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Graphite Oxidation Behavior: NRC Graphite Behavior Model

July 2022

William E Windes

Changing the World's Energy Future

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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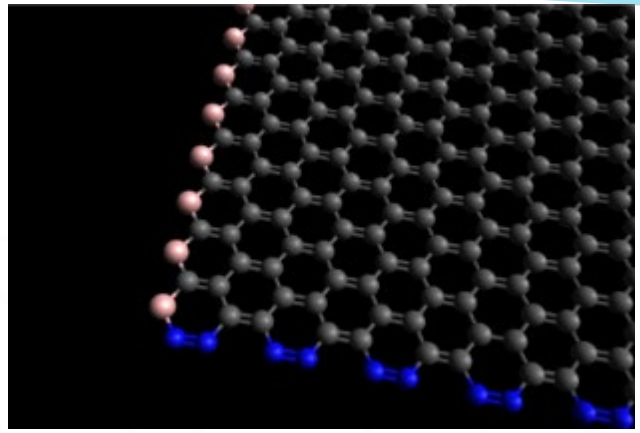
Graphite Oxidation Behavior

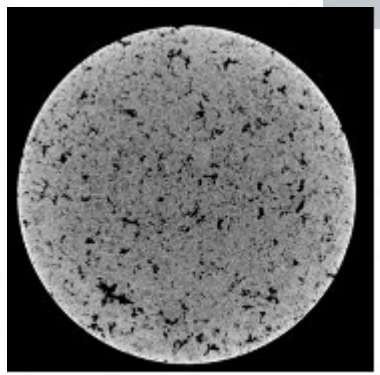
NRC Graphite Behavior Model

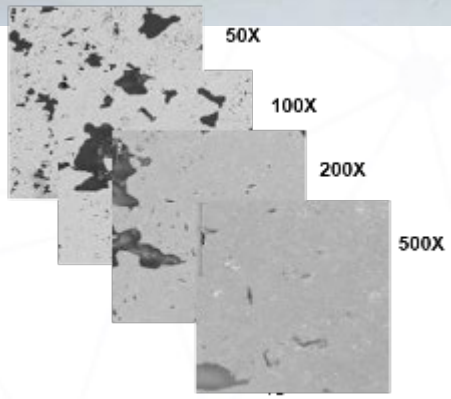
ADVANCED REACTOR TECHNOLOGIES

Graphite oxidation behavior: Topics

- Graphite microstructure and oxidation
  - Graphite crystal structure and basal planes
  - Reactive surface area sites
    Zig-zag and Arm-chair
  - Pore microstructure effects
    - *Interconnectivity*
- Reactivity and oxygen transport
  - Oxygen-**graphite** reaction
    - *Not C-O reaction!*
    - *Temperature effects*
  - Oxygen diffusion to graphite
    - *Diffusion into the microstructure*
    - *High temperature vs low temperature diffusion*
- Oxidation: It's a gradient of factors







Graphite's unique structure is the key

ADVANCED REACTOR TECHNOLOGIES

- Graphite behavior – *it's because of the weird structure*
  - Anisotropic material (stacked, covalently bonded basal planes)
  - Multi-scale material (atomic, crystallite, grain, binder, and specimen)
- Crystal structure is key to understanding behavior
  - Forms a benzene-like ring of carbon atoms – covalent bonds
  - Basal planes form a "chicken-wire" structure

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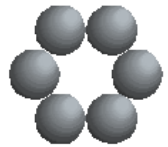
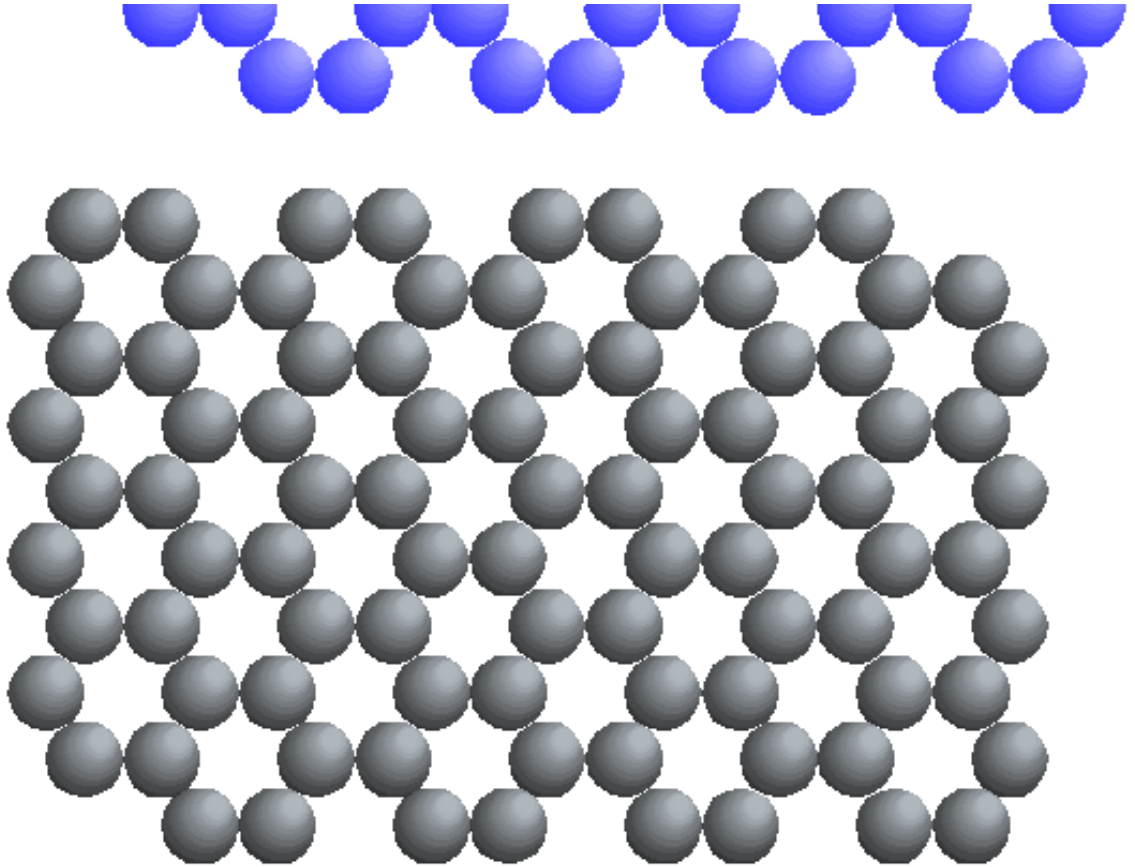


Graphite's unique structure is the key

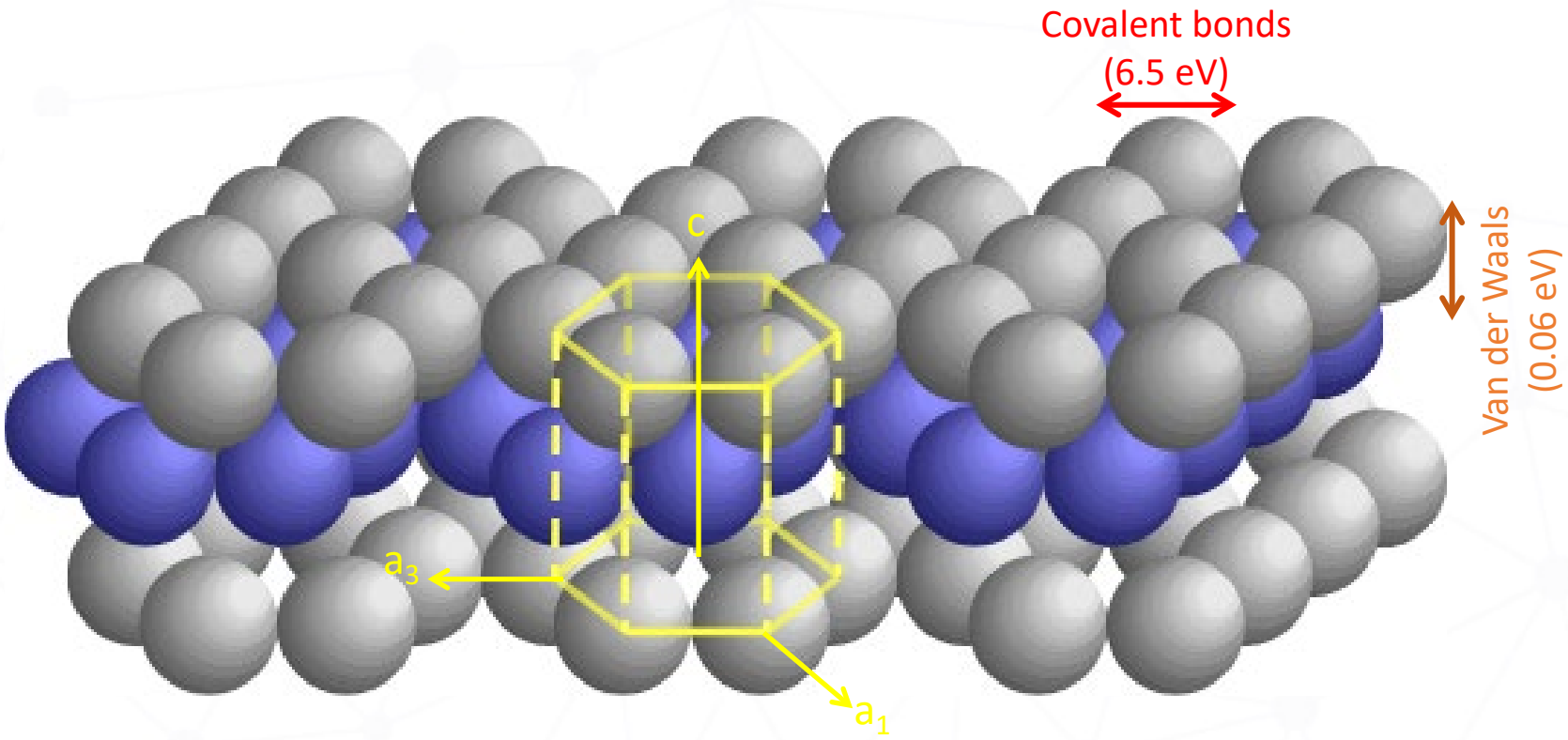
ADVANCED REACTOR TECHNOLOGIES

- Finally the basal planes form an … ABAB… stacking structure



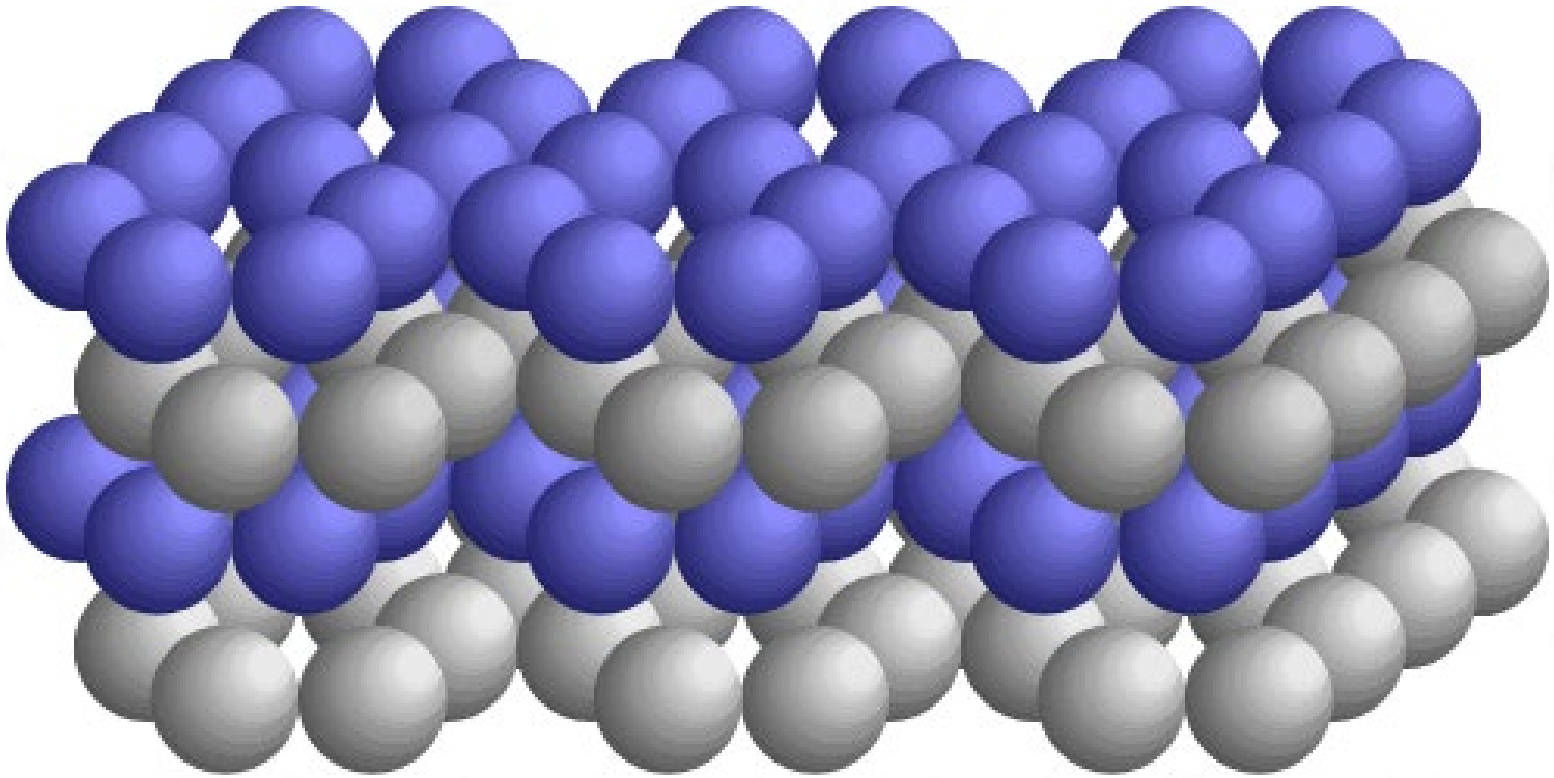
Graphite Crystal Structure

- Hexagonal close pack (HCP)
  - A-B-A-B stacking of basal planes
  - Covalent in basal planes, Van der Waals between basal plane



Multi-scale “composite” material

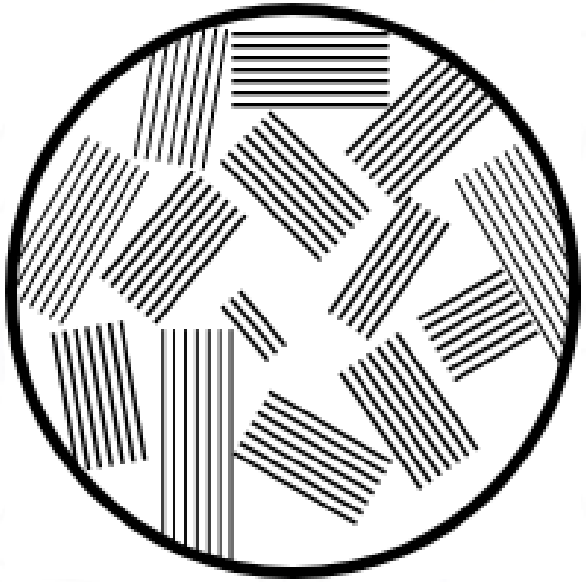
- It’s not just a a uniform cluster of neatly stacked basal planes
  - From atomic crystal structure

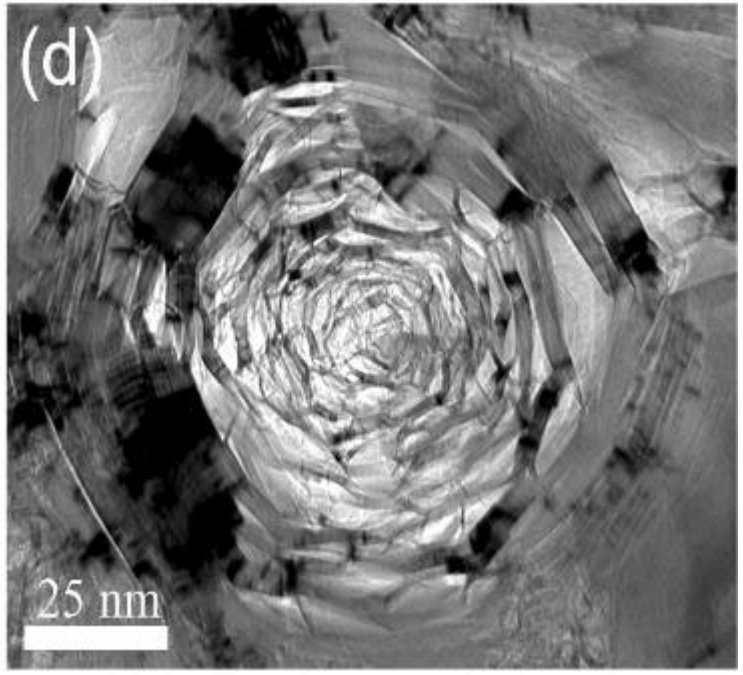


Multi-scale “composite” material

ADVANCED REACTOR TECHNOLOGIES

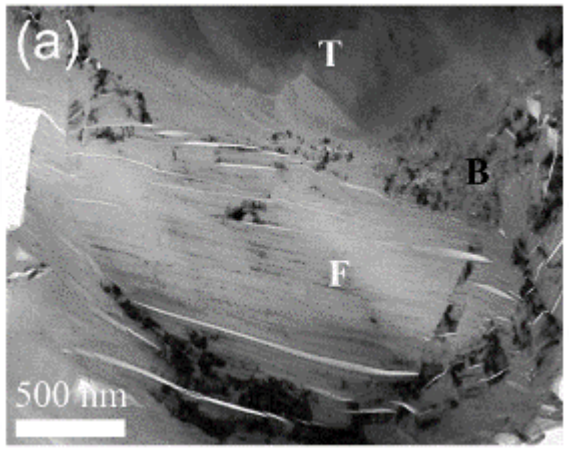
- To crystallites (150X)

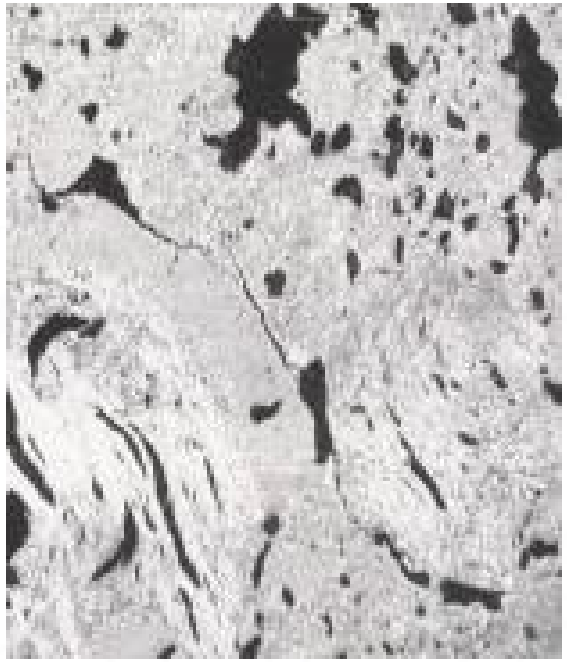


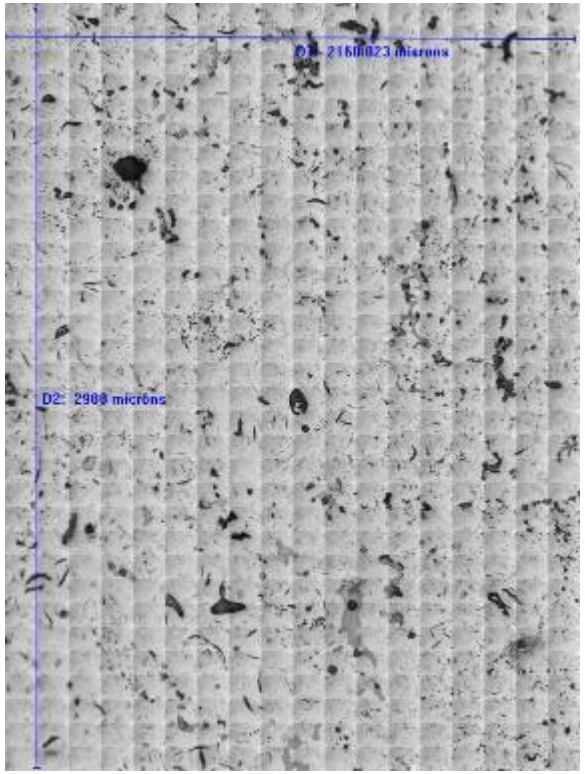


Multi-scale “composite” material

- To grains (filler phase) and binder (5000X) - **Large pores too**!







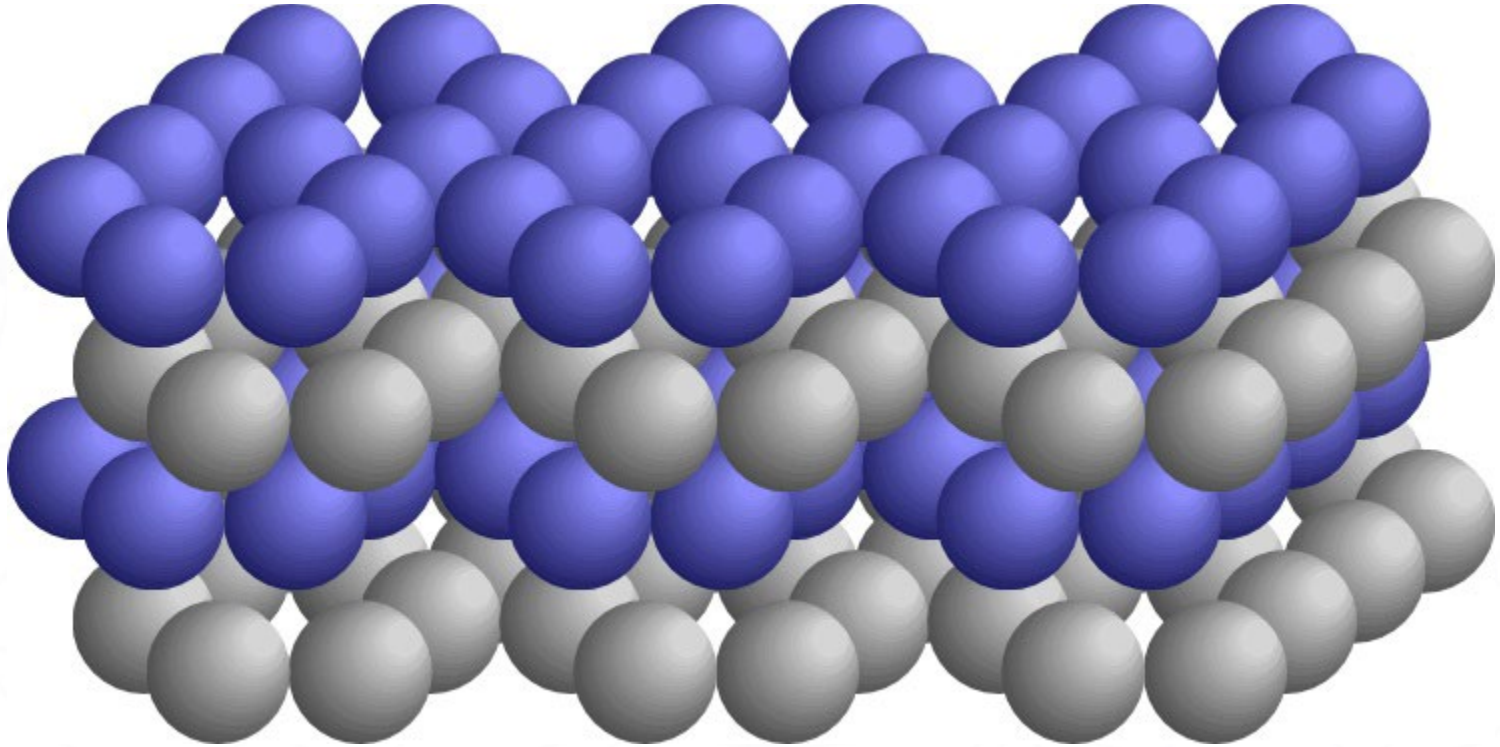
Multi-scale “composite” material

- To the sample and **component level** (100X)

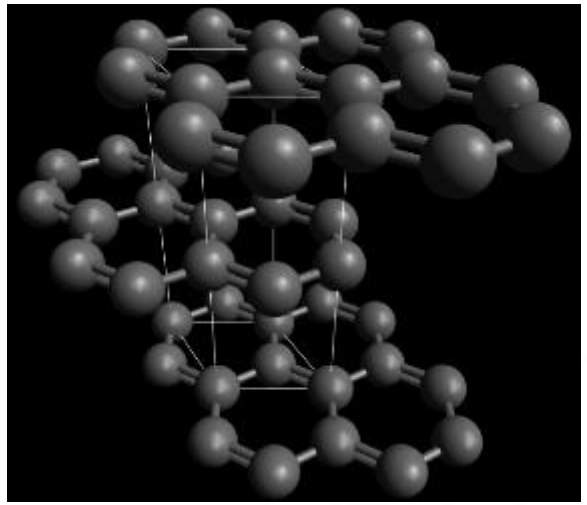
Mechanisms underlying irradiation damage

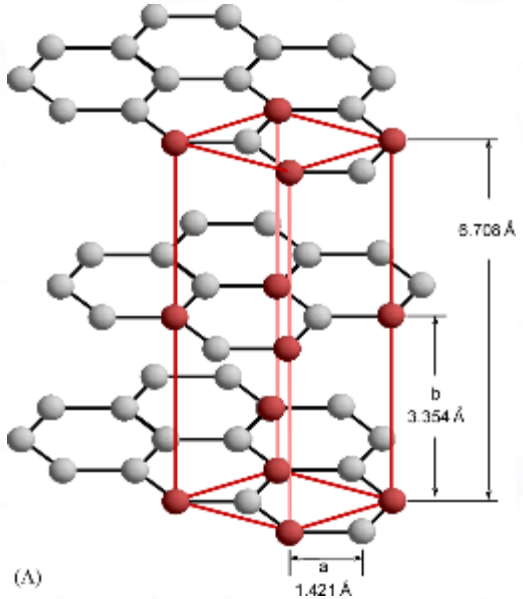
ADVANCED REACTOR TECHNOLOGIES

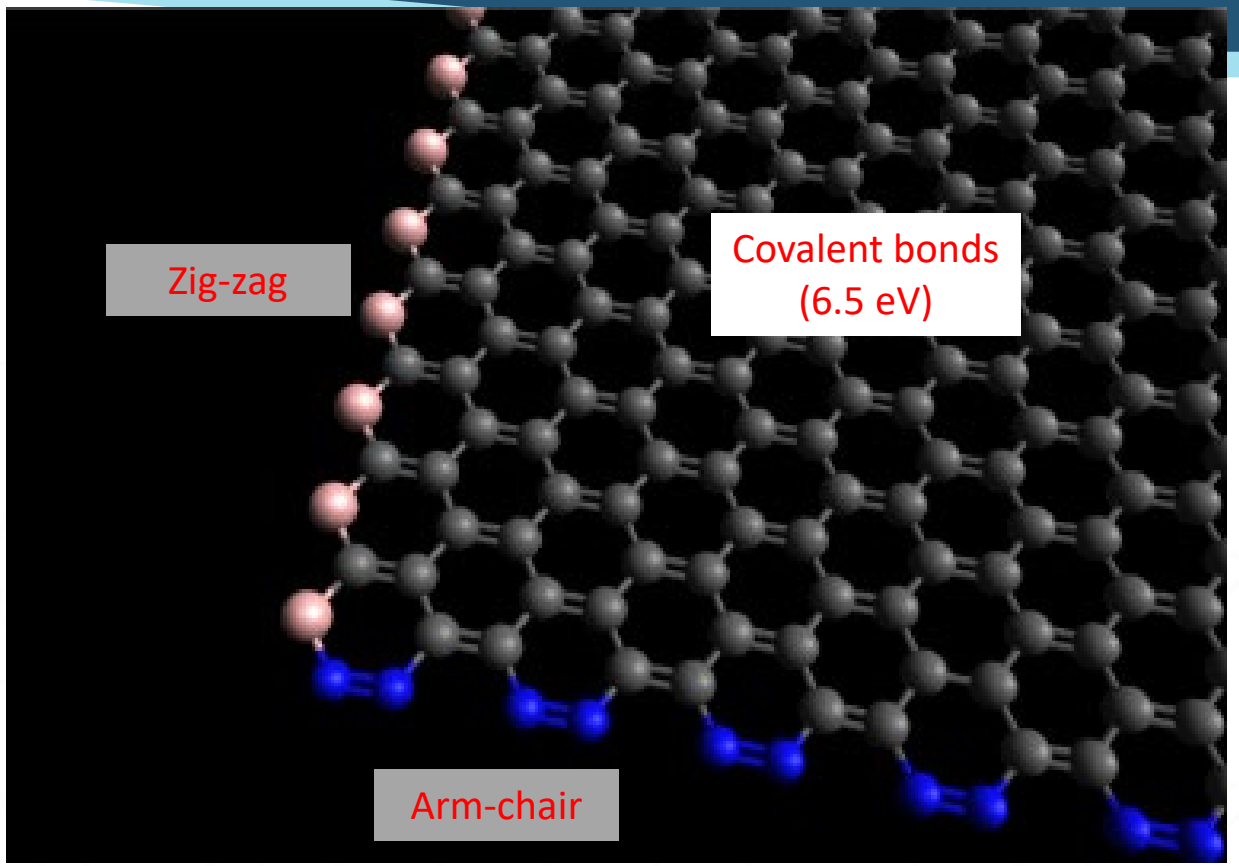
- Ballistic event physically displaces atoms for lattice position
- Sub-plane formation, vacancy clusters



Reactive surface area (RSA) sites





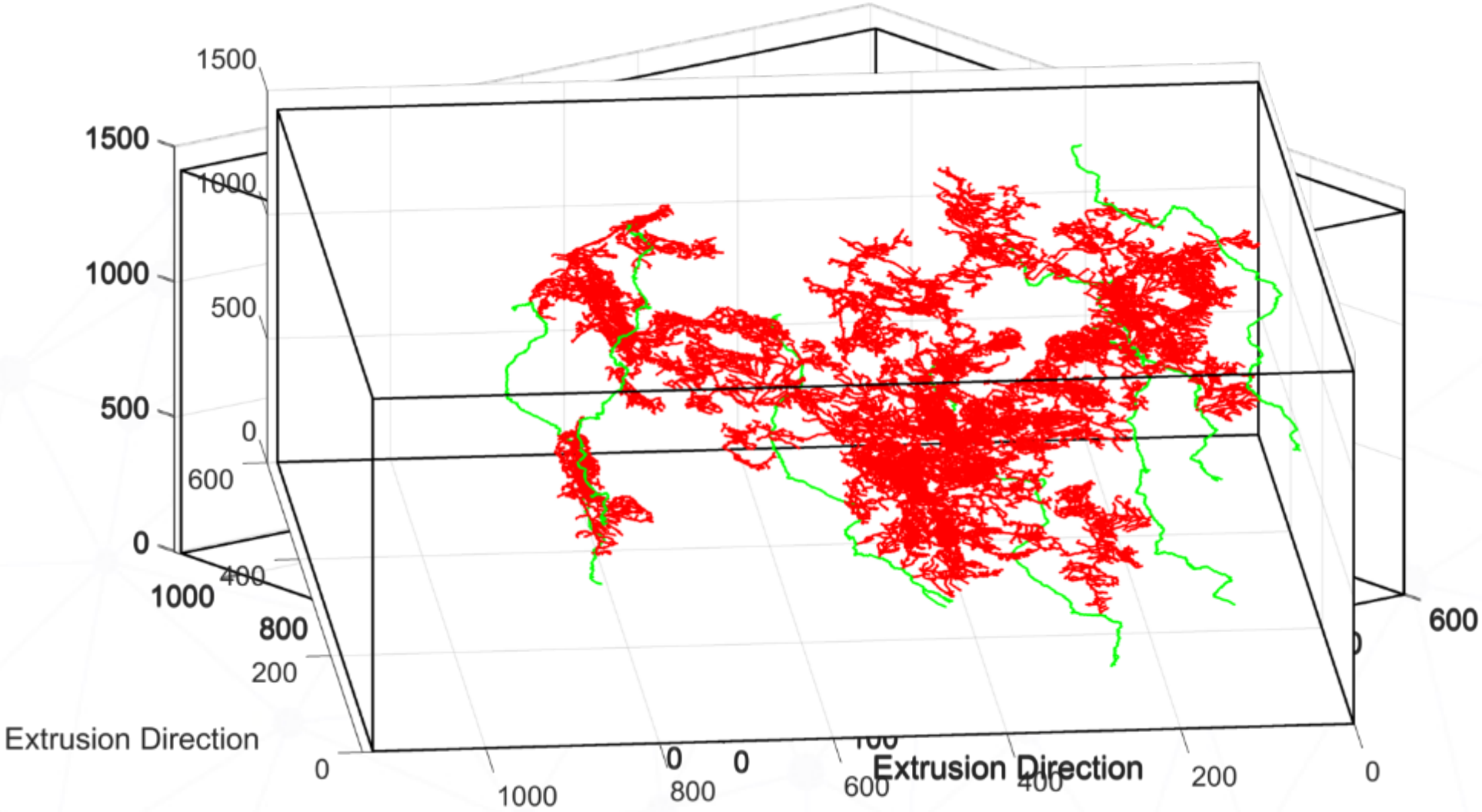


- High energy needed to break covalent bonds in middle of basal plane
- Reaction occurs on the outer atomic layers of carbon atoms
  - The Zig-zag and arm-chair sites

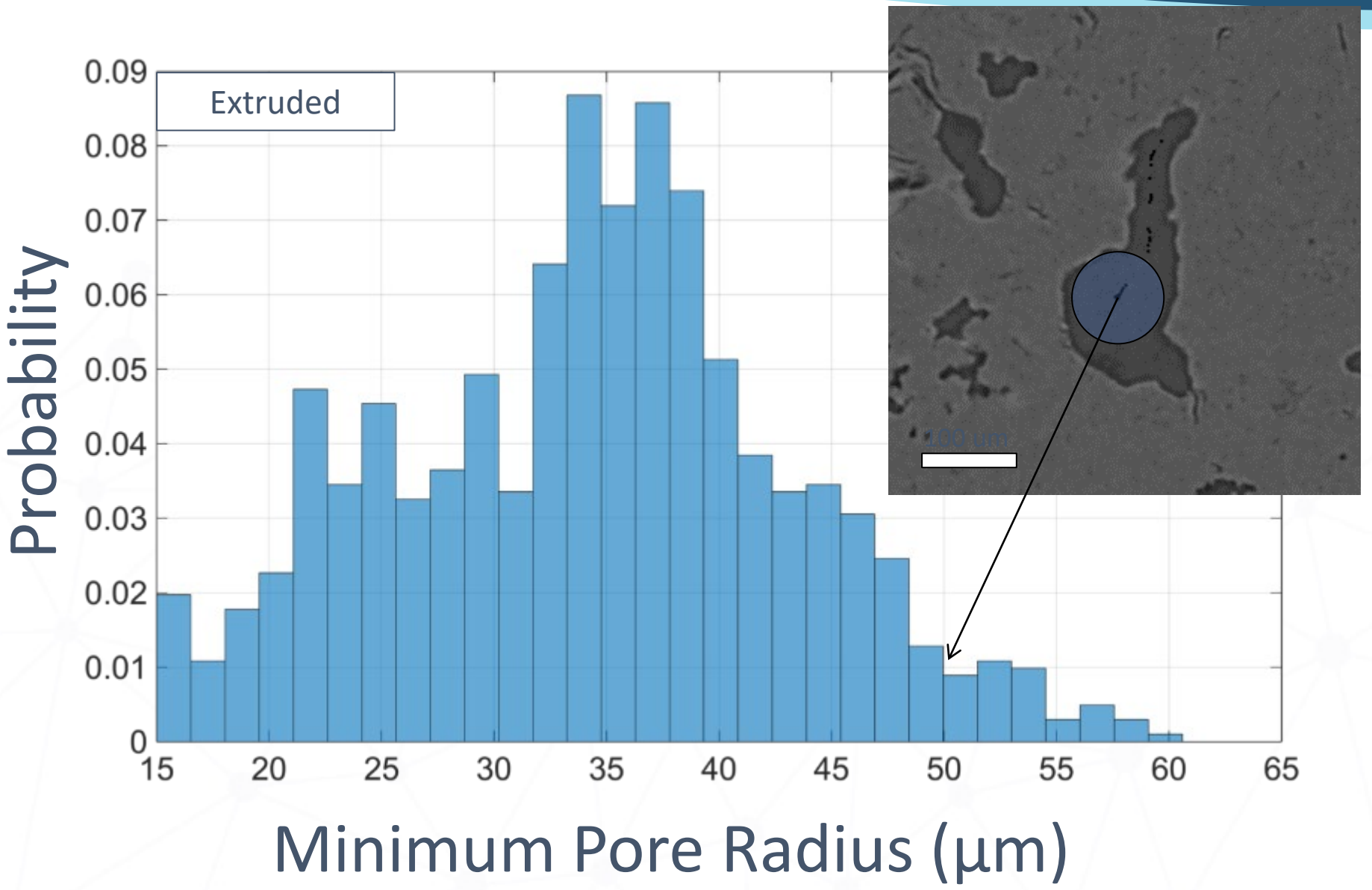
Using the 3-D data: *Interconnected pore structure*

τ_y=1.66±0.6, $\tau_{Primary}$=1.16±0.05, τ_{Branch}=1.70±0.46

Extruded



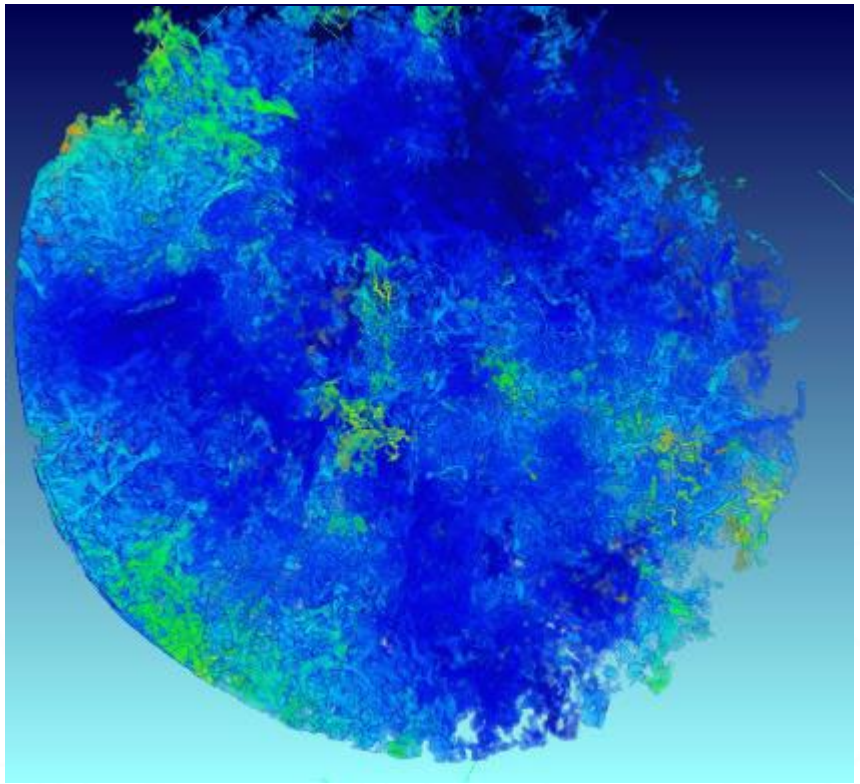
Using the 3-D data: *Flaw size*



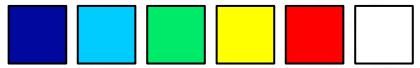
How we characterize pore structure:
Geodesic Distance Transform (GDT)

ADVANCED REACTOR TECHNOLOGIES

Iso-molded



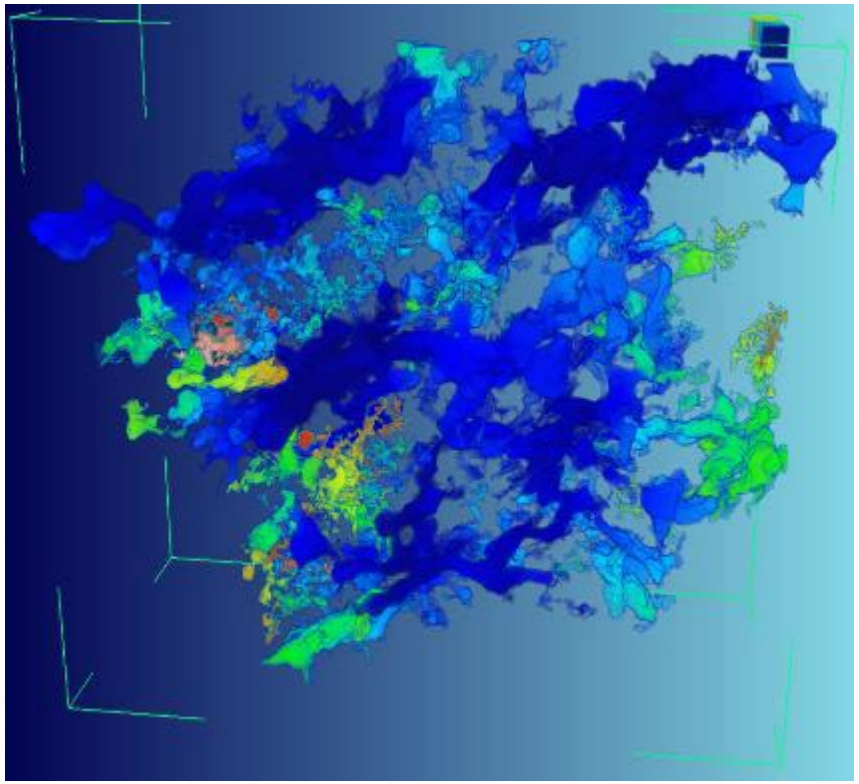
τ_x=1.56±0.07
τ_y=1.56±0.06
τ_z=1.53±0.05



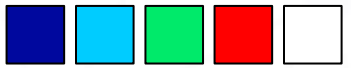
1.25 2.75

Extruded

$\tau=\langle\tau\rangle\pm\sigma$



τ_x=2.58±0.7
τ_y=1.66±0.6
τ_z=1.82±0.6

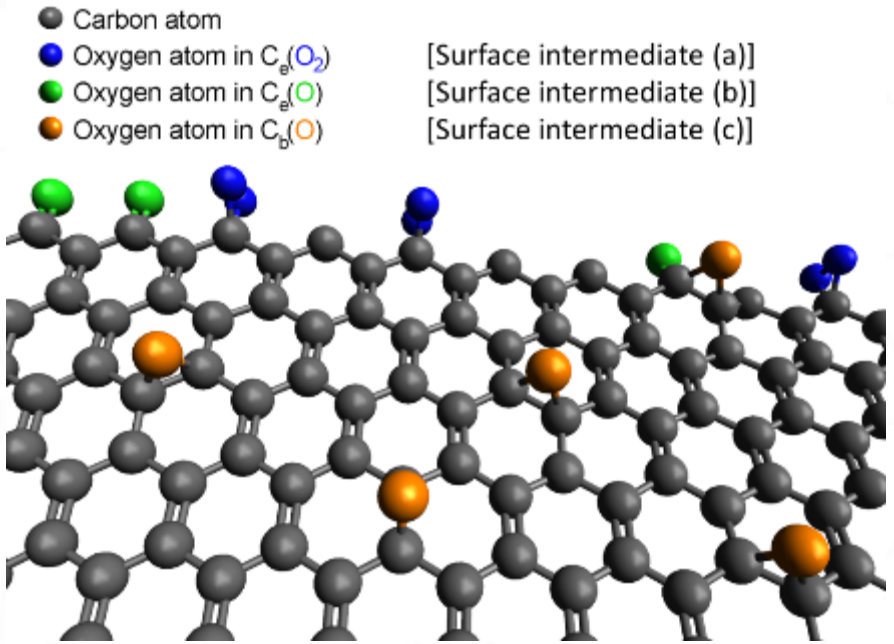


1.1 4.0

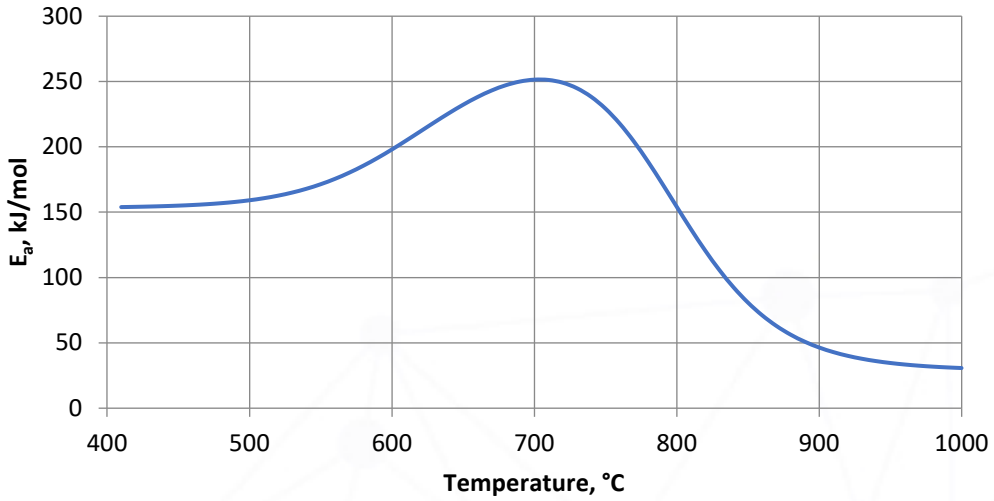
Graphite – oxygen reactions

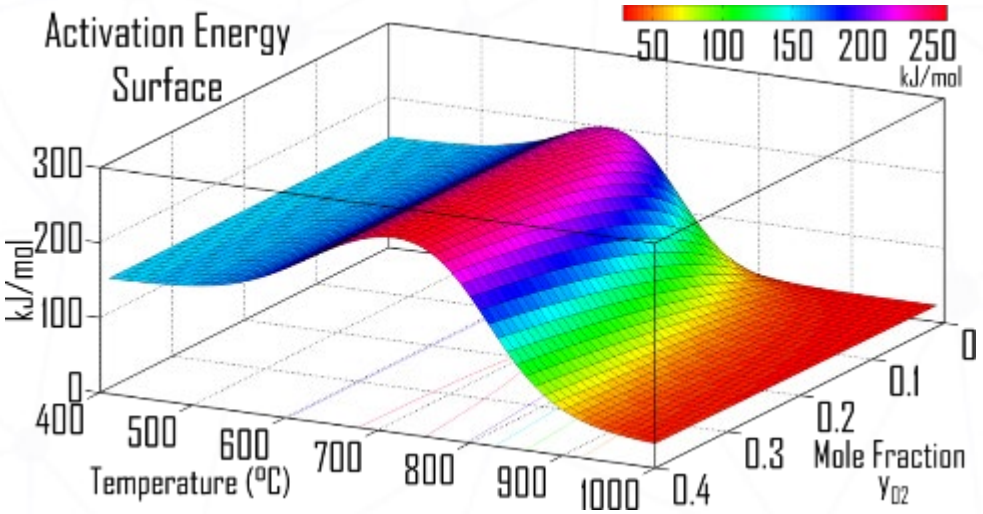
- The crystal structure of the carbon atoms (graphite) dictates the reaction
  - This is not just combining carbon atoms with oxygen atoms
  - The crystal structure precludes reactions with vast majority of carbon atoms except on the edges
- Reactions still only occur at edges of basal planes
  - Zig-zag and arm-chair RSA sites
- Reactions of graphite (carbon) to oxygen
  - Reaction rates for each mechanism drive overall macroscopic reaction
  - Temperature of system dictates the preferred mechanism
- Analogy: burning of pages in a thick book

$C_e + O_2(g) \xrightarrow{k_{A1}} C_e(O_2)$	Molecular Oxygen Chemisorption
$2C_e + O_2(g) \xrightarrow{k_{A2}} 2C_e(O)$	Oxygen Dissociative Chemisorption
$C_e(O_2) + C_b \xrightarrow{k_S} C_e(O) + C_b(O)$	Oxygen Spillove
$C_e(O) \xrightarrow{k_{D1}} CO(g)\ (+2C_e)$	Direct CO Desorption
$C_e(O) + C_b(O) \xrightarrow{k_{D2}} CO_2(g)\ (+C_e)$	Indirect CO_2 Desorption
$C_e(O_2) \xrightarrow{k_{D3}} CO_2(g)\ (+2C_e)$	Direct CO_2 Desorption



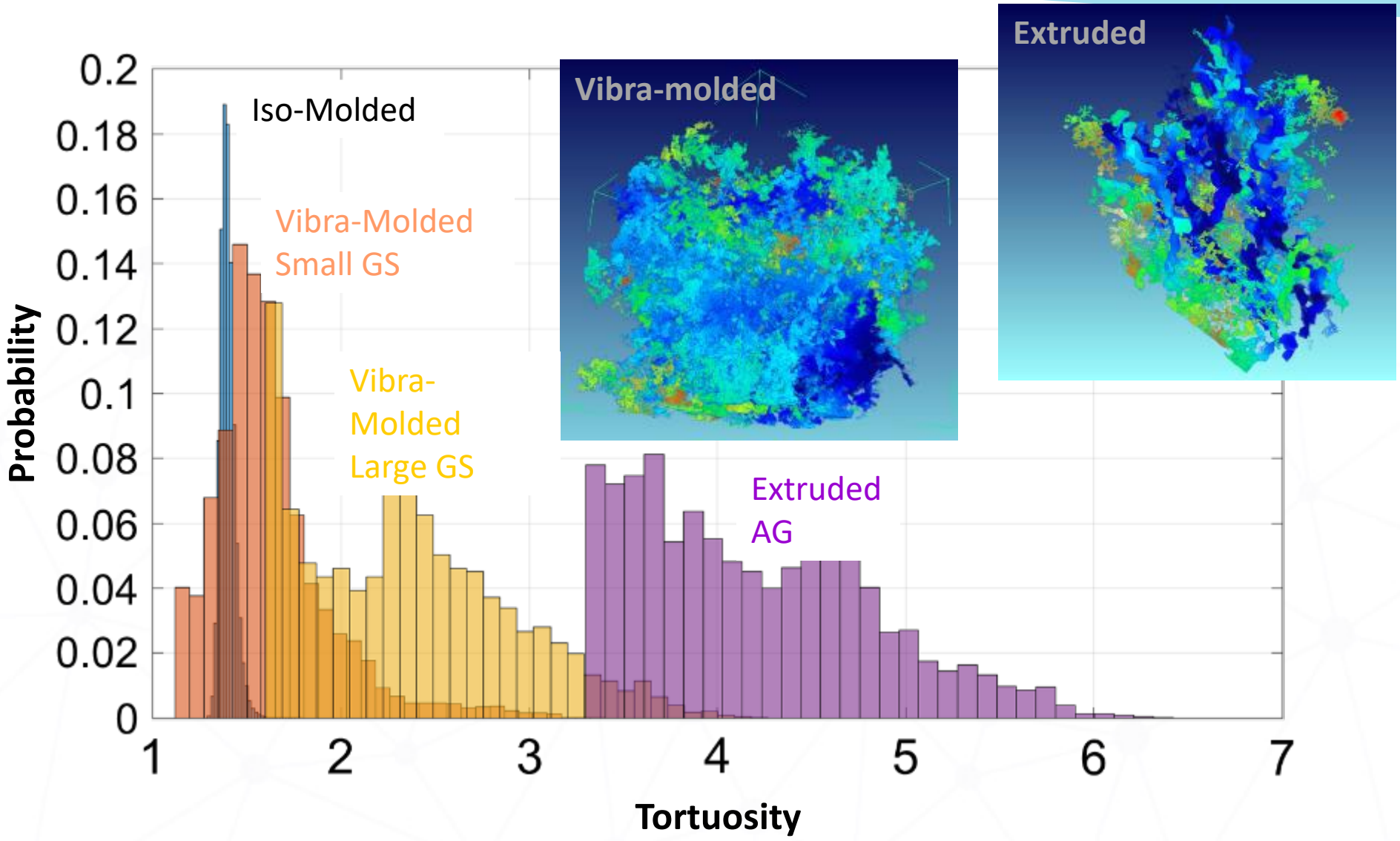
Temperature and diffusional effects



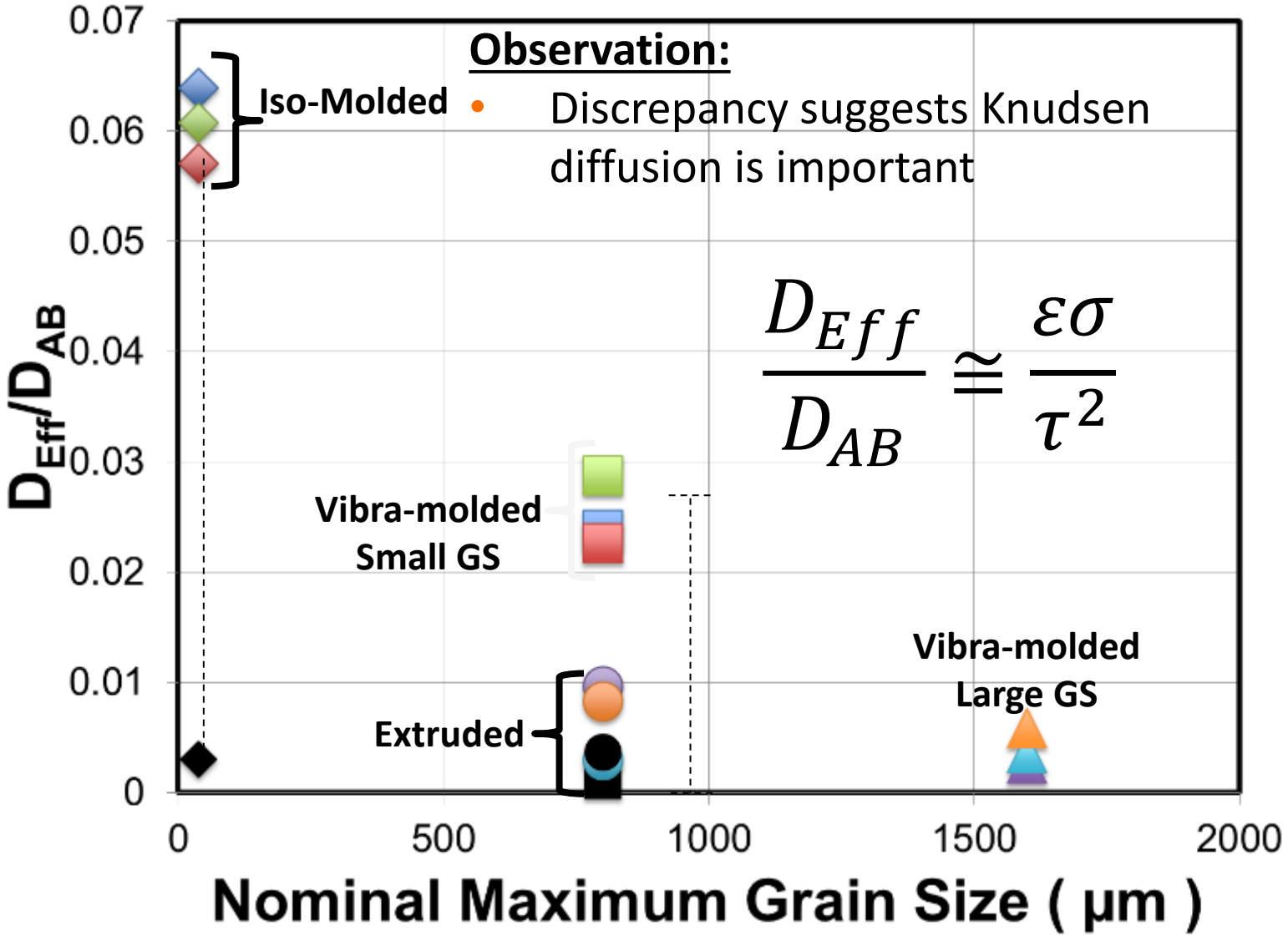


- Temperature effects
  - The macroscopic (combined oxygen transfer mechanisms) oxidation activation energy is dependent upon the system
  - As seen for a typical graphite, the Kinetic Controlled (oxidation dominated by the reaction kinetics) ranges between 550C to 850C.
    - **Key word**: Ranges
- Diffusion of oxygen
  - The other half of the equation
  - Efficiency of oxygen diffusion affects macroscopic response
  - Diffusion efficiency is related to reactivity (Oxygen doesn't diffuse if it has reacted), temperature, and pore microstructure
  - A complex interrelationship between temperature (chemical reactivity) and availability of reactants

Understanding structural differences

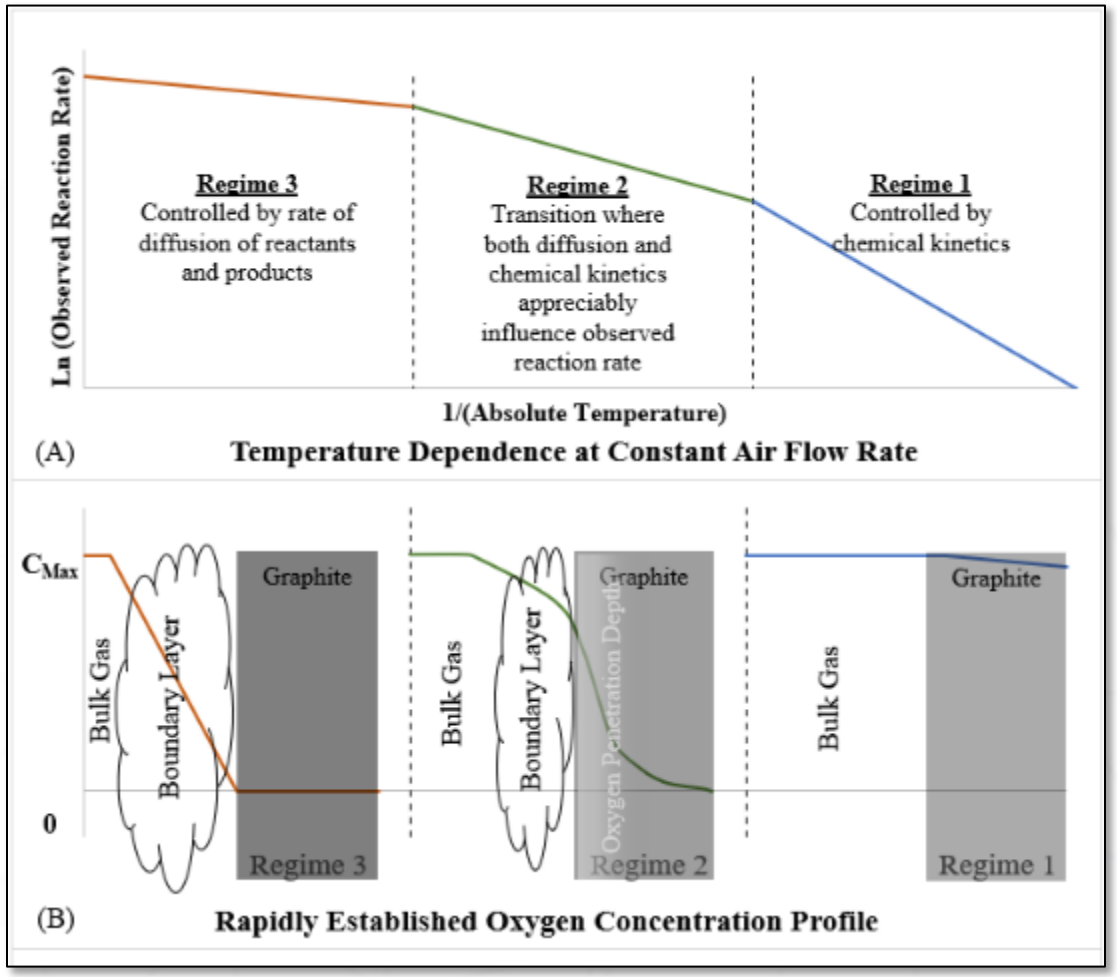


Dominant diffusion mechanism



Conclusion: Oxidation is a gradient

- Traditional way of understanding oxidation
  - *Walker Diagram: Three Regimes*
- Not really accurate (too simplistic)
- Proper response is actually a gradient
  - *Complete Regime 3 (diffusion control) only occurs at infinite temperatures*
  - *Complete Regime 1 (Kinetic control) only occurs at zero temperature*
- Oxidation is a complex relationship between reactivity and diffusion of oxygen
  - *Very sensitive to temperature*
  - *A little Diffusion and a little Kinetic controlled response at all temperatures*
  - *In general:*
    - ***Higher temperatures (> 650C): more diffusion***
    - ***Lower temperatures (< 650C): more kinetic***



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