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Performance of Graphite Oxidation with Environment and Specimen Geometry

September 2021

Changing the World's Energy Future

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Idaho National Laboratory

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For
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Performance of Graphite Oxidation with Environment and Specimen Geometry

ASTM STP Symposium on Graphite Testing for Nuclear Applications: The Validity and Extension of Test Methods for Material Exposed to Operating Reactor Environments

23-24 September 2021

Virtual Meeting

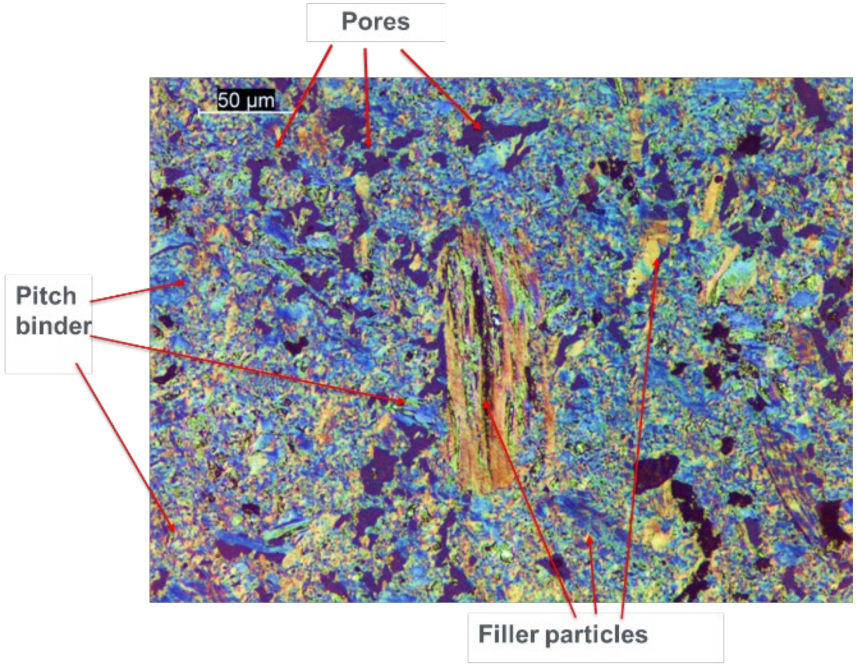
Advanced Reactor Technologies

Presentation outline

- Introduction
  - Motive for the study (a modest request)
    - *Issues that must be considered*
  - Pertinent oxidation background information
    - *Three oxidation regimes*
  - ASTM D7542
- The primary parameters for oxidation control
  - Energy of the System
  - Atmosphere
  - Reaction Interface

- Conclusions and future studies

Graphite Oxidation: a vision statement

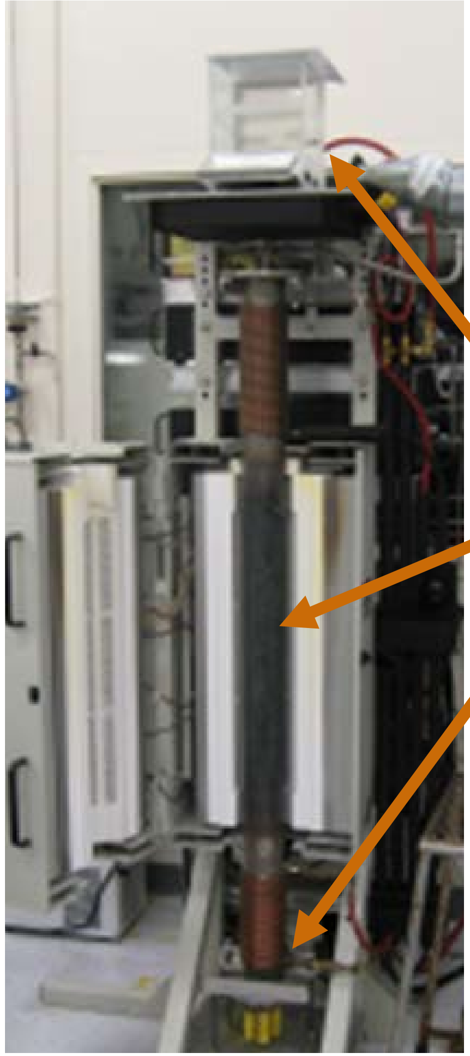


- Oxidizing graphite is easy!
  - Heat up graphite and expose to oxygen
- Controlling oxidation of graphite is nearly impossible
  - Subtle changes to oxidizing environment can dramatically alter the oxidation behavior
    - ***Why there are so many different results***
  - Due primarily to:
    - ***Stacked basal plane crystal structure***
    - ***Complex microstructure (pore structure)***
  - Oxidation is severely restricted

Motivation for this study (a modest request)

INL initiated oxidation studies of <u>irradiated</u> graphite (AGC Exp)

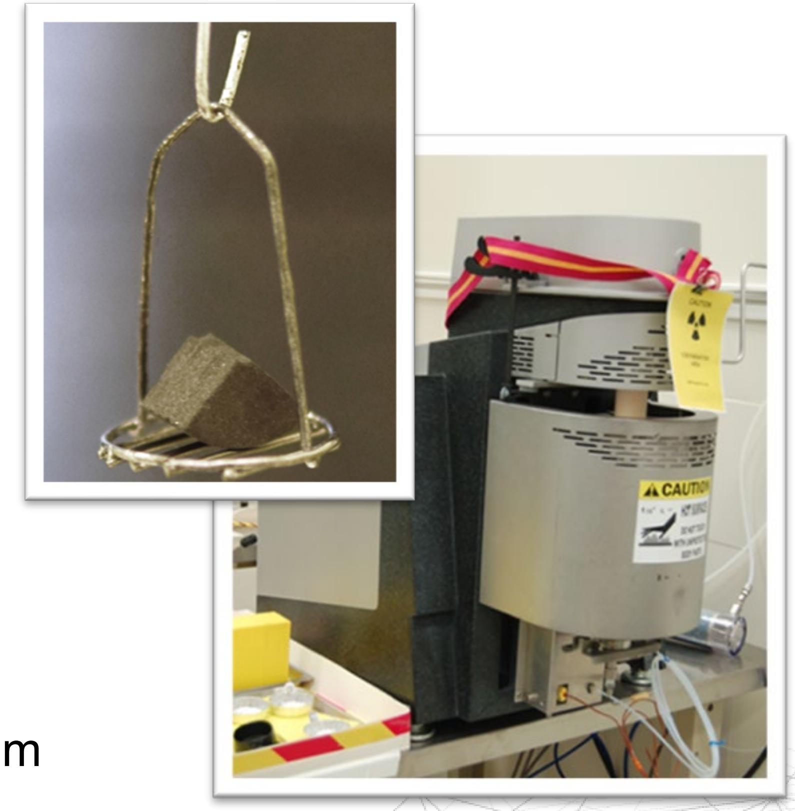
- Need to use the Thermo-gravimetric Analyzer (TGA)
- Very small samples
  - ***Sectioned from AGC samples***



Scale

Hot zone

Gas input



- Large sample 25.4mm X 25.4mm (Specified in ASTM D7542)
- Small TGA specimen (6mm thick X 6mm height)

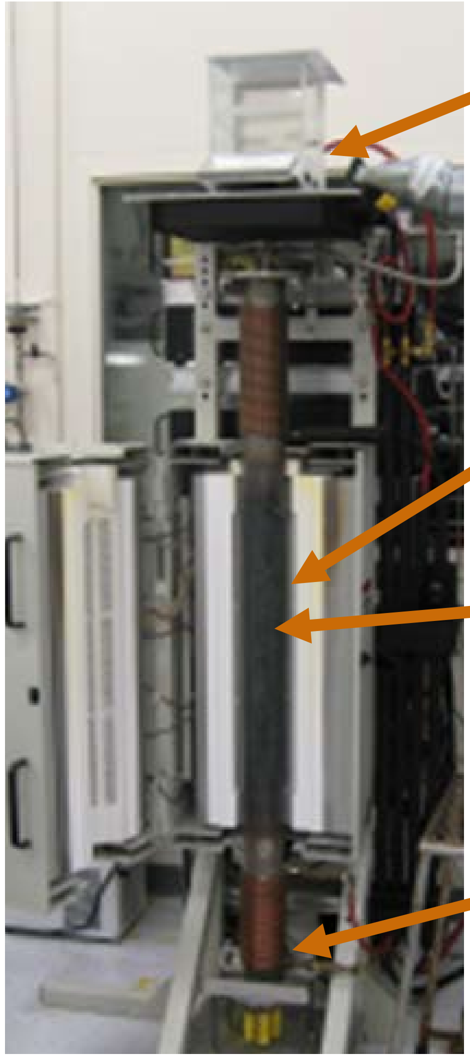
Introduction – 3 Keys to Graphite Oxidation Performance

- Energy of the System
  - Local Temperature
  - Activation Energy
  - Exothermic Reaction (NOT self sustaining)
- Atmosphere
  - Dry Air (20% O_2 at Atmospheric Pressure)
  - Products (primarily CO_2 under test conditions)
  - Flow Rate (O_2 supply, boundary layer diffusion)
- Reaction Interface
  - Active Sites (concentration varies with extent of reaction)
  - Density (Porosity) Evolution
  - Mechanisms within the Microstructure
  - Impurities (catalytic/inhibitor/interferences mechanisms)

} Kinetic controlled oxidation regime

Very complicated to obtain same oxidizing conditions

ASTM D7542
Vertical furnace



Mass loss

- Mass variability (***Grain separation)***
- **Masking of sample**

Hot zone

- Temperature control
- Oxidation chamber volume
  - vs **sample size**
  - vs sample geometry

Sample

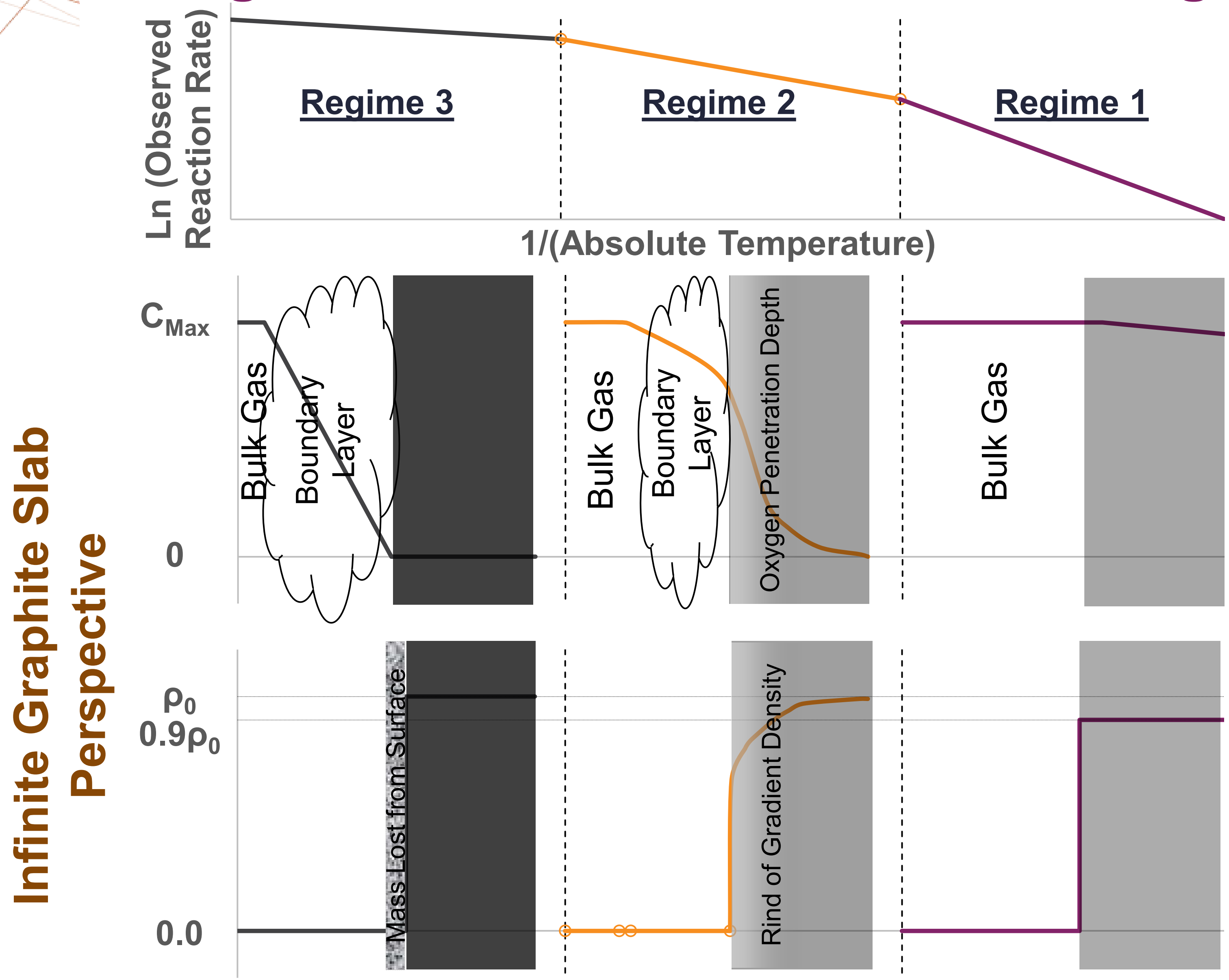
Grain orientation

Impurities

Gas input

- **Gas flow rate**
- Gas composition

Background: Three Views of Three Regimes

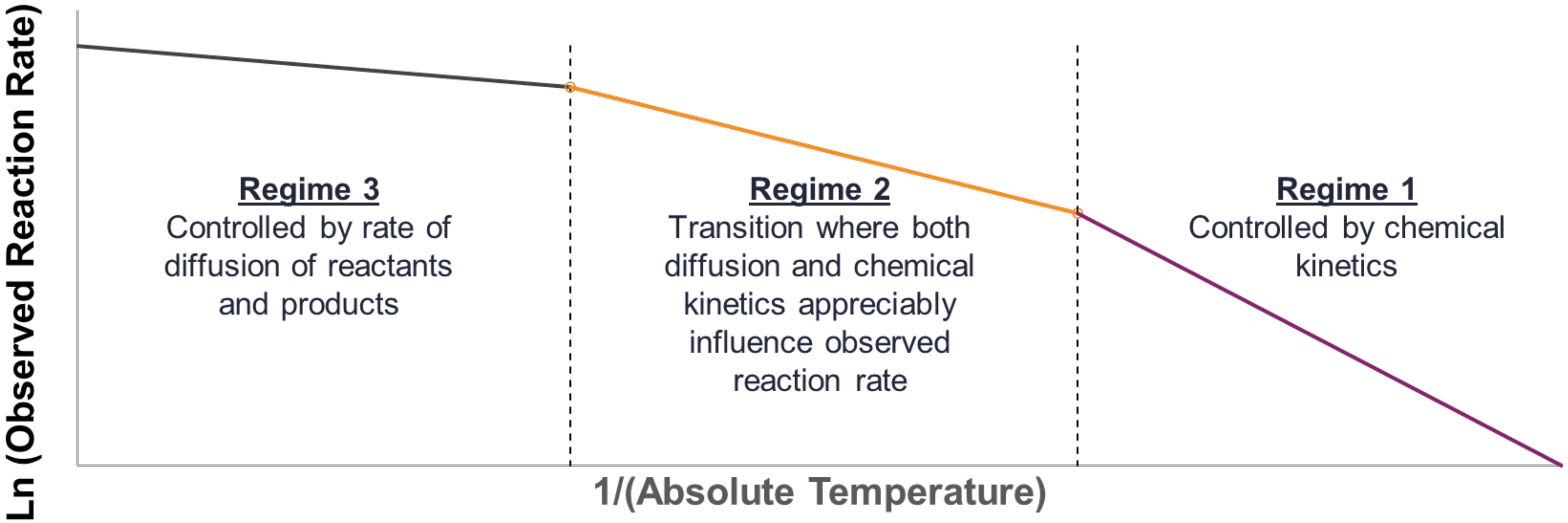


Arrhenius Temperature Dependence

Oxygen Concentration Profile

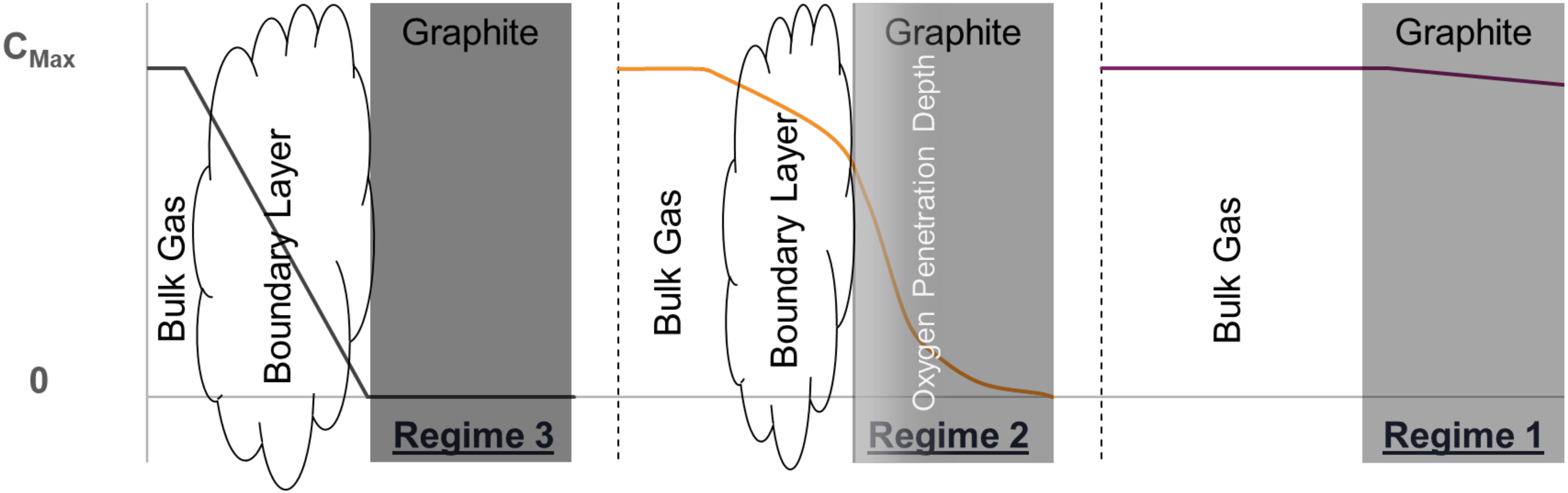
Density Profile (Evolution of Porosity after 10% mass loss)

The Progression of Oxidation – with Temperature



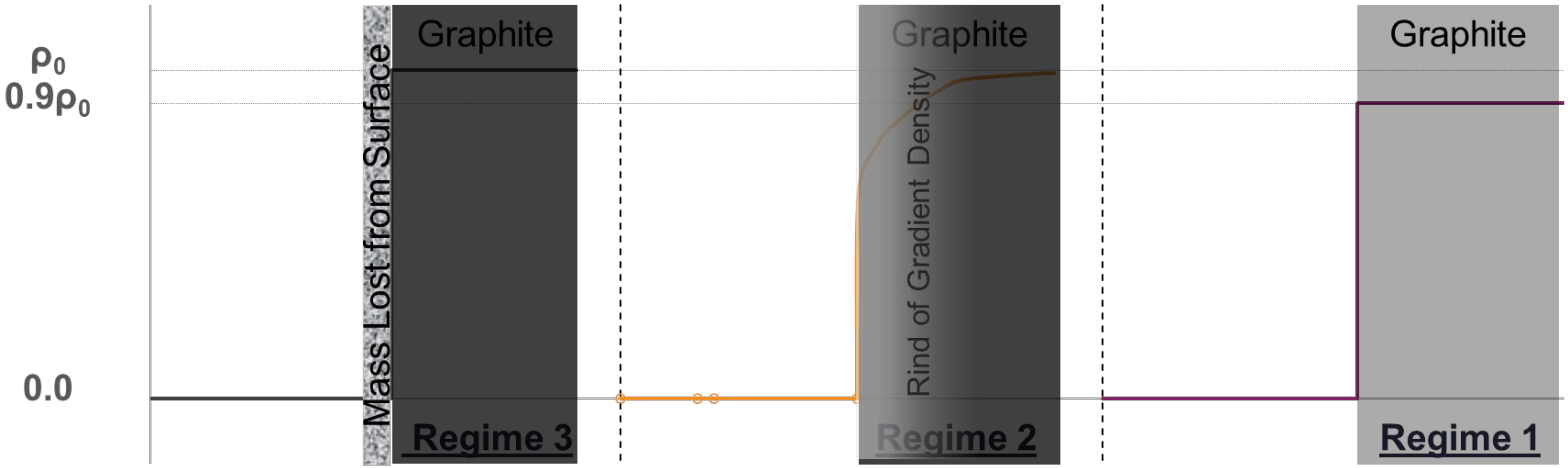
Temperature Dependence at Constant Air Flow Rate

Oxygen Concentration Gradient during Oxidation – Visualized for an "Infinite Graphite Slab"



Rapidly Established Oxygen Concentration Profile

Porosity Evolution with Oxidation



Cross-Sectional Density Profile after ~10% Mass Loss

ASTM D7542 – Why it works (comparing different grades)

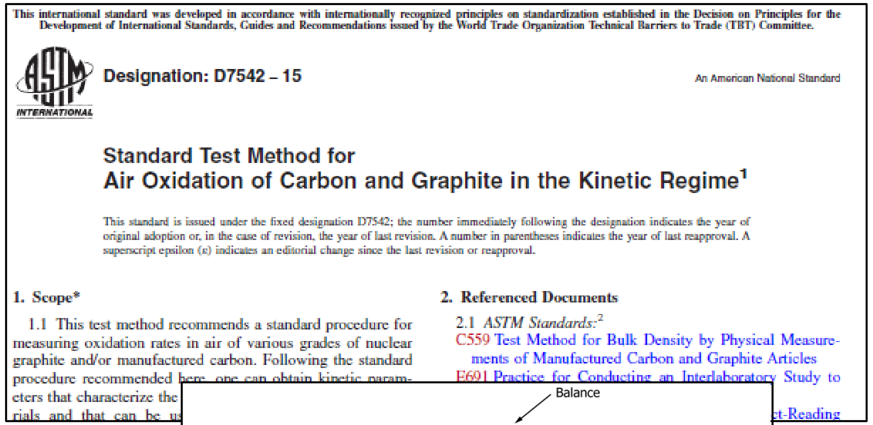
Oxidizing condition

Oxidation within the **Kinetic Regime**

- Furnace tube
  - Specific chamber size
  - Specific sample size and geometry and orientation
  - Limited temperature range (450°C to 800°C)
- Atmosphere
  - Strict <u>air</u> flow rate (10 ℓ/min)
    - ***Excess of oxygen***
    - ***Plug flow (flat flow profile)***
    - ***No He (or other gases) in system***

Inherent material properties

- ***Kinetic oxidation behavior (for comparison with other grades)***
  - Active Sites (concentration varies with extent of reaction)
    - ***Source material, binder/filler ratio, impurities***
  - Density (Porosity) evolution
    - ***Oxygen diffusion within the unique microstructure***



This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D7542 – 15

An American National Standard

Standard Test Method for
Air Oxidation of Carbon and Graphite in the Kinetic Regime[1]

This standard is issued under the fixed designation D7542; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

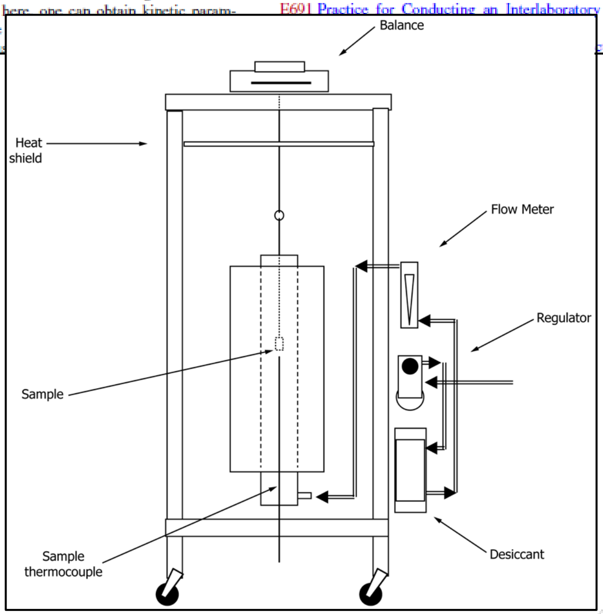
1.1 This test method recommends a standard procedure for measuring oxidation rates in air of various grades of nuclear graphite and/or manufactured carbon. Following the standard procedure recommended here, one can obtain kinetic param- eters that characterize the … rials and that can be us…

2. Referenced Documents

2.1 ASTM Standards:[2]

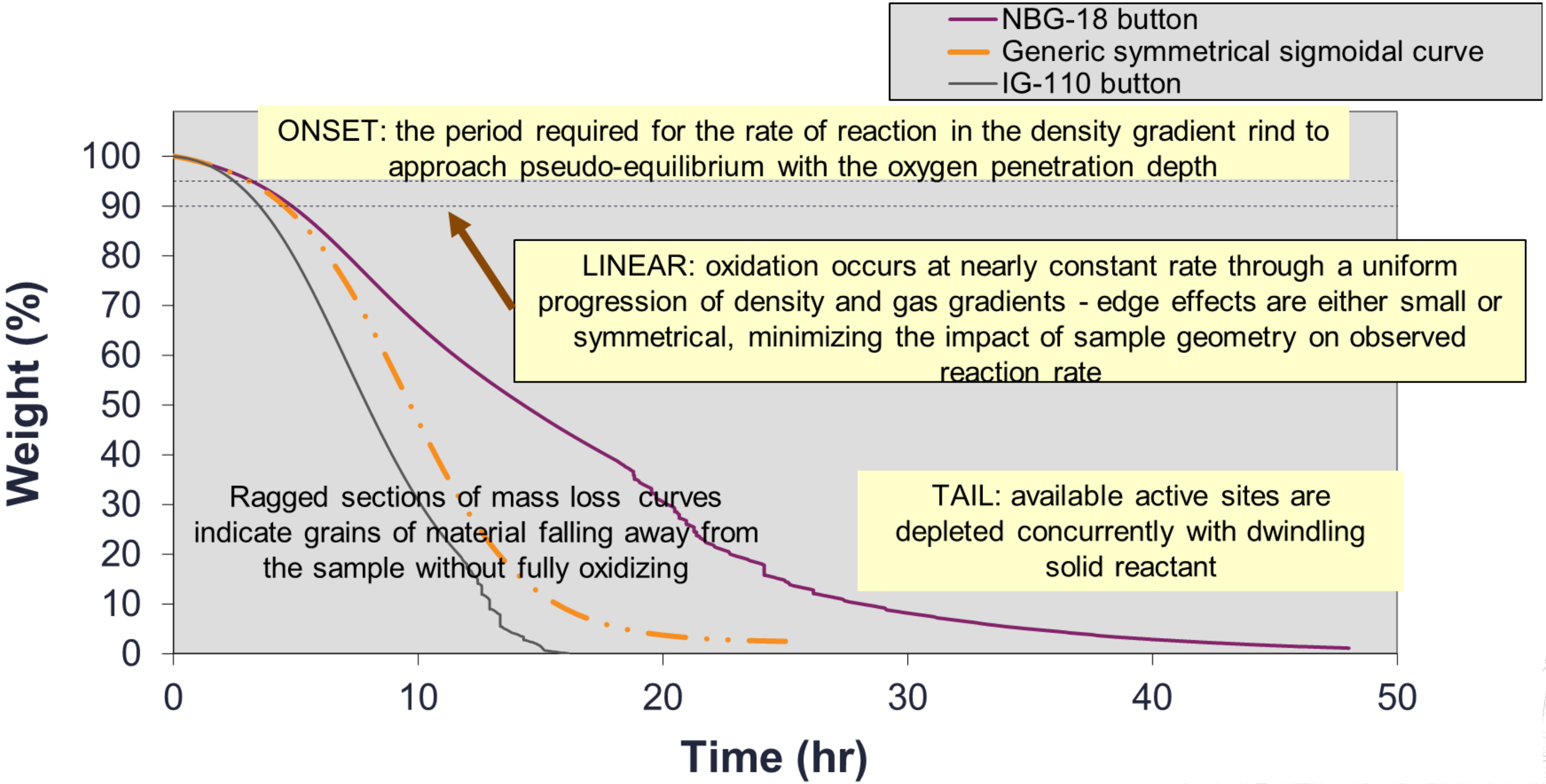
C559 Test Method for Bulk Density by Physical Measurements of Manufactured Carbon and Graphite Articles

E691 Practice for Conducting an Interlaboratory Study to … …t-Reading

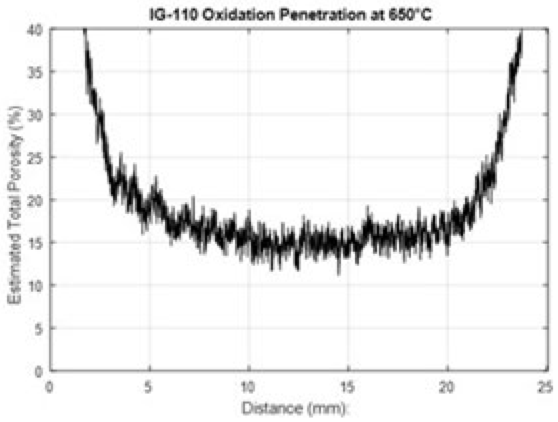


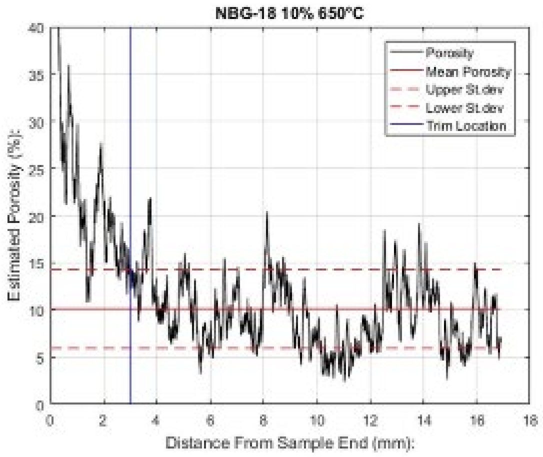
ADVANCED REACTOR TECHNOLOGIES

Progression of Mass Loss with Isothermal Oxidation: Up to ~99% mass loss in 10 L/min. air at ~700°C

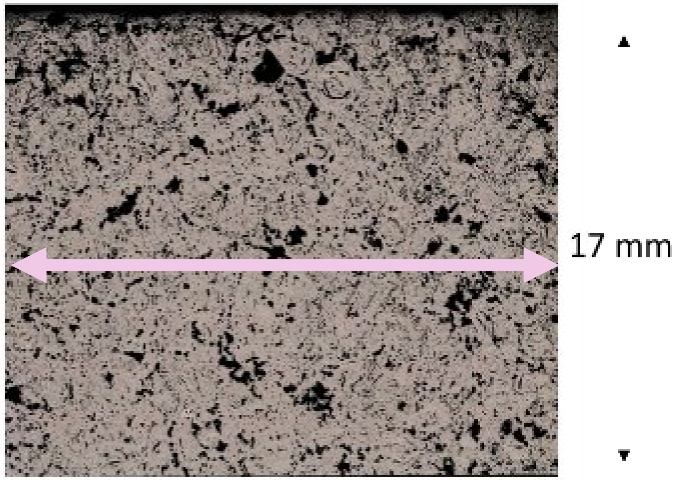


Penetration depth of graphite oxidation





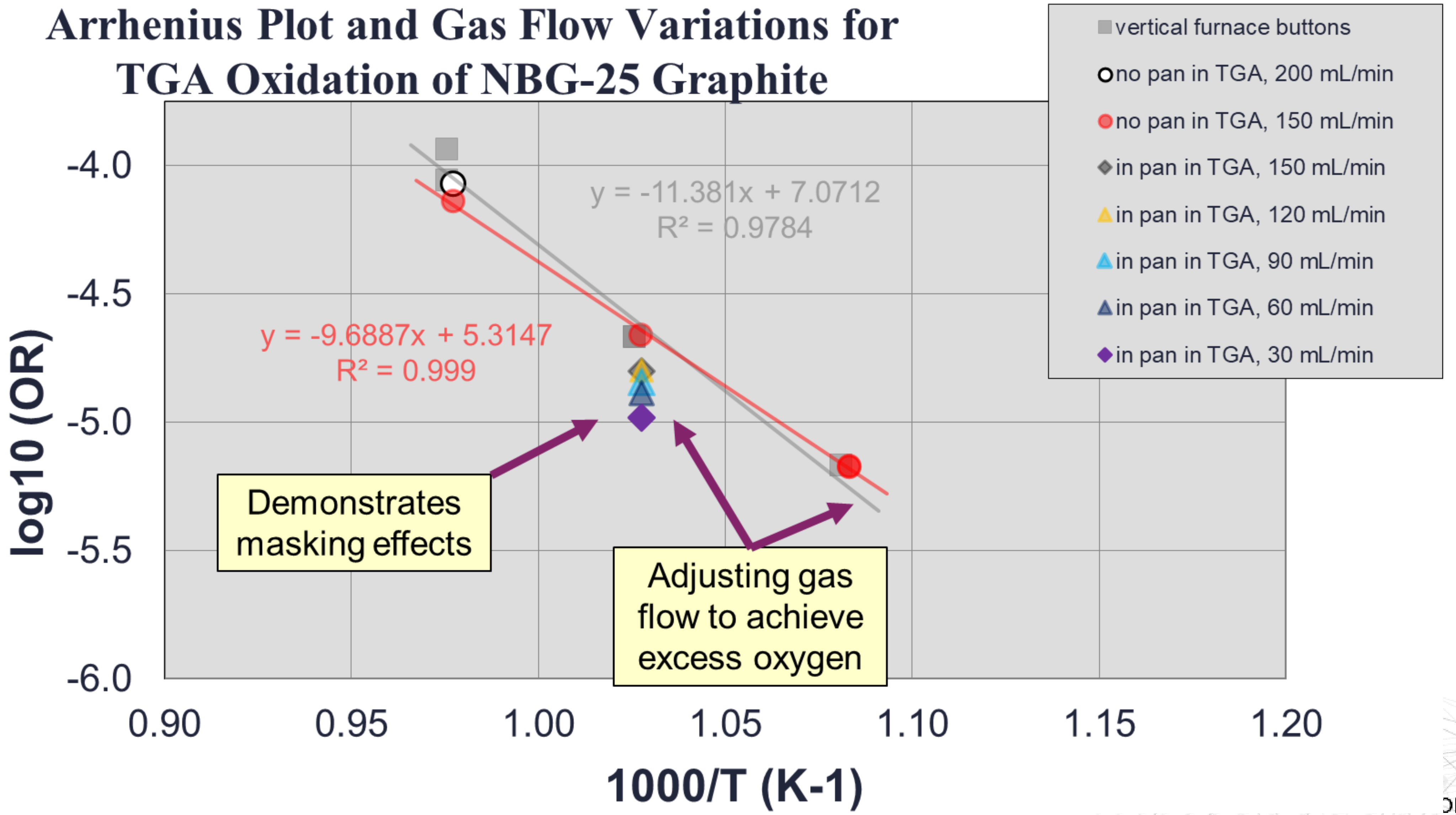
NBG-18 Oxidation Profile for 650°C



NBG-18 Oxidized Image

- Oxidized graphite penetration profile
  - Optical analysis – pore structure difference
- Penetration depth (from outer sides):
  - ~ 3mm for fine grain IG-110
  - ~ 4mm for medium grain NBG-18
  - Unoxidized center ~ 18-19mm
- Oxidation conditions:
  - 100% dry air
  - Temperature: 650°C
  - Sample: 25.4-mm diameter by 50.8-mm height
  - 10% Mass loss
- Penetration profile dependent upon graphite grade

Masking effects: TGA with and without Pan



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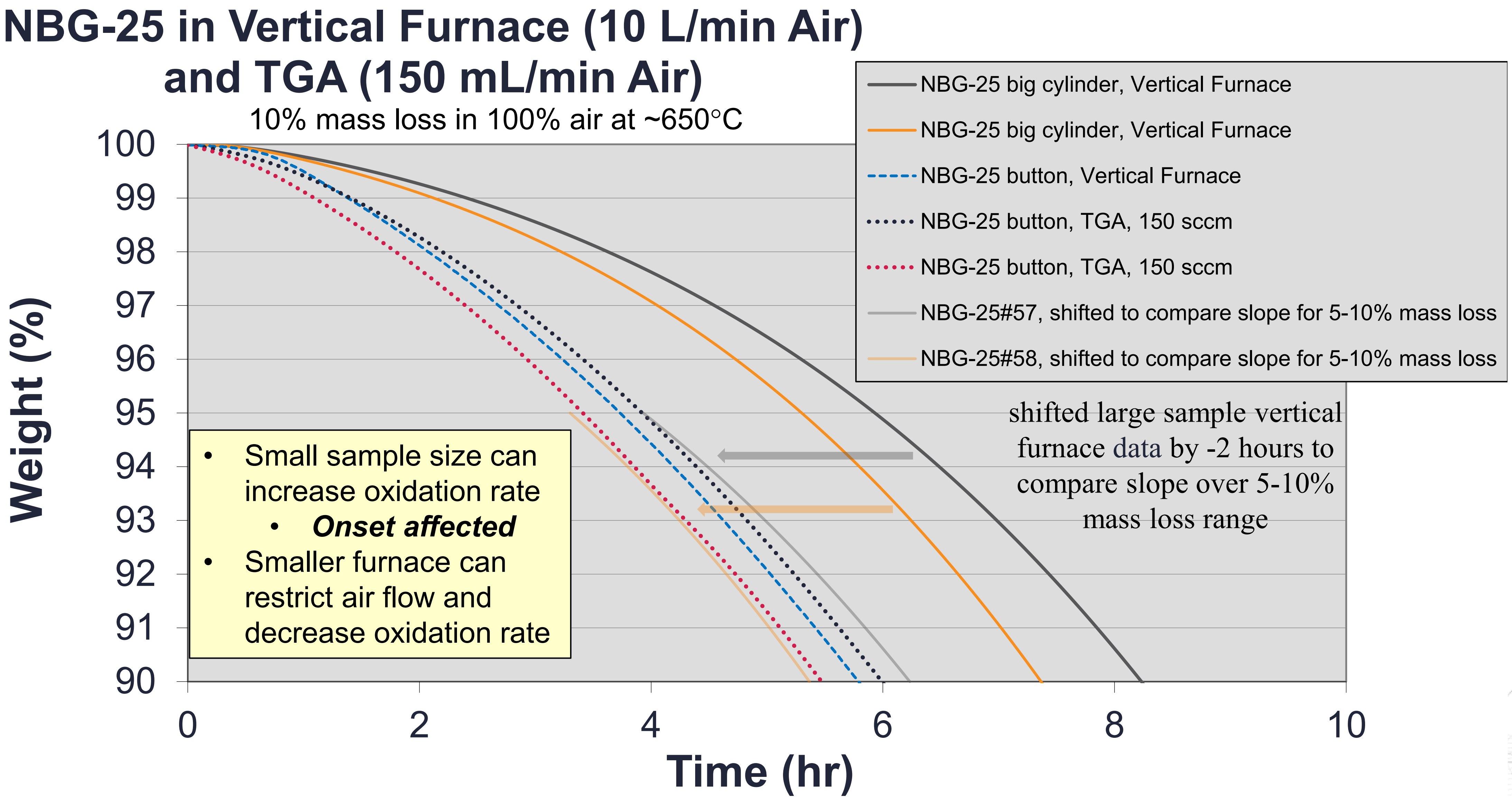
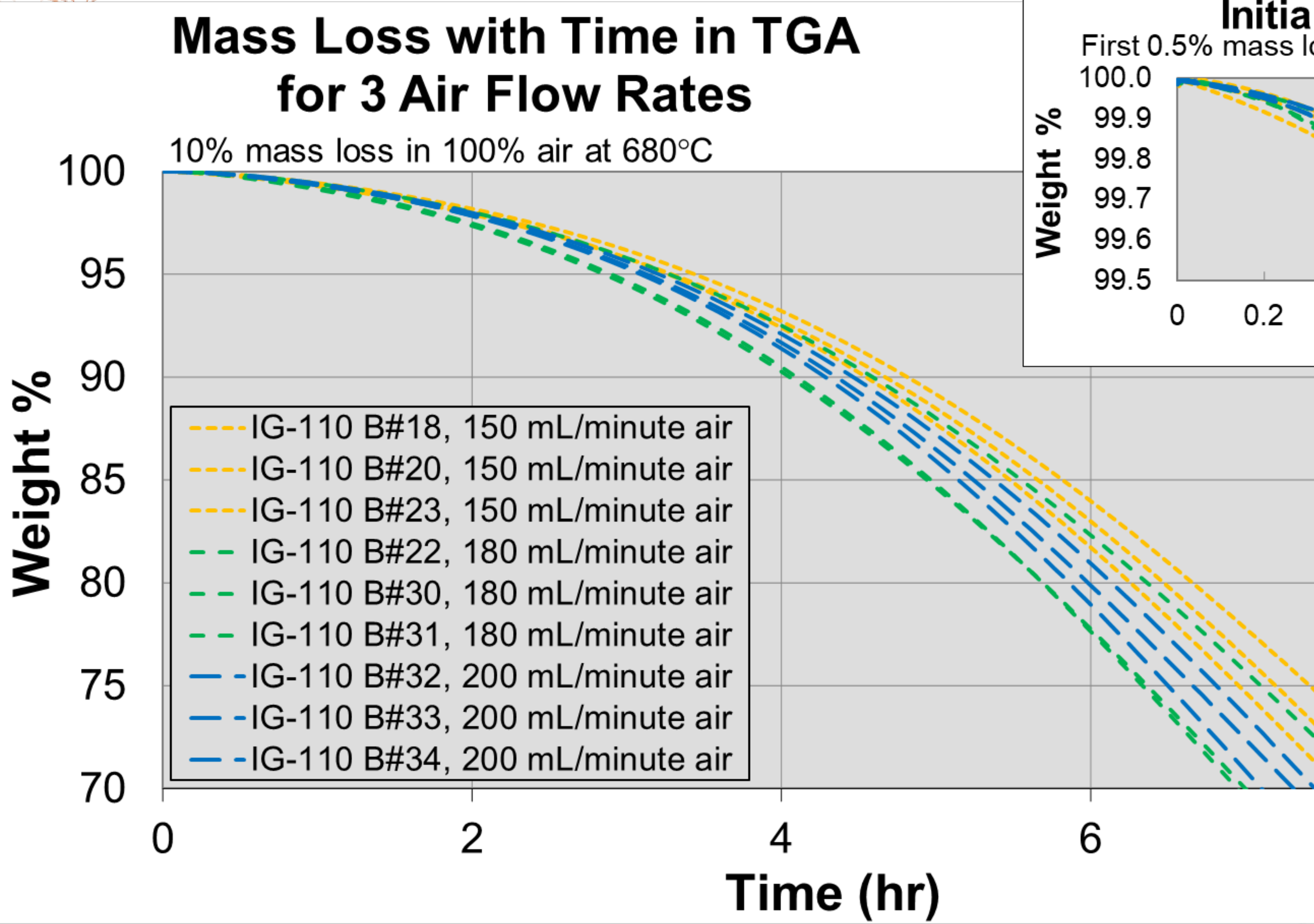
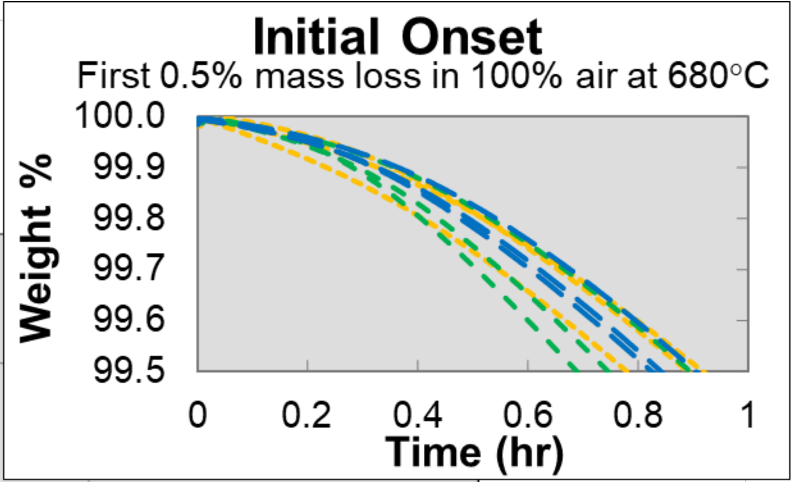
Sample size and furnace volume: Vertical furnace to TGA



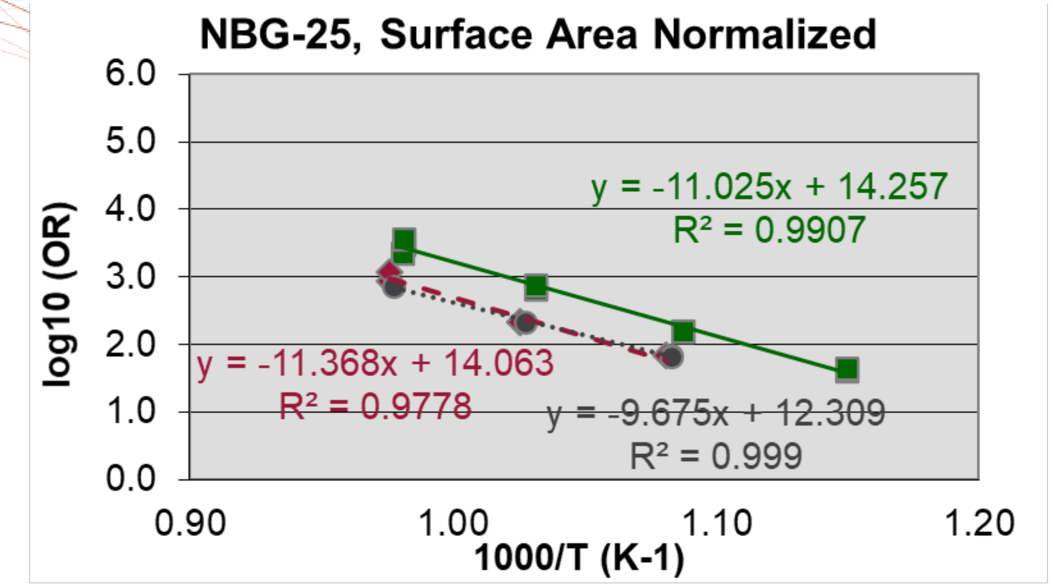
Effects of air flow: IG-110 in TGA

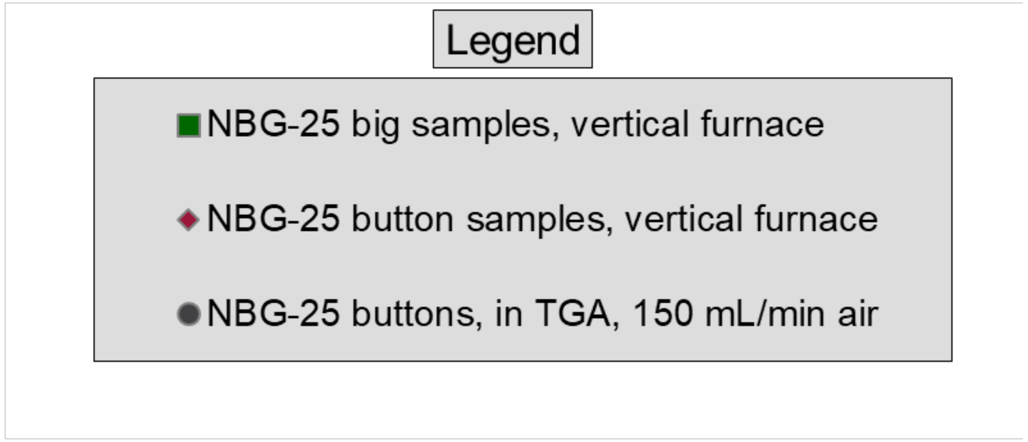


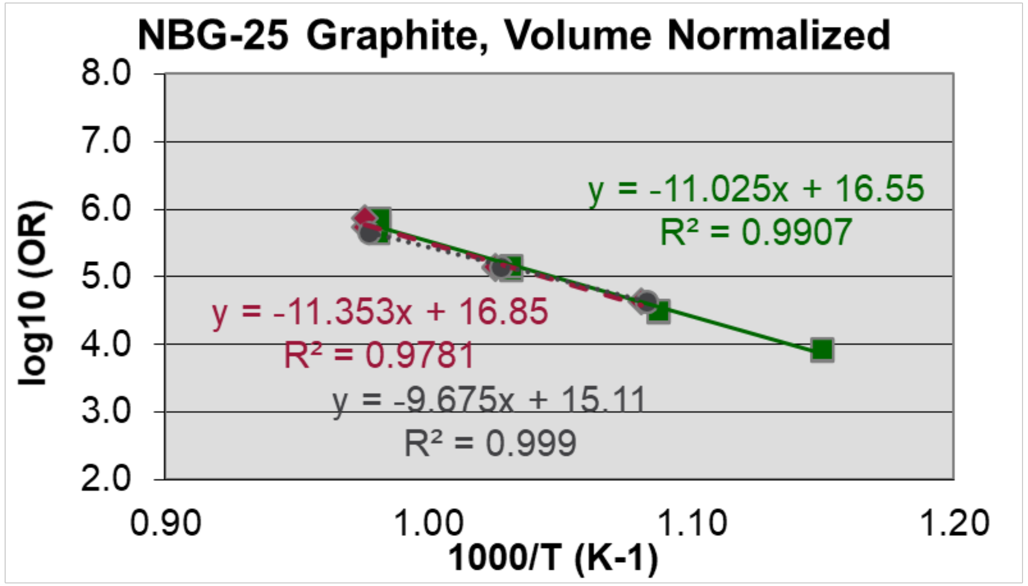


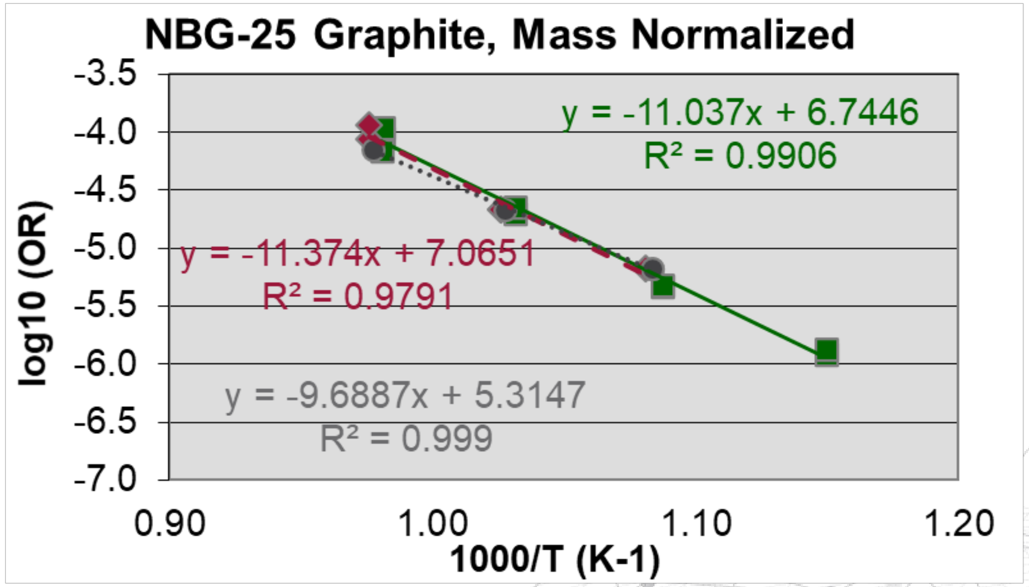
- Increasing air flow rate increased oxidation rate
- 200 mL/min = achieved excess oxygen state
  - ***At 680°C***

Normalization Practices: Sample size effects

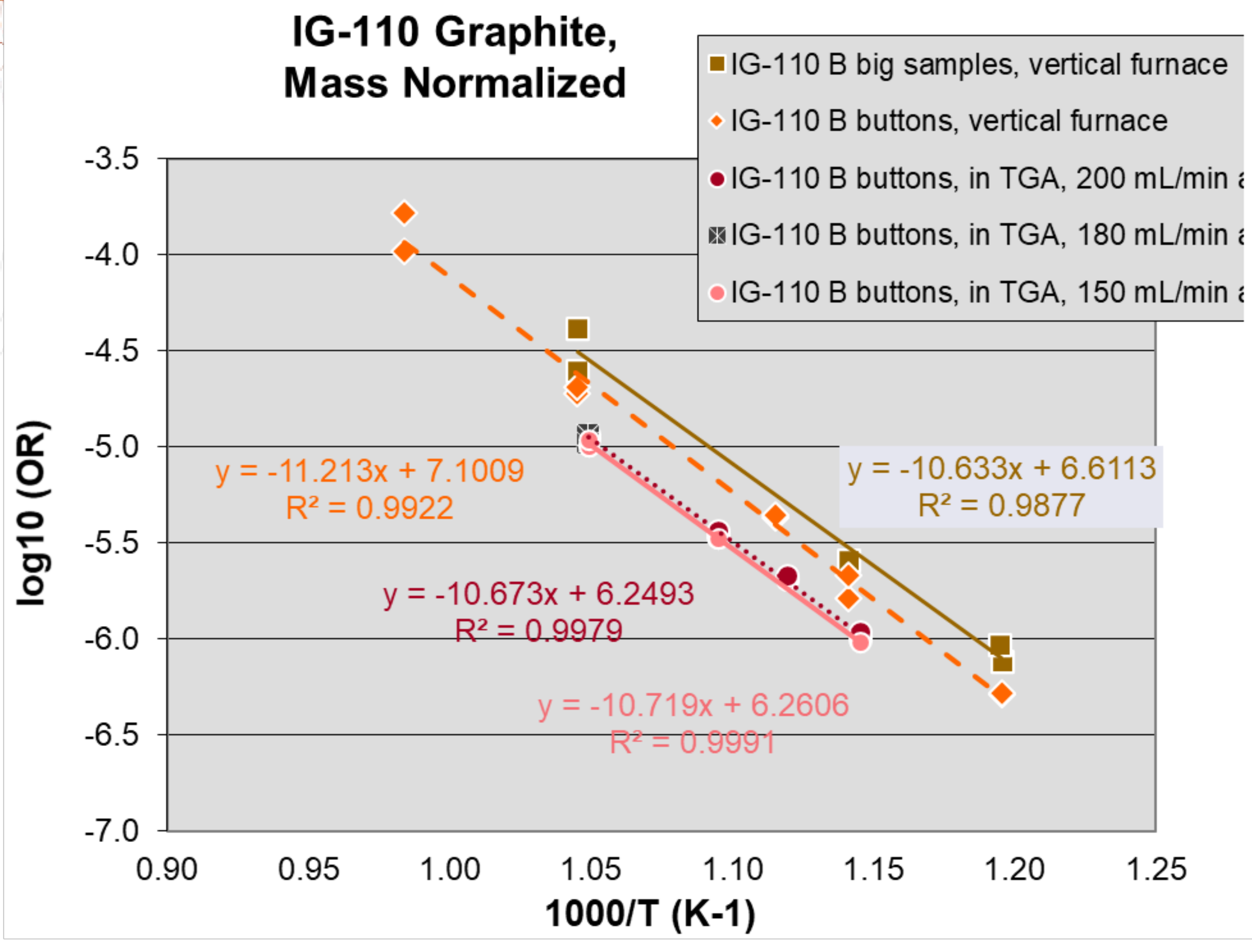


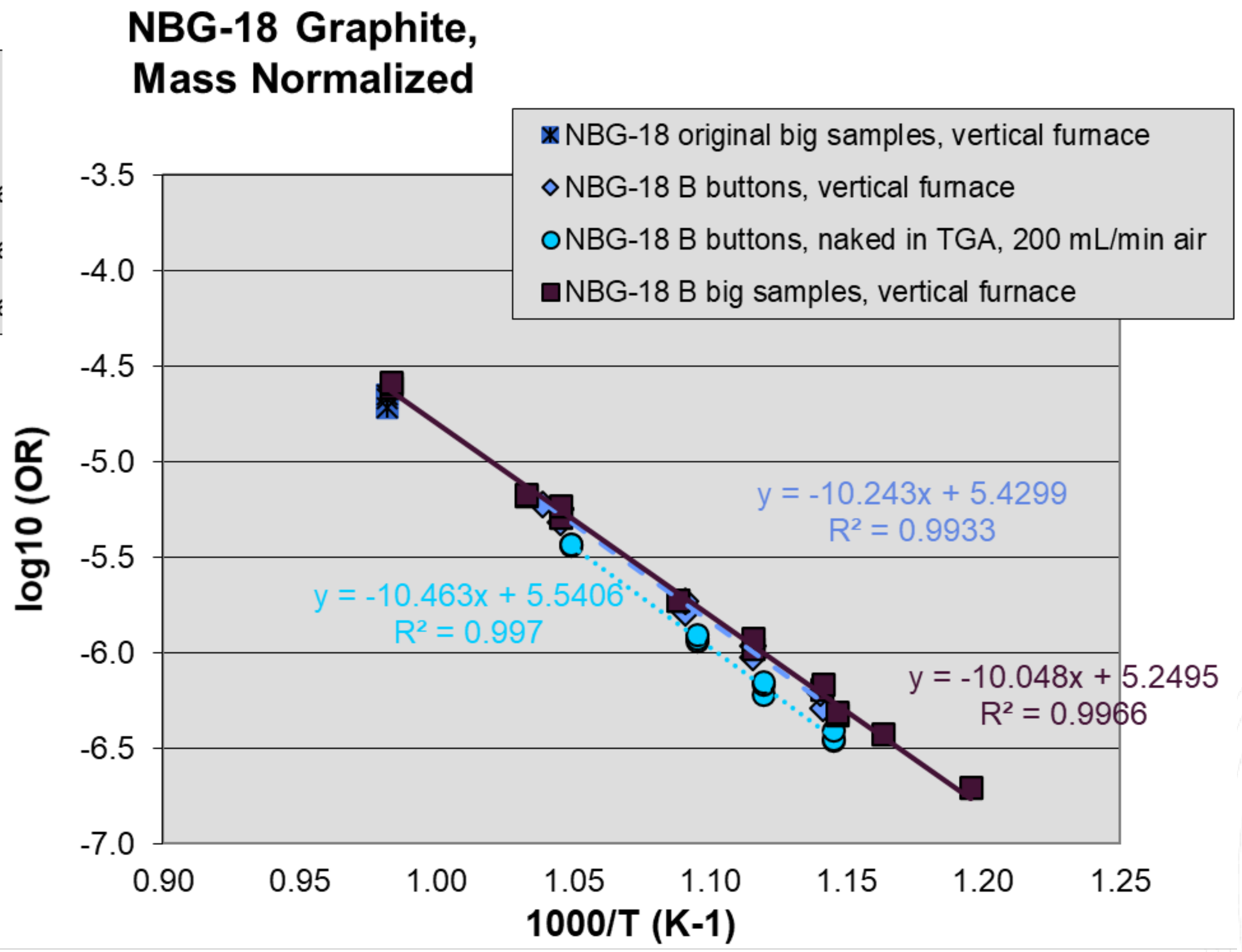






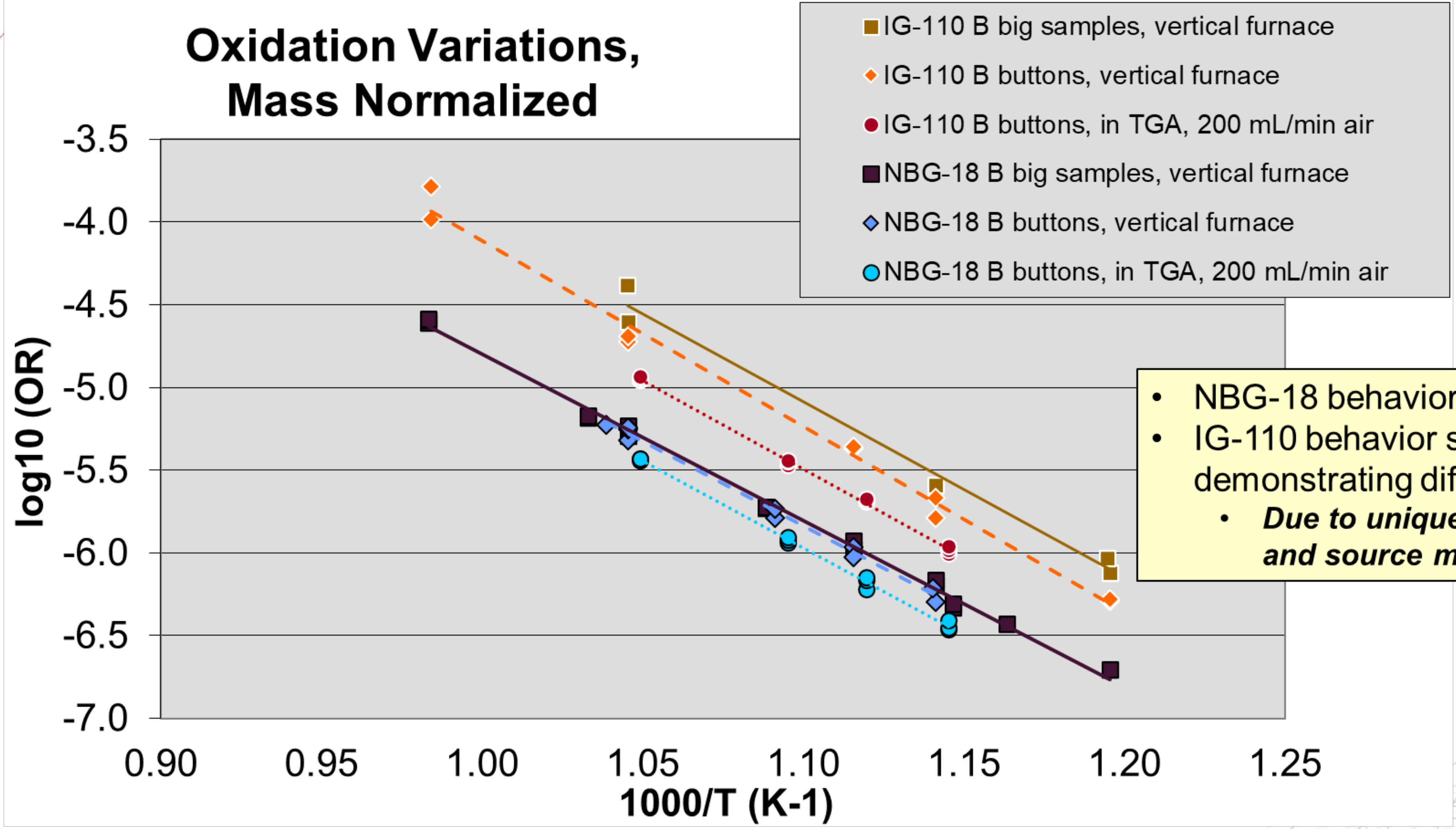
Each grade behaves differently: Self-consistent Families of Data





Vertical furnace and TGA oxidation behavior beginning to demonstrate consistent results

Performance of Systems and Sample Geometry for Fine and Medium Grain Graphites



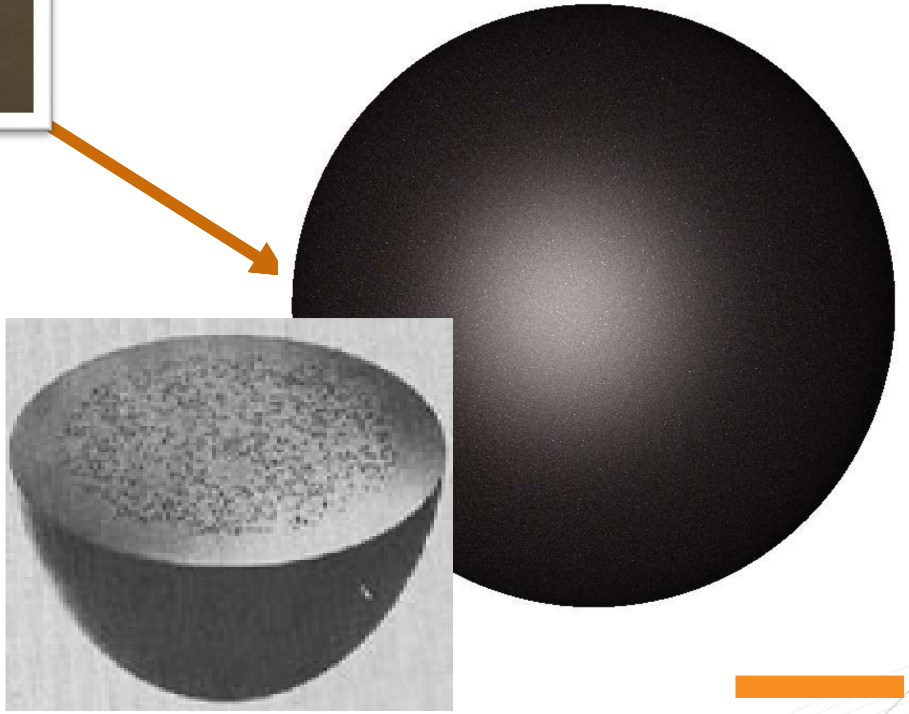
- NBG-18 behavior is consistent
- IG-110 behavior still demonstrating differences in TGA
  - ***Due to unique microstructure and source materials***

Conclusion

- Kinetic controlled regime required to compare oxidation behavior between grades
  - Measures inherent oxidation properties of graphite
    - ***Reactive surface area (RSA) sites, pore microstructure, impurities, and filler/binder ratio***
  - Not measuring the oxidation conditions
    - ***Oxidizing environment: air flow, temperature, sample size, sample geometry, reaction chamber***
- Diffusion-controlled and Transition regimes are problematic
  - Transition creates a varying penetration profile making comparisons difficult
  - Diffusion is temperature dependent - only reacts at the surface
- Careful control of oxidizing environment is required to achieve Kinetic-controlled oxidation

Future Work

- Large (50-60mm dia) samples
- Oven
  - *Non-vertical furnace*
- Multiple samples



- Fuel Pebbles
- Vertical Furnace
- Not graphite
  - *Fuel matrix material*

Questions?

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