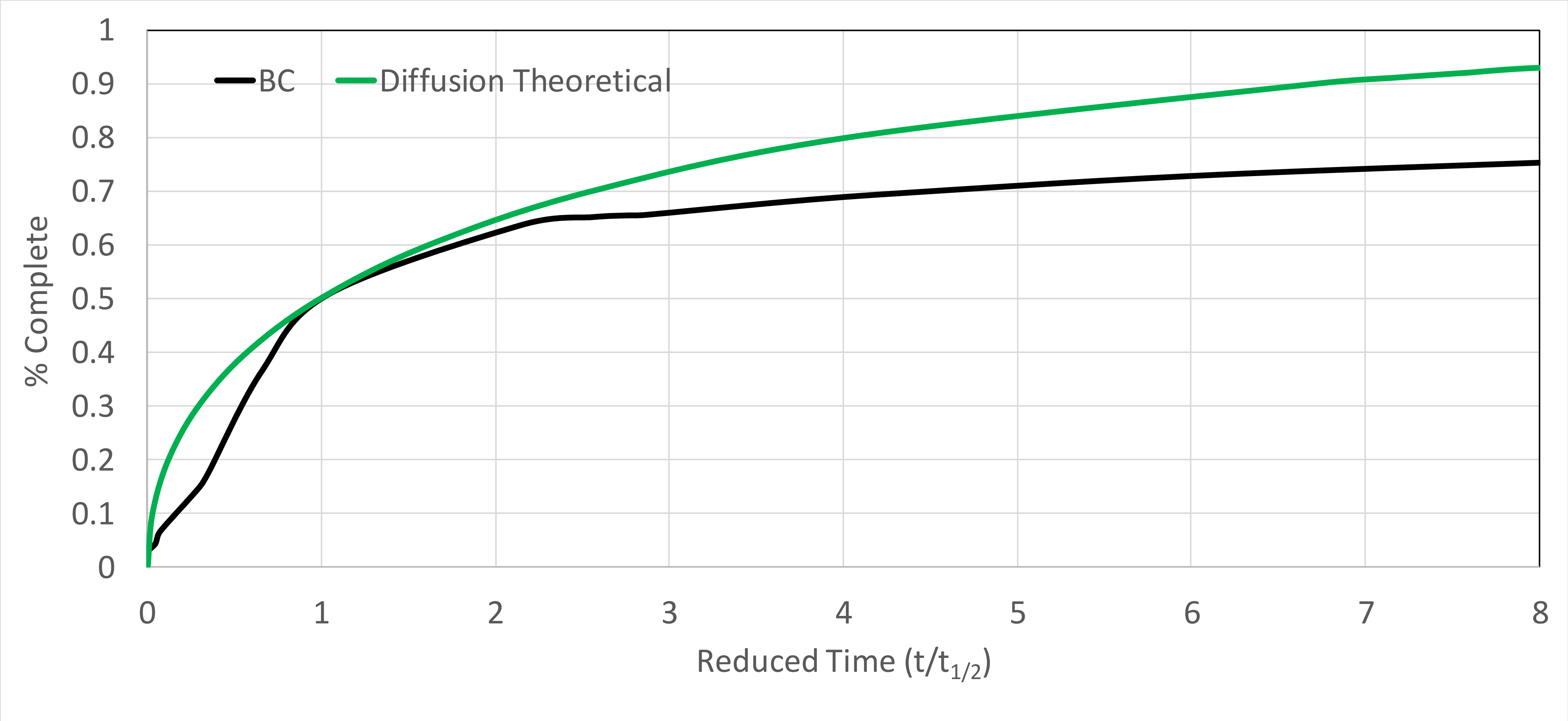
Mechanism	Symbol	G(α)	A
Phase boundary controlled reaction (contracting area; bidirectional shape)	*R2*	$2\left[1-\sqrt{(1-\alpha)}\right]$	0.3670
Phase boundary controlled reaction (contracting volume; heating)	*R3*	$3\left[1-\sqrt[3]{(1-\alpha)}\right]$	0.3793
Unimolecular decay law (first order reaction) Instantons growth; unidirectional growth	*F1*	$-\ln(1-\alpha)$	0.4057
Random nucleation/growth (Johnson-Mehl-Avrami equations)	*A2*	$\sqrt{[-\ln(1-\alpha)]}$	0.6368
	A3	$\sqrt[3]{[-\ln(1-\alpha)]}$	0.7402
1-D diffusion	*D1*	α^2	0.110
2-D diffusion	*D2*	$(1-\alpha)\ln(1-\alpha)+\alpha$	0.0630
3-D diffusion	*D3*	$\left[1-\sqrt[3]{(1-\alpha)}\right]^2$	0.0160
3-D diffusion (Ginstein-Brounshtein Eqn)	*D4*	$(1-\frac{2\alpha}{3})-(1-\alpha)^{\frac{2}{3}}$	0.0146

(Sharp et al. 1966)

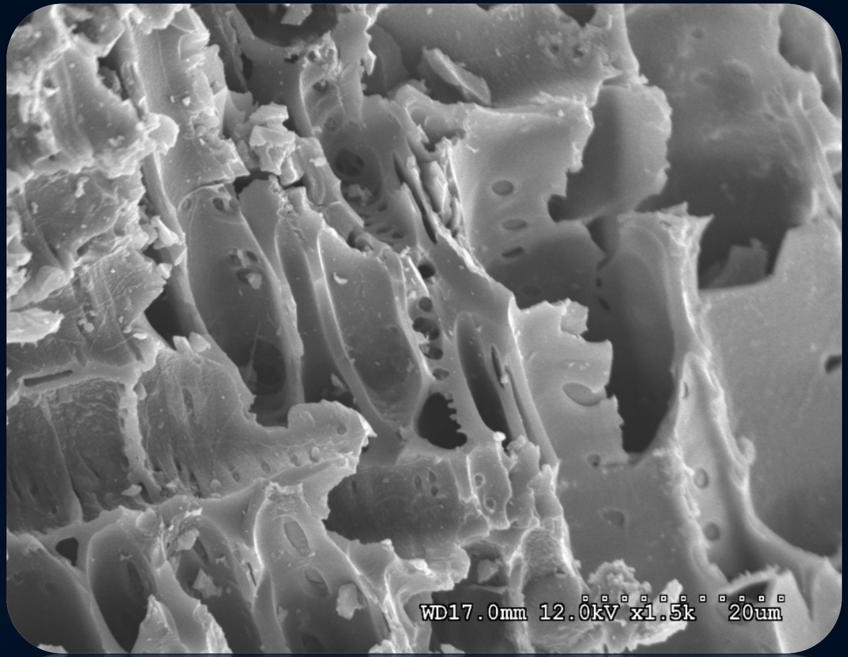
Sharp Reduced Time Curves

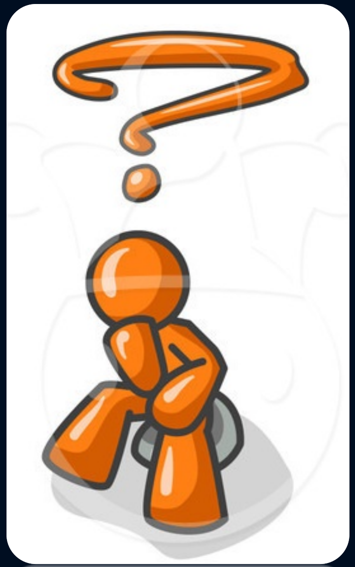


Biochar Kinetic Analysis -

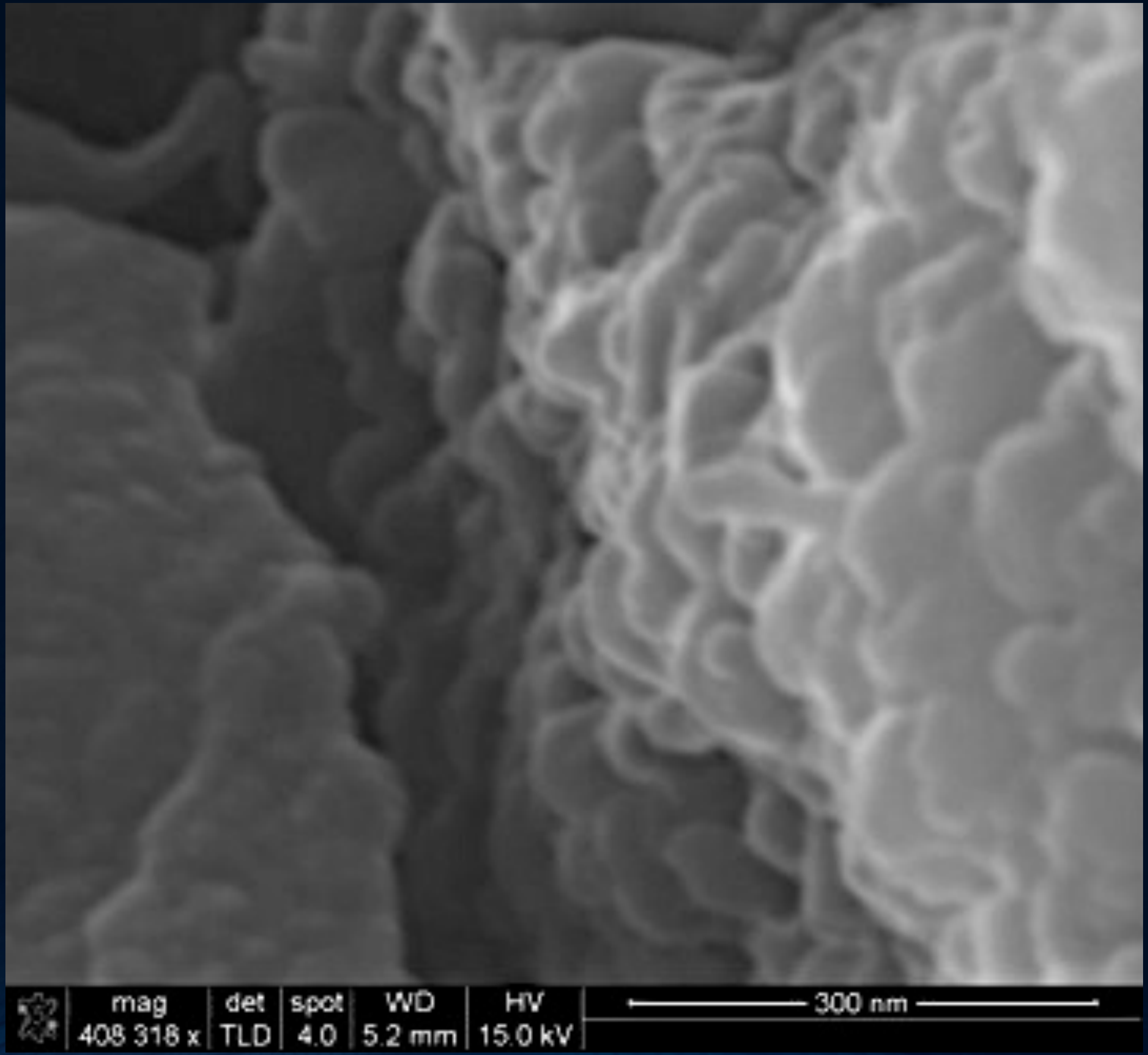


Biochar Sorption – Maybe its not the carbon ?



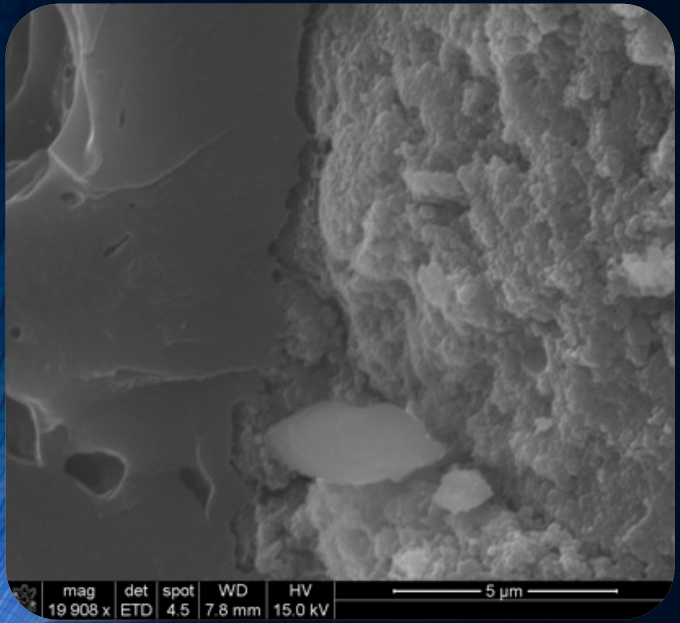


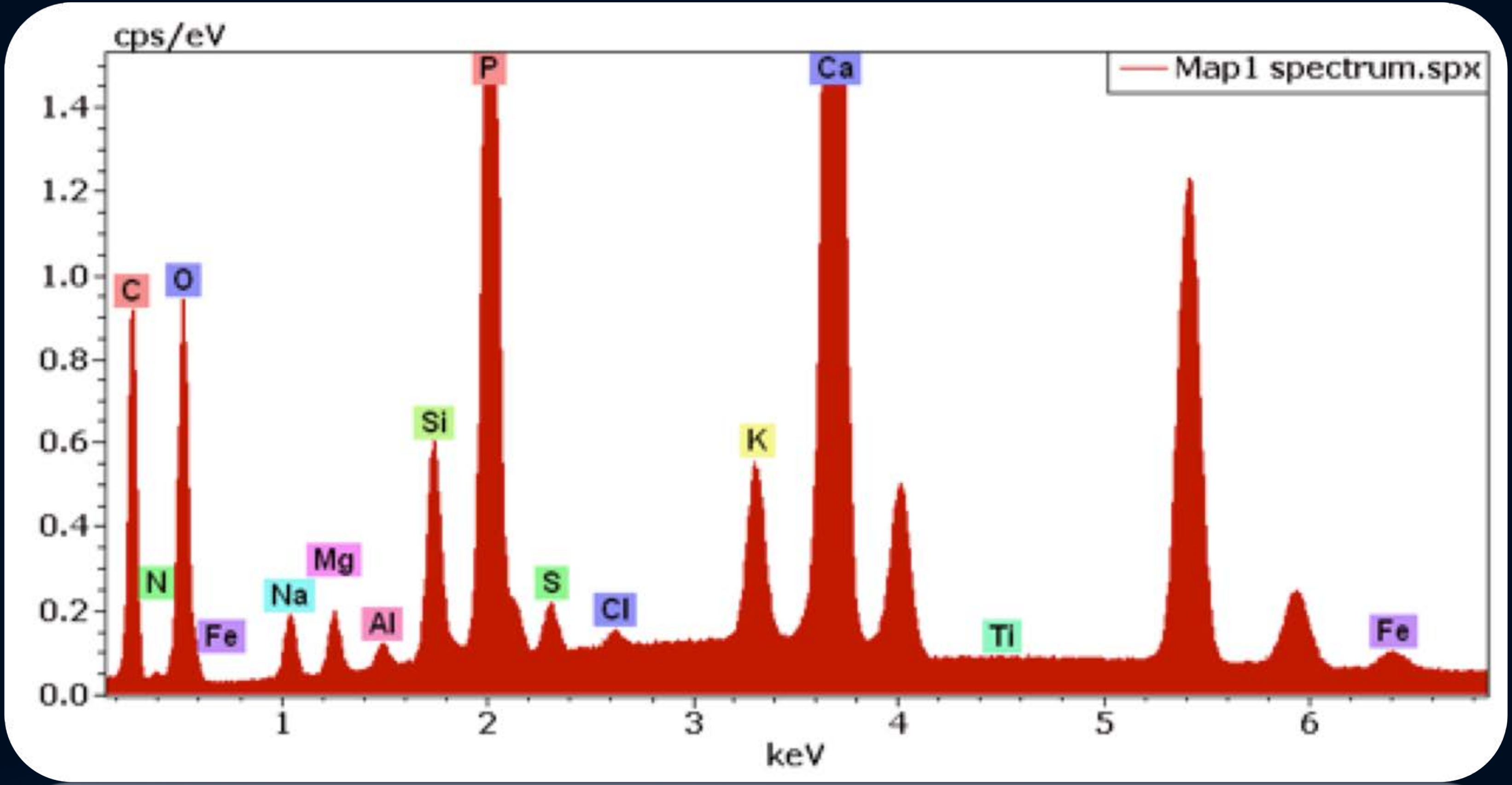
Aged Biochar - Fairly Uniform Coating



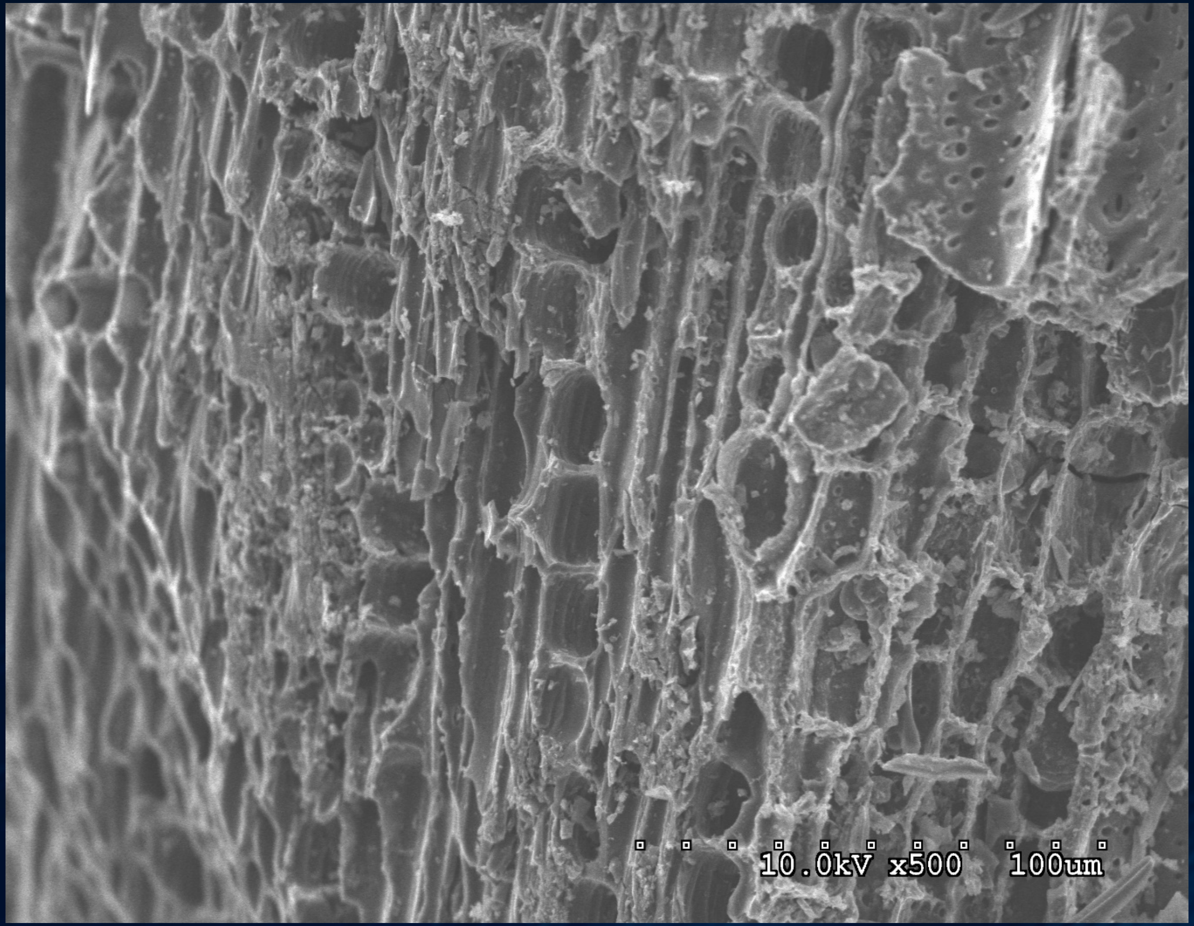
Biochar

- Cations – but where is N, P, Cl, Br, OH, O ???



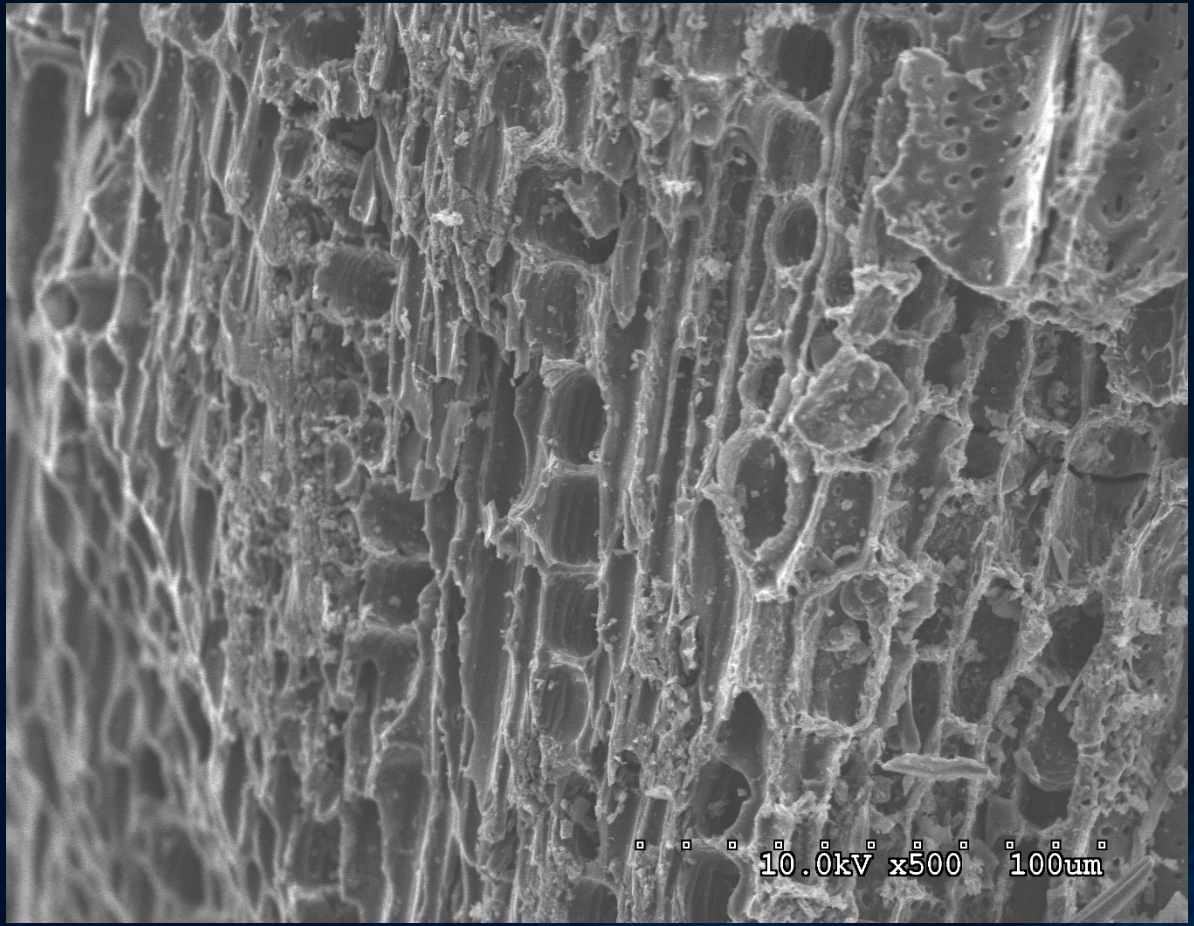


Biochar : Fluorescent dyes

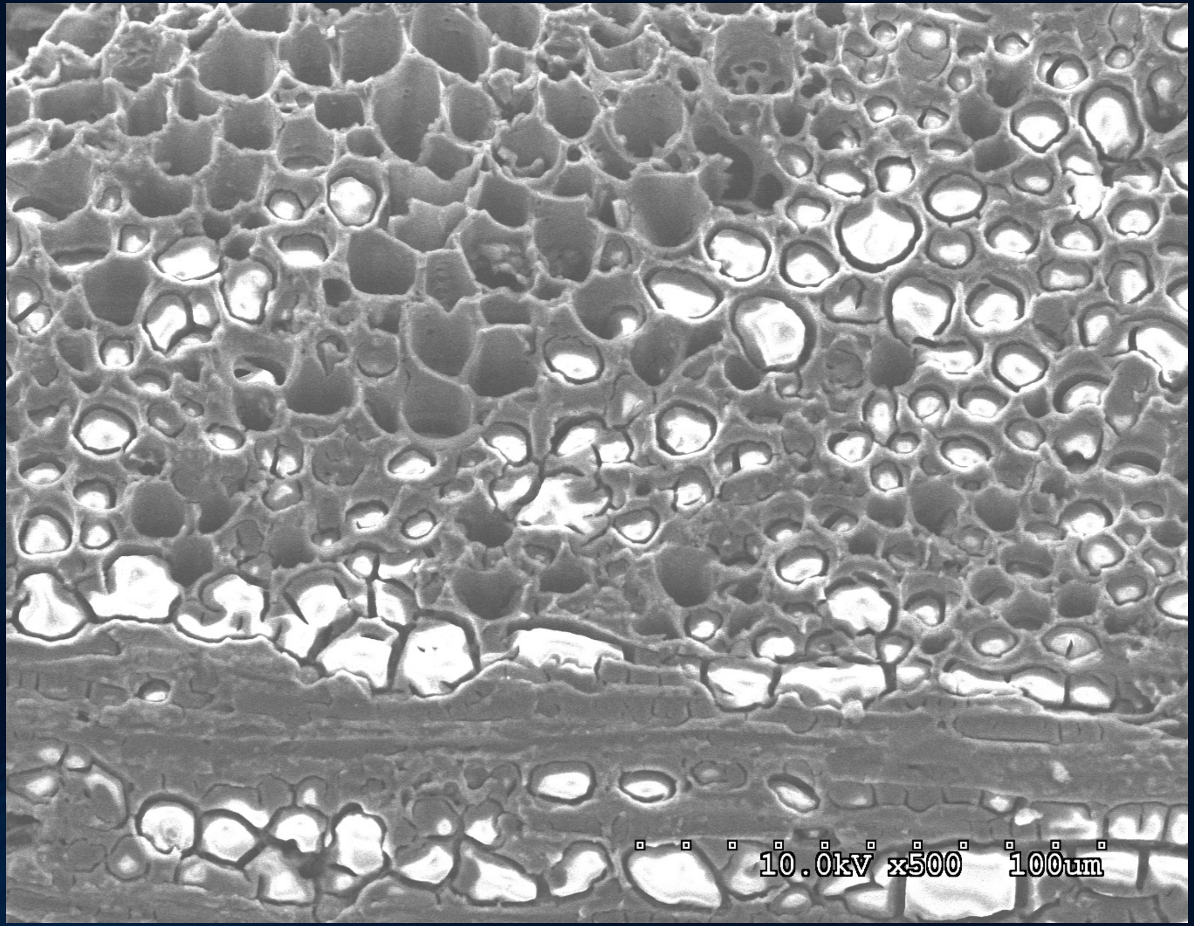


Initial

Biochar : Fluorescent dyes



Initial



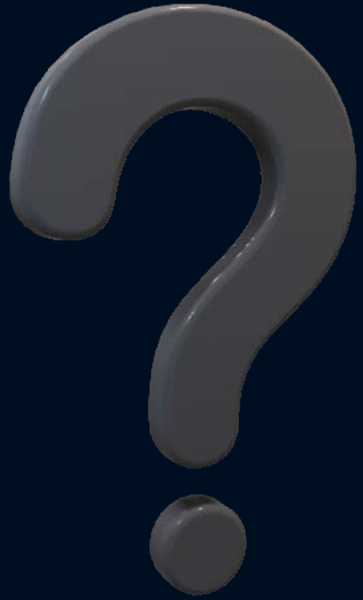
With dye

Dipole-Dipole Interactions

- Comparing evaporation rates of various solvents from saturated biochar samples

Correlation Matrix: BC Drying Rate vs. Solvent Properties

	Pearson Correlation (R^2)
Solvent Dipole Moment	**0.432**



Dipole-dipole interactions ?

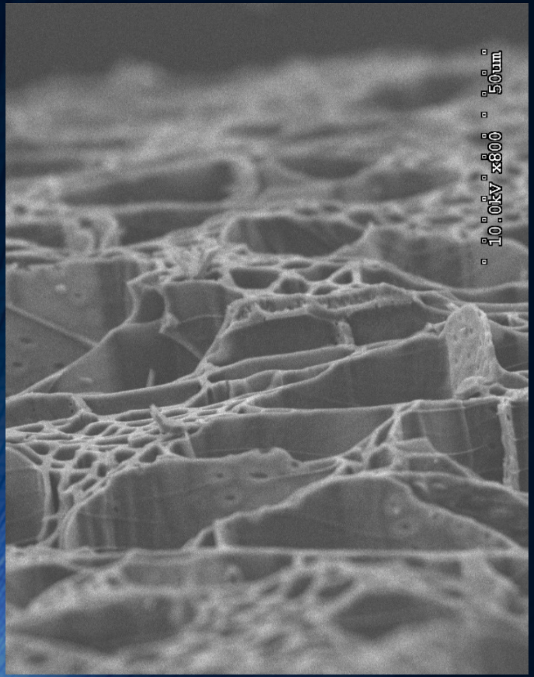
- Comparing evaporation rates of various solvents from saturated biochar samples

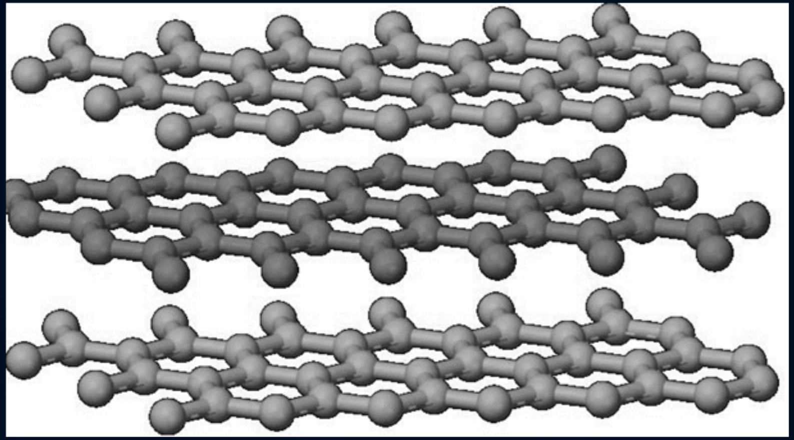
Correlation Matrix: BC Drying Rate vs. Solvent Properties

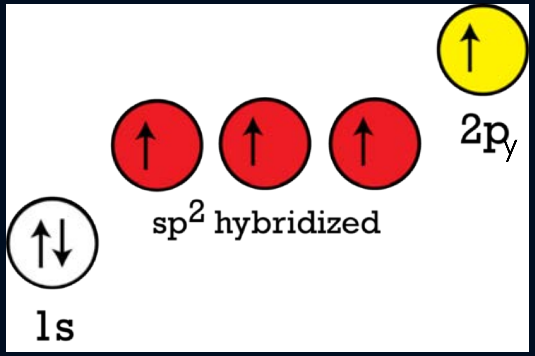
	Pearson Correlation (R^2)
Dipole Moment	0.432
Dipole Length	0.433
Solvent Boiling Point (^oC)	0.225
Magnetic Susceptibility (cm^3/mol)	**0.942**

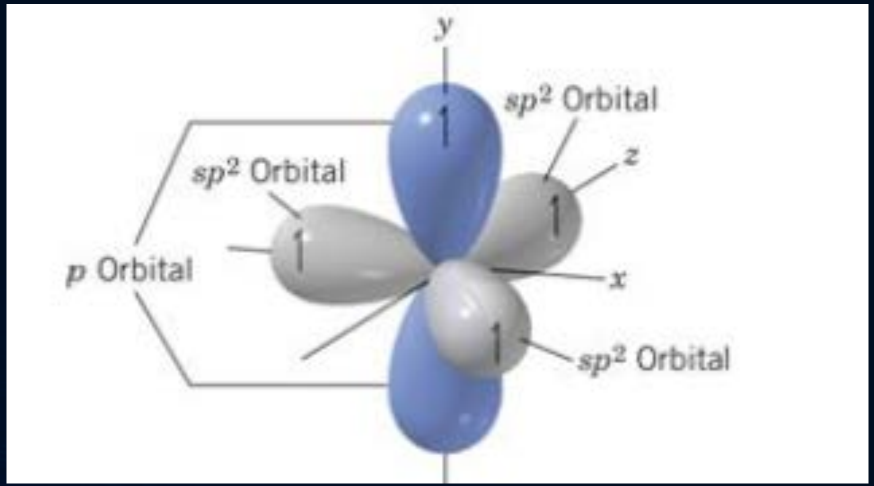
At the molecular scale

GRAPHITIC CARBON STRUCTURES (sp^2 HYBRIDIZATION)

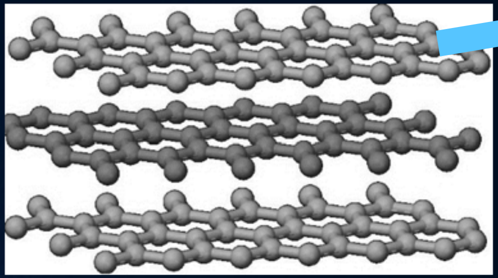


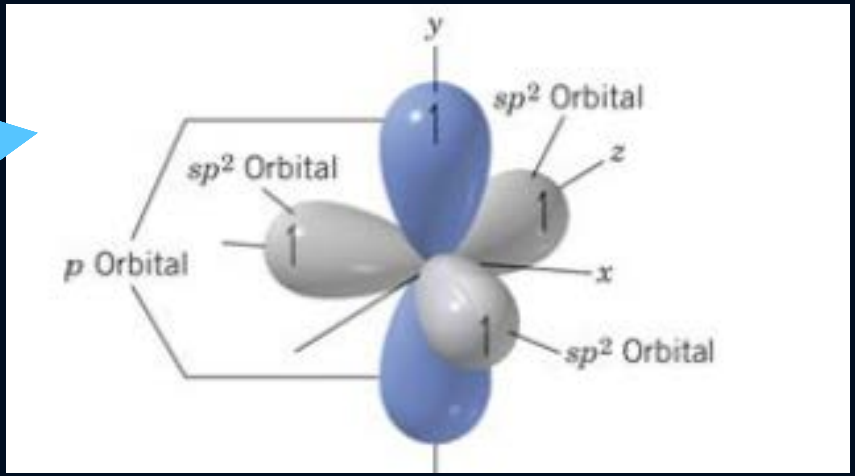






Calculation of electric field at biochar surface

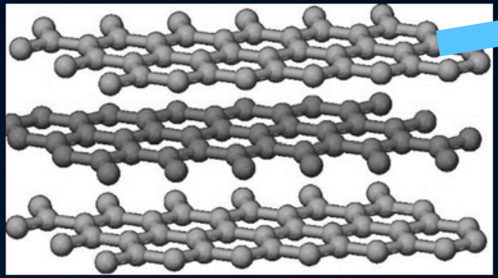


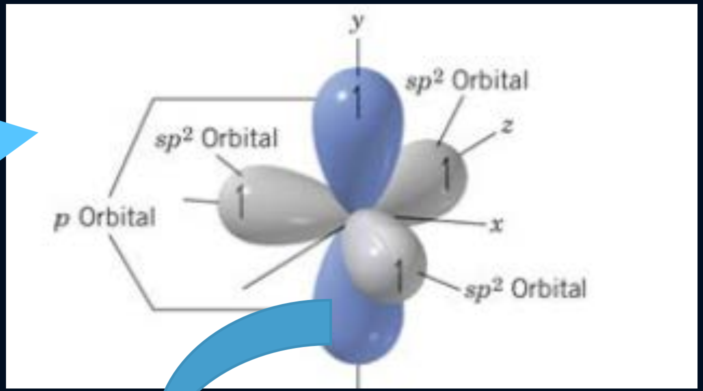


USING SCHOTTKY'S ASSUMPTION FOR METALS
ELECTRIC FIELD ALSO PRODUCED BY OUT-OF-PLANE ELECTRONS

$$E \approx \frac{\in}{4r^2}$$

Calculation of electric field at surface





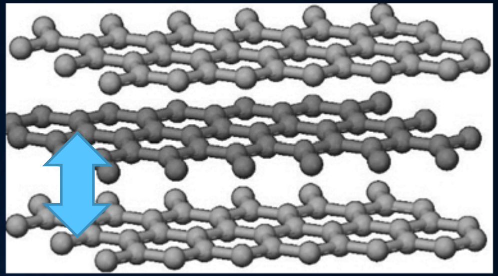
$$\varphi = \frac{\in}{4{r_o}^2}$$

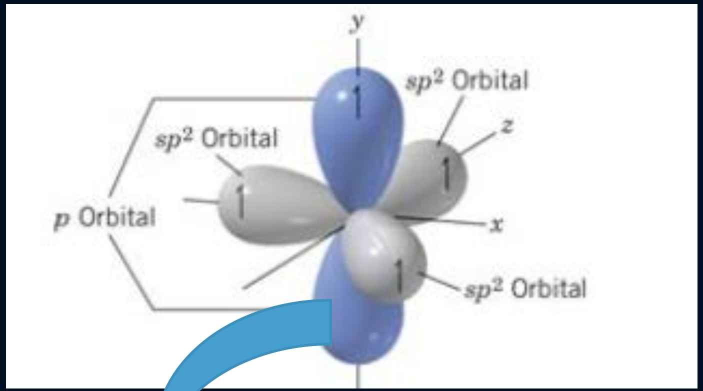
CARBON → 4.34 eV

r_O = 1.6 X 10^{-8} m (0.16 nm)

Calculation of electric field at surface

0.34 nm

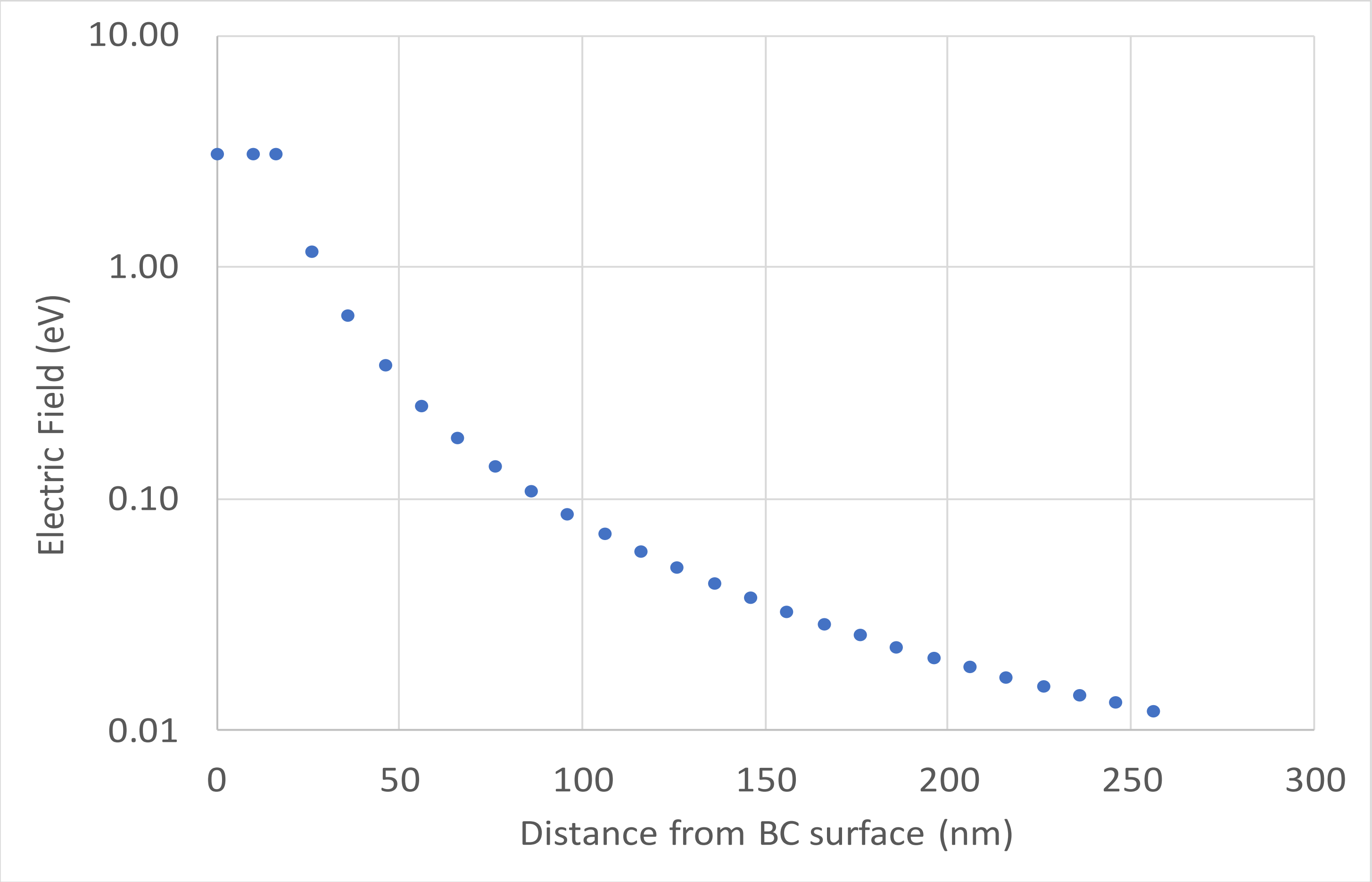


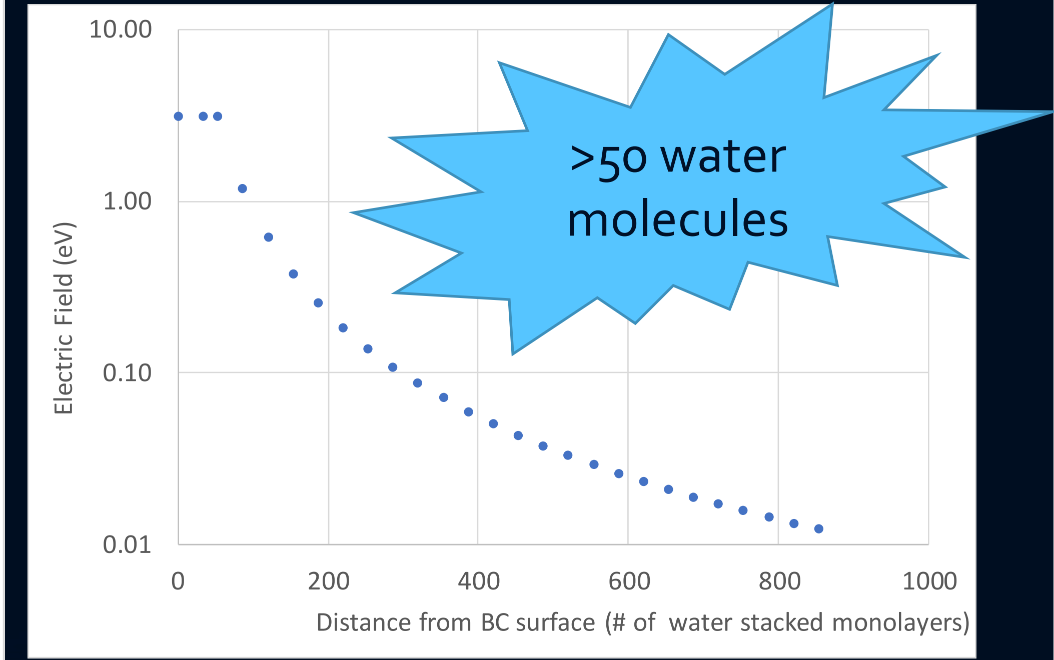


CARBON → 4.34 eV

r_o = 1.6 X 10^{-8} m (0.16 nm)

Can this electric field impact water sorption?





USING SCHOTTKY'S ASSUMPTION FOR METALS $E \approx \frac{\in}{4r^2}$

However -

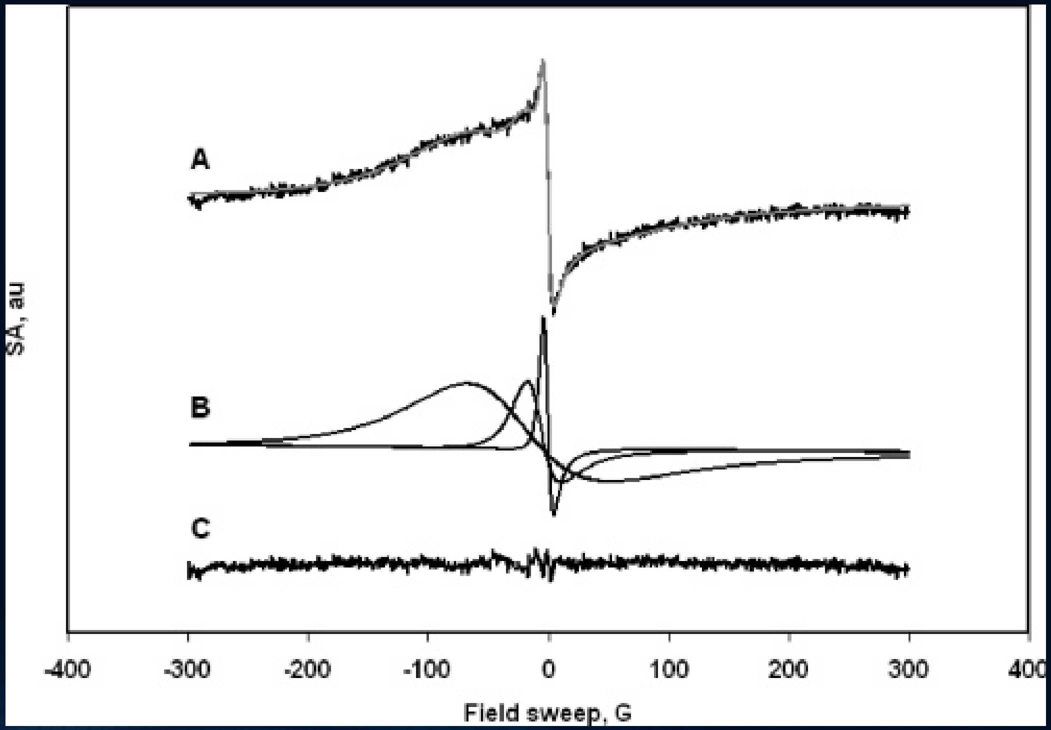
- The work function is not a static characteristic of a bulk material

  - A property of the current surface state
    - Crystal face
    - Contamination (water/CO_2/chemisorbed O_2)
    - Other contamination - ash component/soil particles

Heteroatoms – replacements of carbon

EPR DATA CONFIRMS THE G-VALUES INCREASE FOR UNPAIRED ELECTRONS LOCALIZED AT HETEROATOMS (N, O, S) COMPARED TO UNPAIRED ELECTRONS LOCALIZED AT CARBON ATOMS .

WIĘCKOWSKI EXP TECHN PHYS, 36 (1988), P. 299



Why similar biochar composition results in different sorption?

- Heating profile

  >> rate of temp increase and decrease

- Duration and atmosphere composition
- Initial moisture content of feedstock
- “Aging” (interactions with water vapor or carbon dioxide, or **loss of unpaired electrons**)

Biochar Sorption – Surface Area, Oxygen, or ……

Surface Area → **Oxygen Content** → **Unpaired spin number**

Surface Area
- Correlation between biochar from same pyrolysis unit
- Less universally across studies or feedstock types

Oxygen Content
- Improved correlations within same pyrolysis unit
- Improved correlation across different studies
- Although not deterministic for different feedstocks

Unpaired spin number
- Improved predictable especially across different biomass types
- Mechanism?

Why does this happen?

$$\Psi_{total} = \Psi_{ref} + \Psi_{\Pi} + \Psi_{M} + \Psi_{pres} + \Psi_{grav} + \Psi_{electro} + \Psi_{humidity}$$

With biochar addition

Osmotic, electrostatic and humidity ≠ 0

$$\Psi_{\Pi} = -C_m RT$$

$$\Psi_e \rightarrow \frac{1}{r^2}$$

$$\psi = \frac{RT}{M_w} \ln(h_r)$$

- Ash component of BC
- Electrostatic field on biochar
- Impacts on relative humidity

Contact charging phenomenon

RELATED TO THE WORK FUNCTION OF THE MATERIALS

Material	Work function (eV)
BC (charcoal)	**4.32**
Coal	3.93
Brass (old)	4.87
Plexiglass	3.50
Stainless Steel	4.40
Copper	4.38
"Mineral Matter"	**5.40**
Aluminum	4.06 – 4.26

BIOCHAR SIEVED IN PLASTIC SIEVE
POSITIVE SURFACE CHARGE

BIOCHAR SIEVED IN BRASS SIEVE
NEGATIVE SURFACE CHARGE

BIOCHAR SIEVED IN SS SIEVE
NO CHANGE TO NEGATIVE CHARGE

UPON MATERIAL CONTACT:
LOWER WORK FUNCTION MATERIAL ACQUIRES NEGATIVE SURFACE CHARGE

Gupta et al. Powder Technology, 75 (1993) 79-87

Additional complications:

What if biochar particles and mineral matter collide

mixing or flow stream (pouring)
small particle sizes <50 micron

Material	Work function (eV)
BC (charcoal)	4.32
"Mineral Matter"	5.40

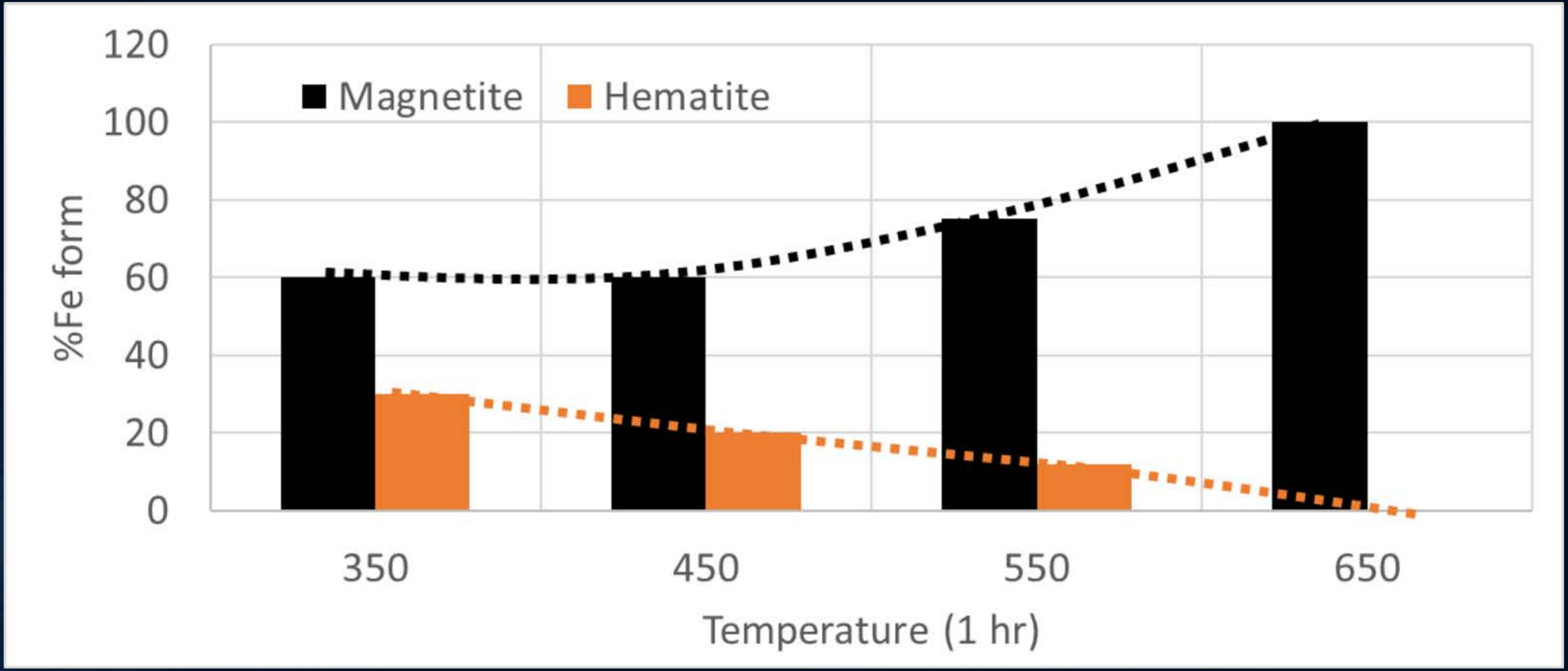
UPON MATERIAL CONTACT:

LOWER WORK FUNCTION MATERIAL ACQUIRES NEGATIVE SURFACE CHARGE
BIOCHAR NEGATIVE CHARGED

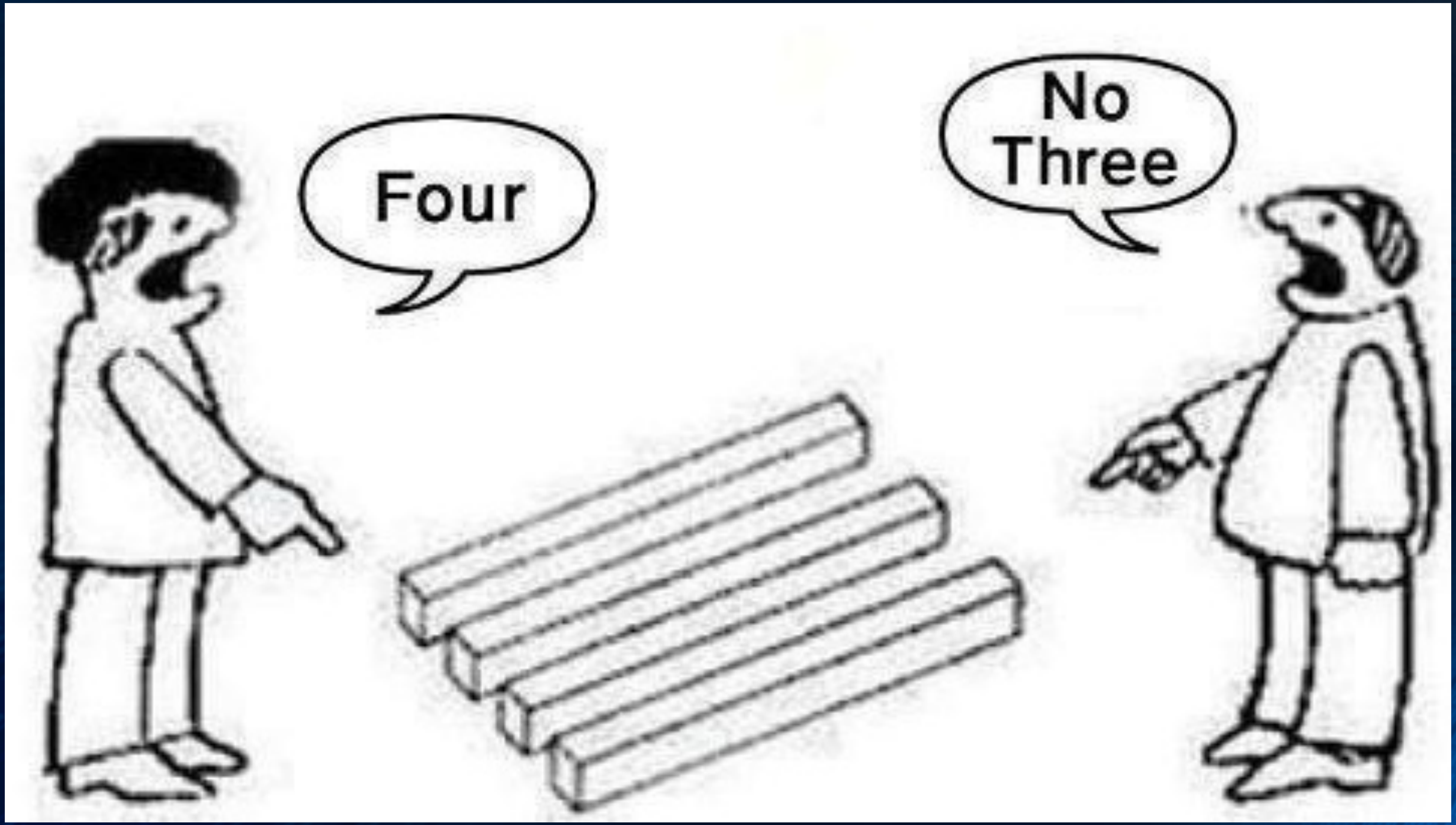
Iron Mineralogy : Impacts SA/Pore Volumes

Iron Mineral	Surface Area (m^2/g)	Pore volume (cm^3/g)
Magnetite	6	0 (non-porous)
Goethite	80	0.23
Hematite	12	0.25
Ferrihydrite	800-1000	0.40

Iron Mineralogy – Temperature Impacts



- Spokas (unpublished) and Regenspurg et al., 2004



Thank-you for your attention.