Graphitization of Pennsylvania Anthracites

Harold Schobert
Professor of Fuel Science, Penn State University
Extraordinary Professor, North-West University

Pretoria University, October 2006

Graphite electrodes for electric-furnace steelmaking: a materials synthesis challenge

Typical physical dimensions:

- *30–700 mm diameter*
- *0.6–3 m length*
- *1–1900 kg weight*

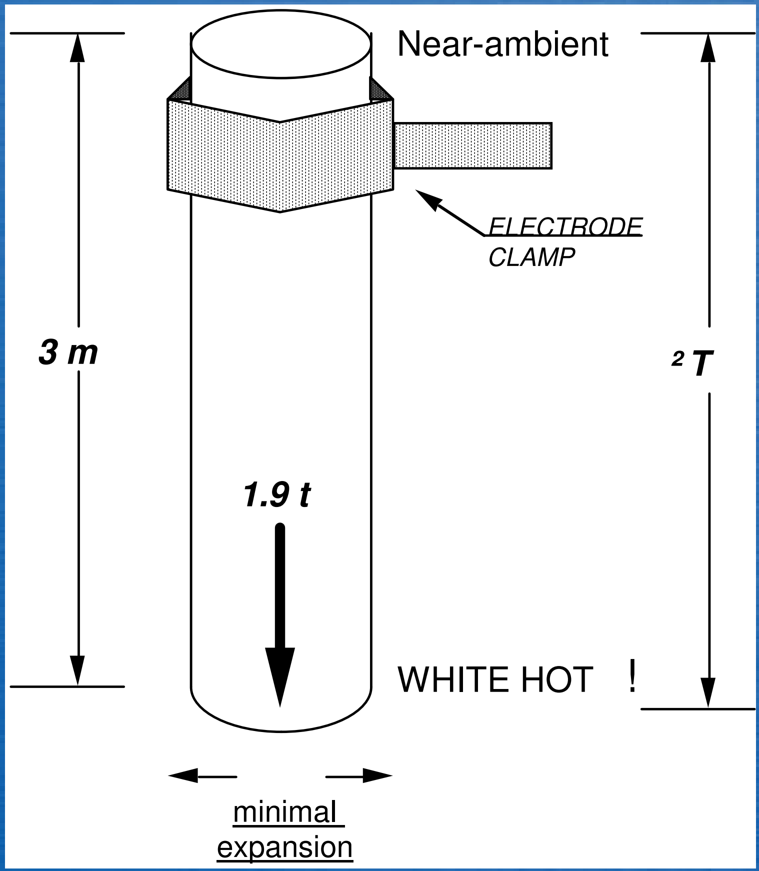
Special properties:

- *Current-carrying capacity (resistivity)*
- *Oxidation resistance*
- *Mechanical strength*
- *Coefficient of thermal expansion*

The Graphite Electrode as a Triumph of Materials Engineering

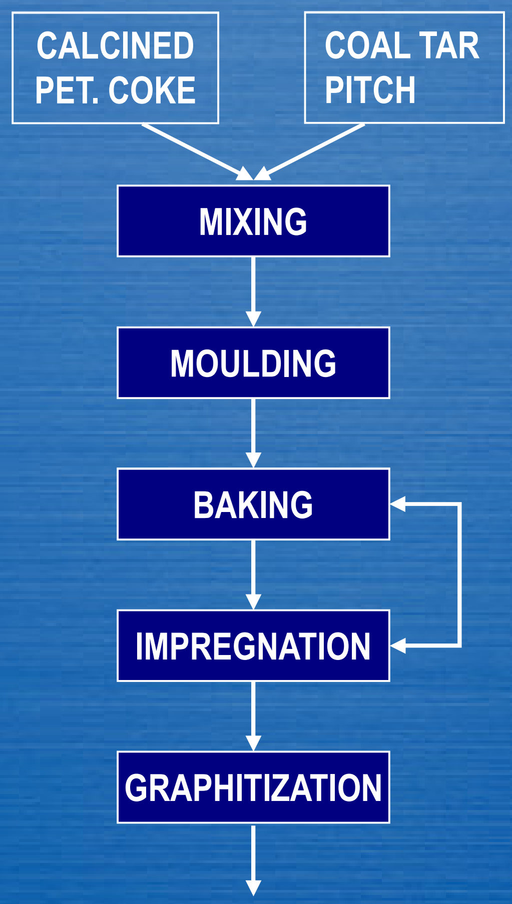
Requirements include

- mechanical integrity
- low CTE
- ability to sustain enormous ΔT
- oxidation resistance



Production of Molded or Extruded Graphites

- Process uses calcined petroleum coke as filler and coal tar pitch as binder.
- May involve multiple re-impregnation and re-baking steps.



Petroleum Coke Quality Issues

- Sulfur—Presence of residual sulfur compounds causes “puffing” of coke/pitch artifact during baking or early graphitization.
- Nickel and vanadium —These elements are superb oxidation catalysts. Their presence in graphite can accelerate “pin-holing.”

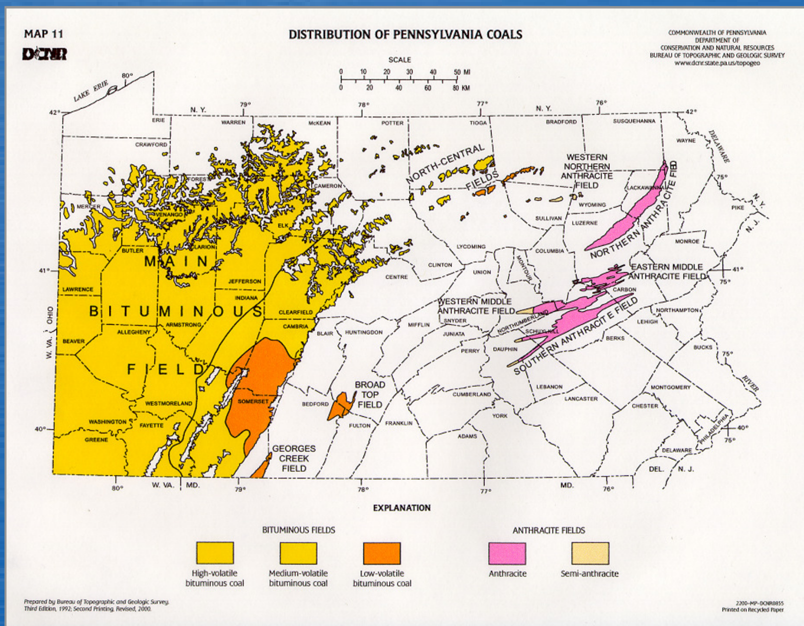
Why Anthracite?

- ≈100% of the carbon is in aromatic structures. If we want aromatic carbon for graphite, here it is.
- Anthracites are ≈90–95% carbon. Anthracite is a carbon material that must be close to graphitic.
- “Because it’s there.” (G. Mallory)

The Economic Driving Force

- The quality of petroleum coke feedstock for graphite electrode production is declining.
- For USA markets, petroleum coke must be imported or be made from imported petroleum.
- High-quality graphite sells for R1200/kg, whereas anthracite sells for R1200/tonne.

Anthracite Reserves in the USA



- Total 7–8 bn tonnes of anthracite in USA.
- Pennsylvania has >96% of these reserves.

The “Great Strike” of 1902

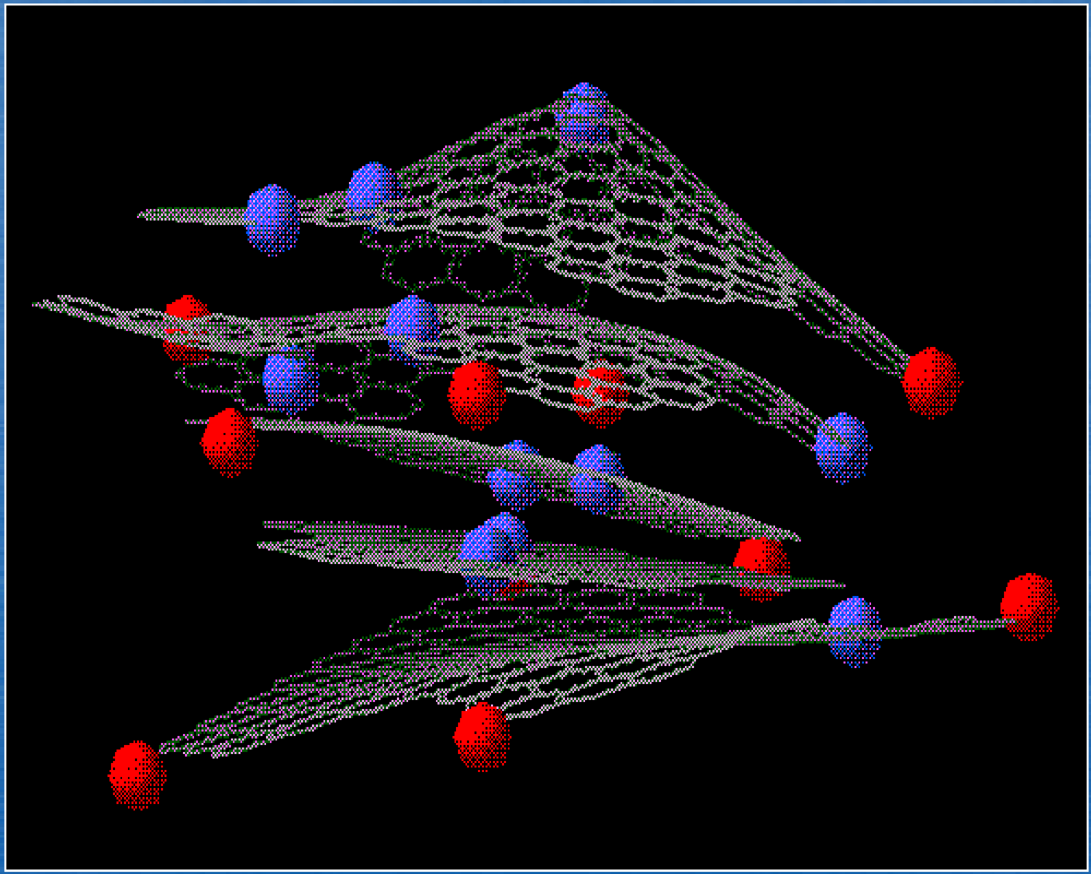
D. L. Miller: R. E. Sharpless, The Kingdom of Coal, Penn, 1985

Compositions of "Typical" Pennsylvania Anthracites

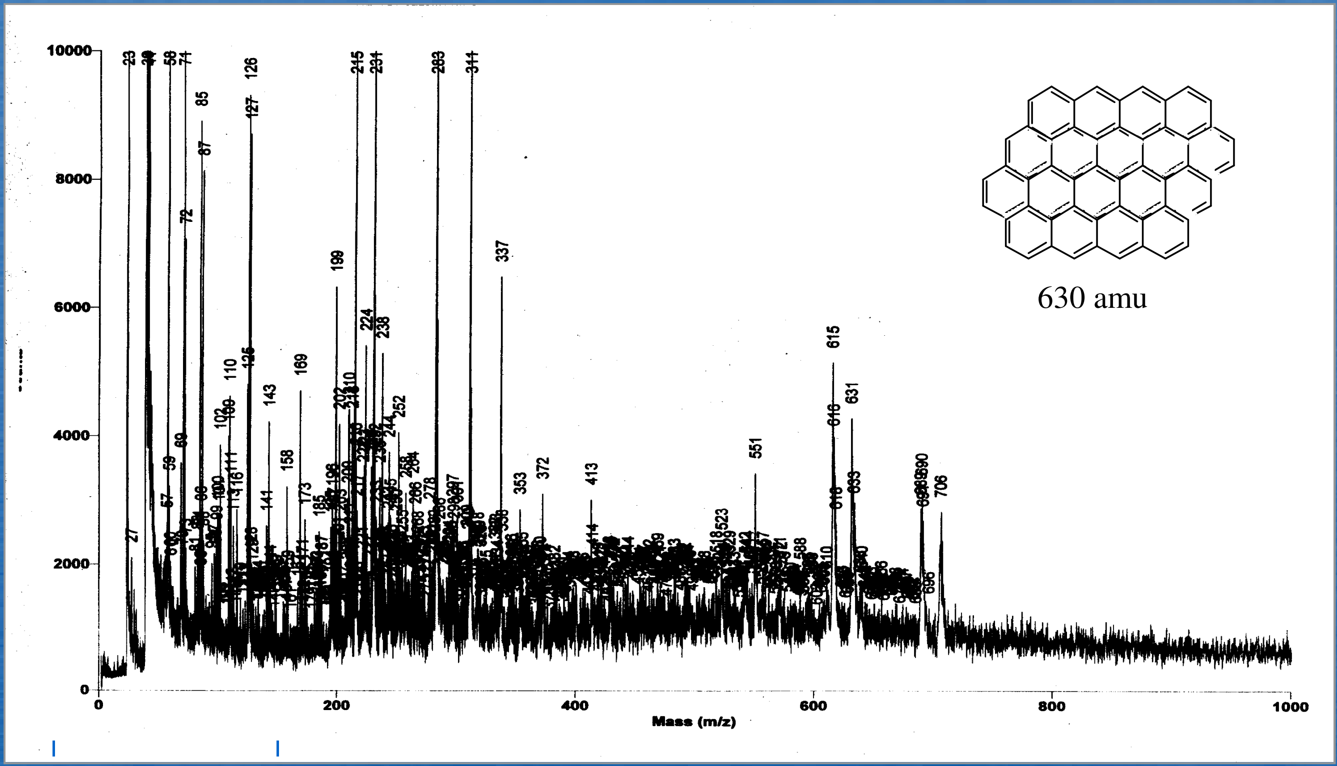
Anthracite	% C	% H	% N	% S	% O[a]	H/C
LCNN	95.7	1.5	1.2	0.5	1.1	0.19
Jeddo	95.2	1.8	1.1	0.6	1.3	0.23
UAE	94.0	2.2	1.0	0.5	2.3	0.28
Summit	93.2	2.5	1.6	0.6	2.1	0.32

[a] By difference

Computer-generated Structural Model of Anthracite



MALDI-MS of LCNN Anthracite



Graphitization of Anthracites in the "Prehistoric" Era

Graphitization of anthracites was investigated in a series of M.S. and Ph.D. theses at Penn State in late 50s and early 60s. Findings included:

1. Microporosity of anthracite decreases on graphitization.
2. Graphitization of anthracite/binder rods gives acceptable ash values but high resistivities (unsuitable for electrodes).
3. Extreme pressures (70–140 MPa) sinter anthracites at ≈900° .

The Conventional Wisdom on Anthracite Conversion

- 1957…The residue can hardly be distinguished from the starting material.
- 1981…Coal with…a carbon content of 91% or higher cannot be hydrogenated at all.
- 1983…Anthracite coals yield relatively large quantities or residue.
- 1990…Anthracites are virtually impossible to process…
- 1994…Anthracite can be classified as “unreactive”…

The Conventional Wisdom on Anthracite Conversion—Corrected

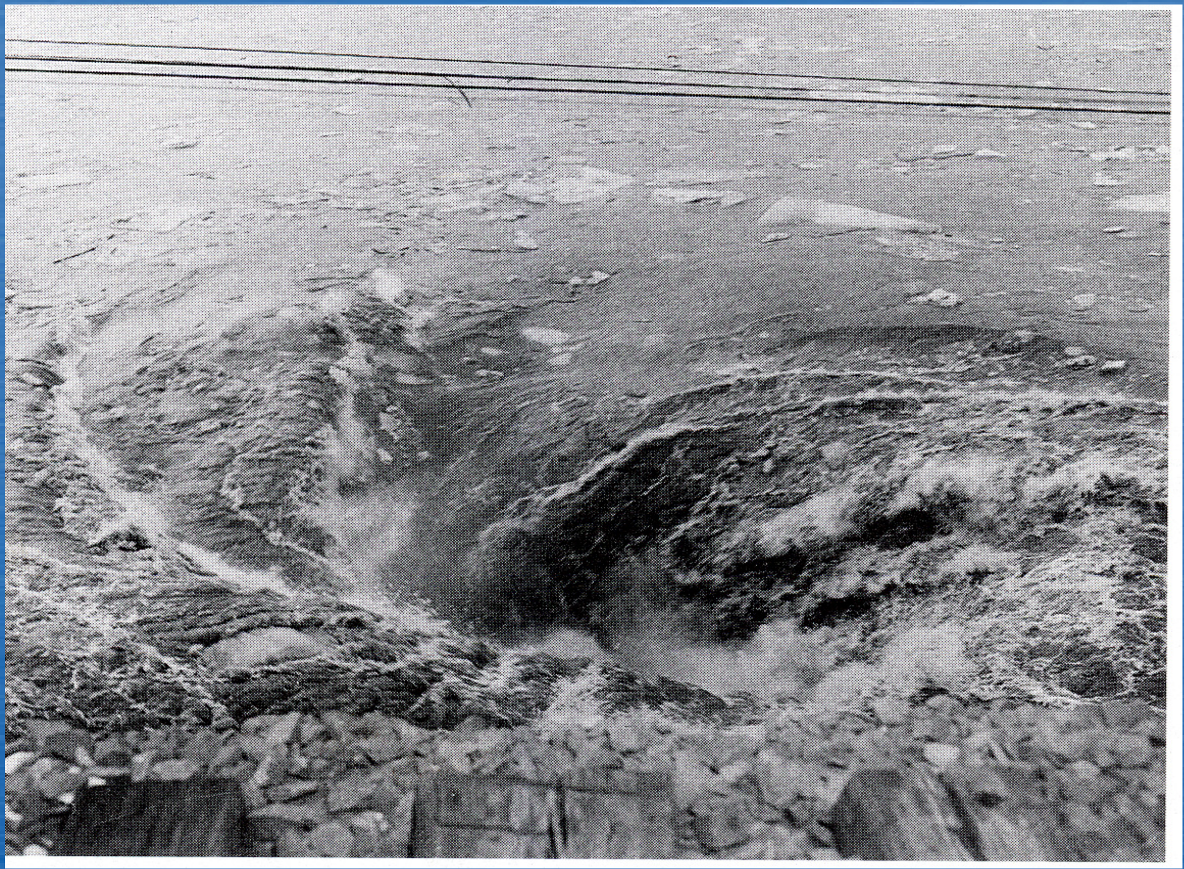
"…anthracites are virtually impossible to process…"

"It is a Tale
Told by an Idiot, full of sound and fury
Signifying nothing"

- Schobert, H. H.; Shakespeare, W. "Macbeth and the Chemistry of Hydrocarbon Fuels"

The Death of Anthracite—1957

“Bones and blood are the price of coal.”



R. P. Wolensky et al., THE KNOX MINE DISASTER, PHMC, 1999

Evan McColl and Peggy Seeger, “The Ballad of Spring Hill”.

Is Coal Dead?

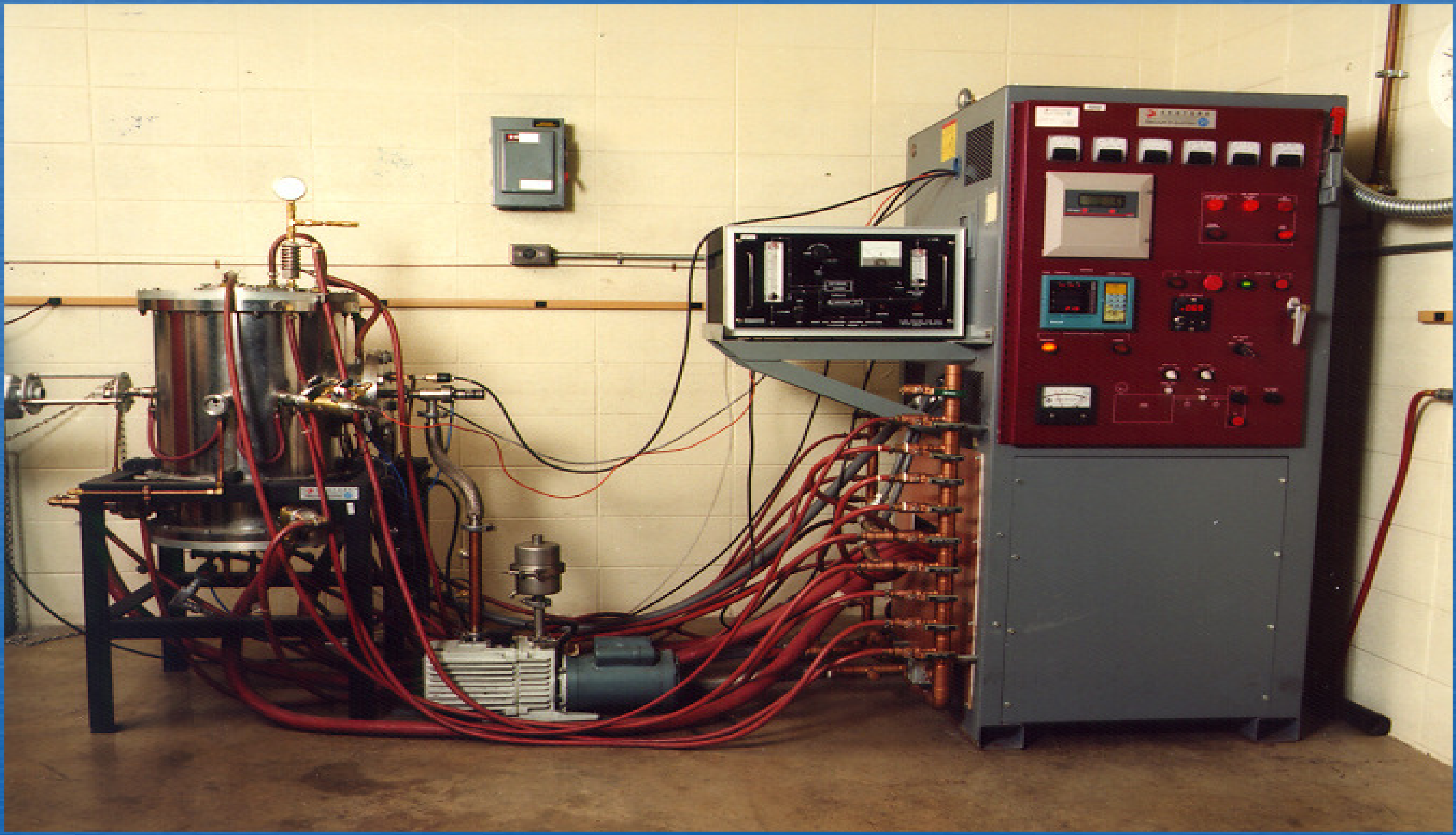
- "The report of my death was an exaggeration."

—Mark Twain

Anthracite Graphitization Research in the Early ‘90s: Aims

- Enhancing the graphitization of anthracites by heat-treatment (400–500°) with strong hydrogen donors.
- Catalytic graphitization with added metal naphthenates.
- Production of test artifacts in industrial trial.

Laboratory-scale Graphitization Furnace



Anthracite Graphitization Research in the Early '90s: Industrial Results

- Pitch level is critical for successful production of graphitized artifacts.
- Very different results were obtained for the two anthracites tested.
- Adding catalyst enhanced the density and strength of a graphitized control sample (petroleum coke).
- CTEs of graphitized anthracites were close to those of control sample; strengths and densities were lower.
- High residual ash levels in the graphitized anthracites.

The Volcano Principle in Heterogeneous Catalysis

- For comparison of the catalytic activities of a row of transition metals.
- Catalytic activity is plotted as a function of, e.g., atomic number.
- Graph rises to a maximum somewhere across the row, and then falls.
- With imagination, the graph looks like a sketch of a volcano.

Violation of the Volcano Principle

- Tests of Fe, Co, and Ni naphthenates as graphitization catalysts show no discernable effect of the metal (!?).

- This suggests that the activity must be due to the nonmetallic part of the catalyst.

A Speculative Mechanism for Catalytic Graphitization

Decomposition of inherent minerals and reaction with carbon forms carbides:

$$3\ M + C \rightarrow M_3C$$

At graphitization temperatures, carbides decompose, liberating highly reactive C atoms ("dicarbenes" :C:)

$$M_3C \rightarrow 3\ M\uparrow + :C:$$

Highly reactive :C: atoms react with "non-graphitizing carbon" (C_{ng}) to form graphite (C_g)

$$:C: + C_{ng} \rightarrow 2\ C_g$$

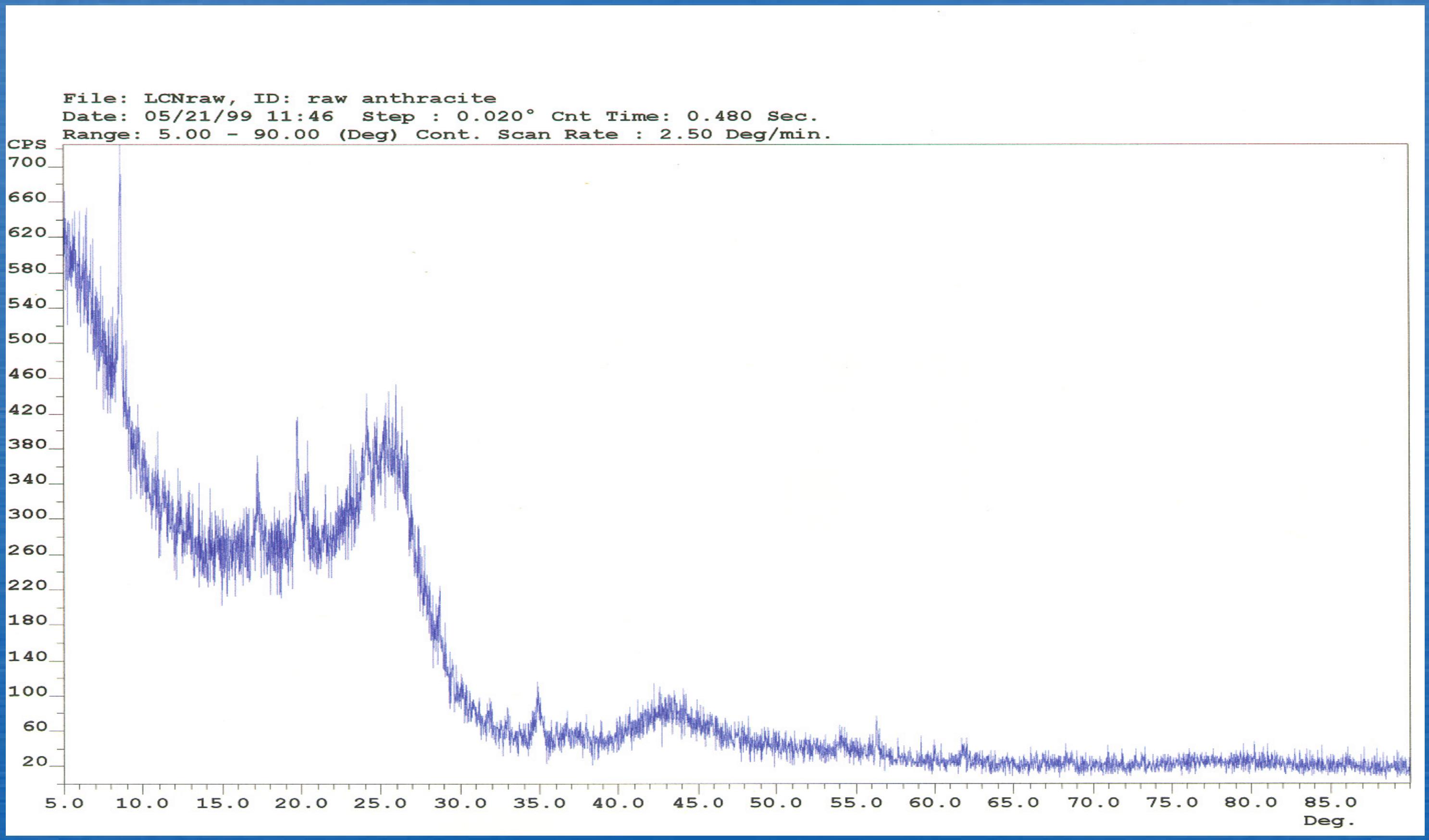
The highly reactive :C: atoms may also facilitate removal of the last of the heteroatoms.

Graphitization Into the New Century

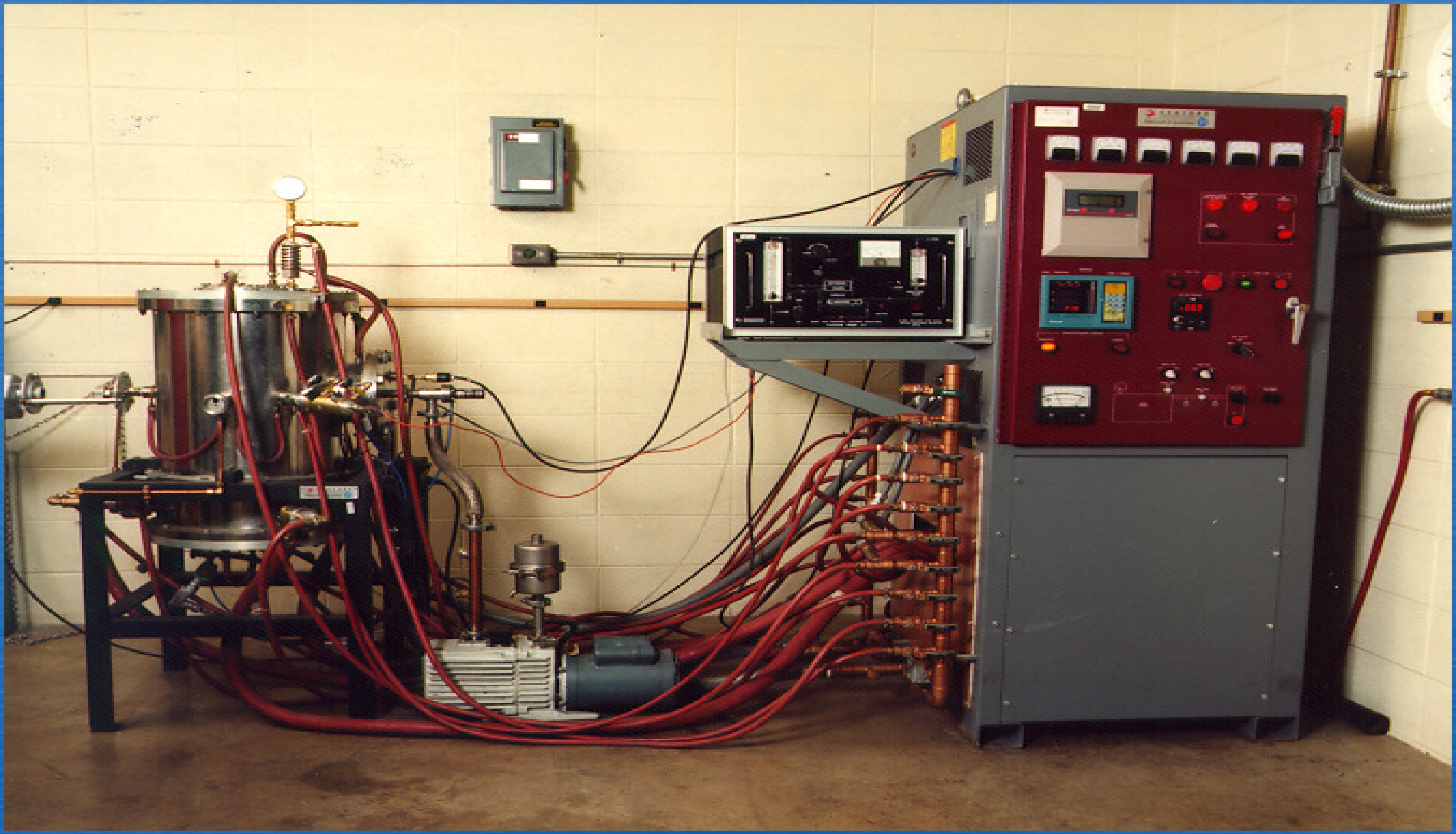
1. Different anthracites show different graphitization behaviors when heat-treated under identical conditions.
2. Different anthracites also have different organic structures and inorganic compositions.
3. A “good” anthracite, on a first try, can produce test billets with properties in the low end of the range for specialty graphites.

Not all anthracites are created equal!

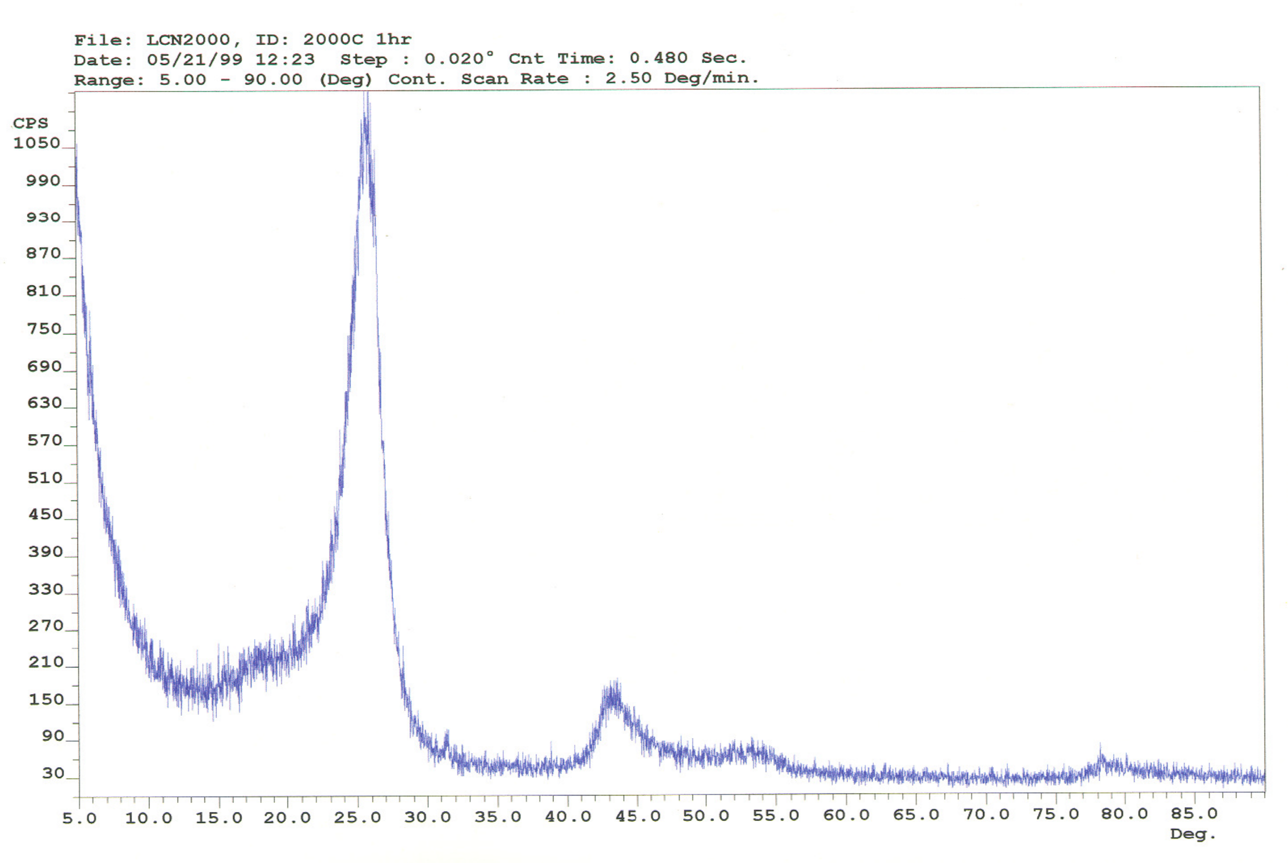
X-ray Diffractogram of Native LCNN Anthracite



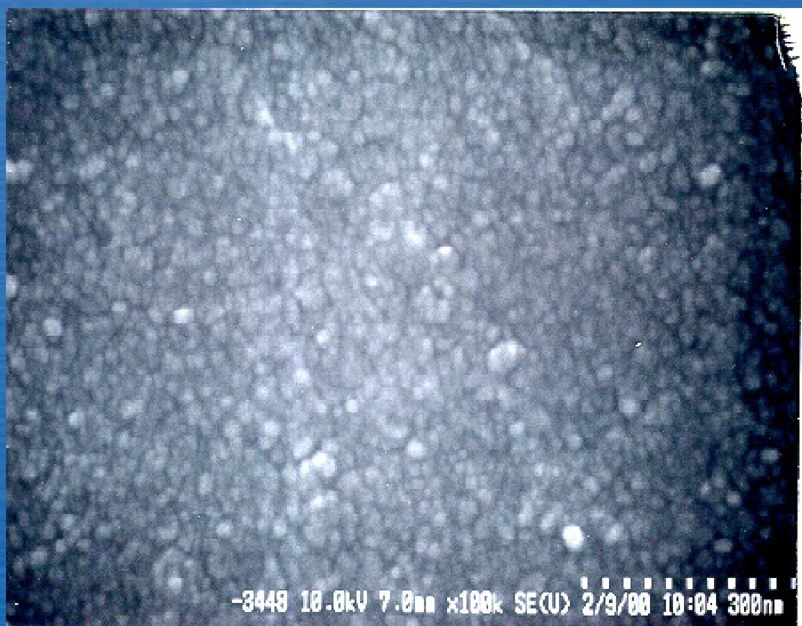
Laboratory-scale Graphitization Furnace



X-ray Diffractogram of LCNN Anthracite Heat-treated to 2000°

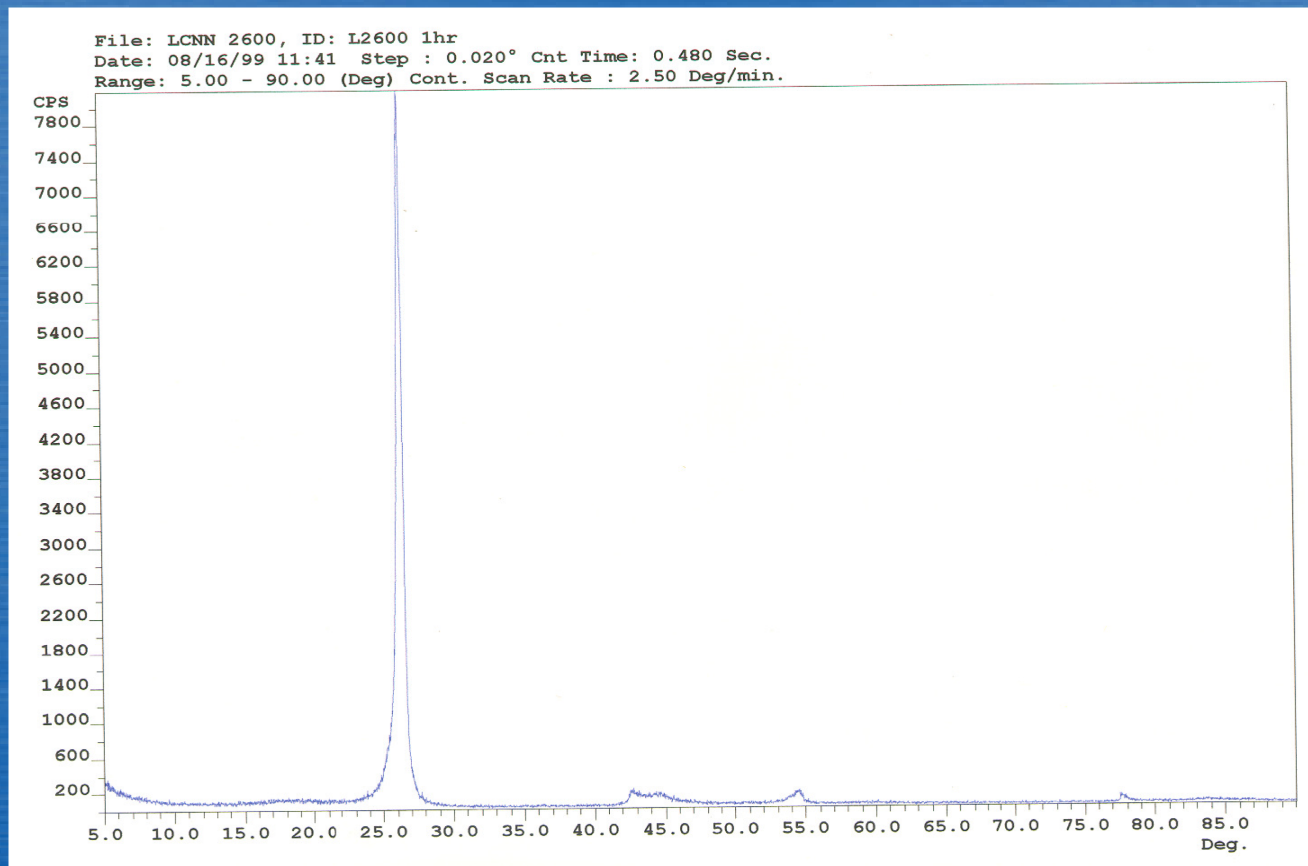


High-magnification SEM Image of LCNN Anthracite Heat-treated to 2000°

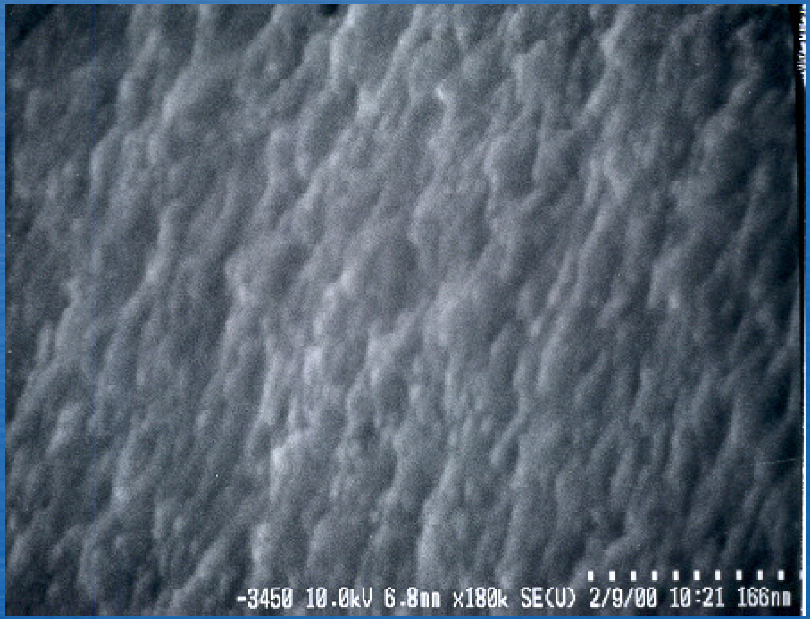


- The non-aligned surface features correlate with the low degree of graphitization obtained at this temperature.

X-ray Diffractogram of LCNN Anthracite Heat-treated to 2600°



High-magnification SEM Image of LCNN Anthracite Heat-treated to 2600°

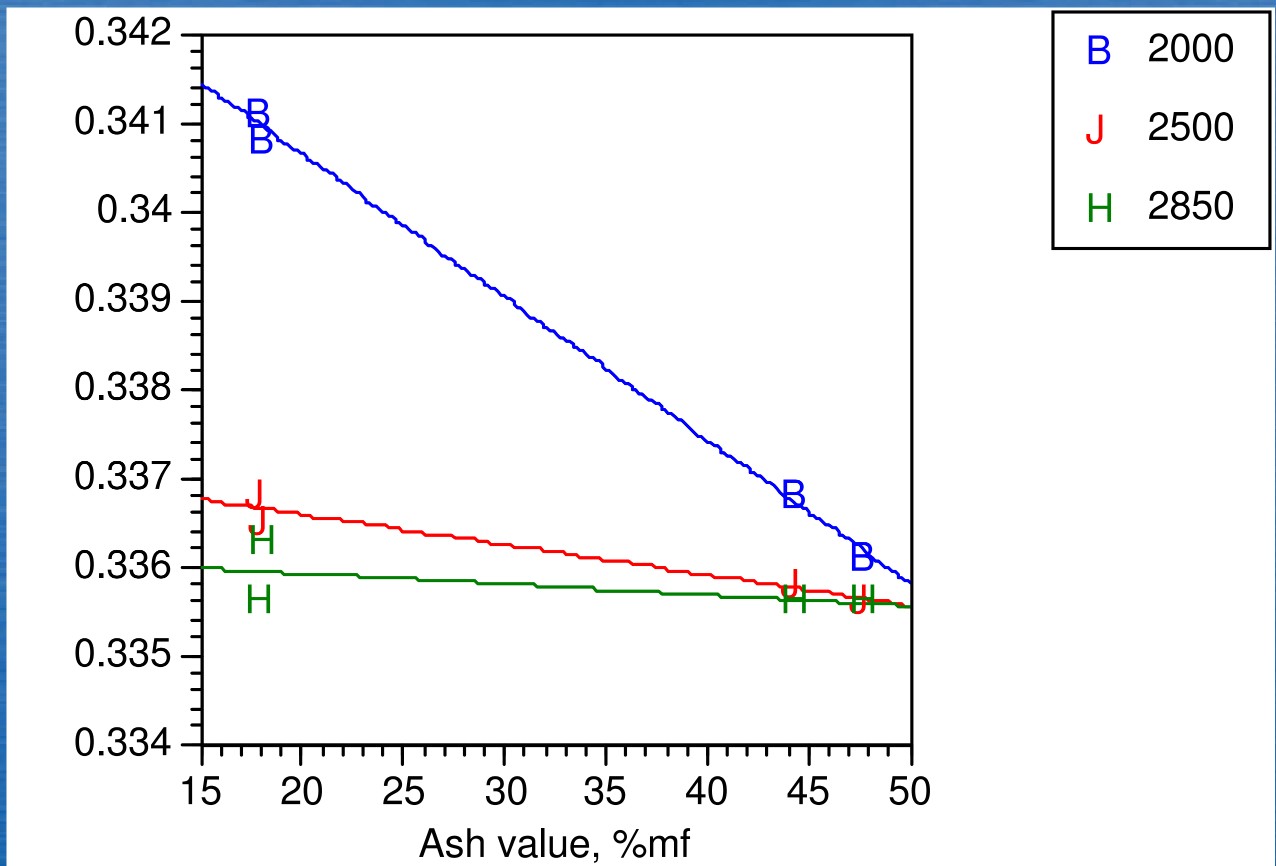


- Clear surface striations appear to correlate with the structure being more aligned at this higher heat-treatment temperature.

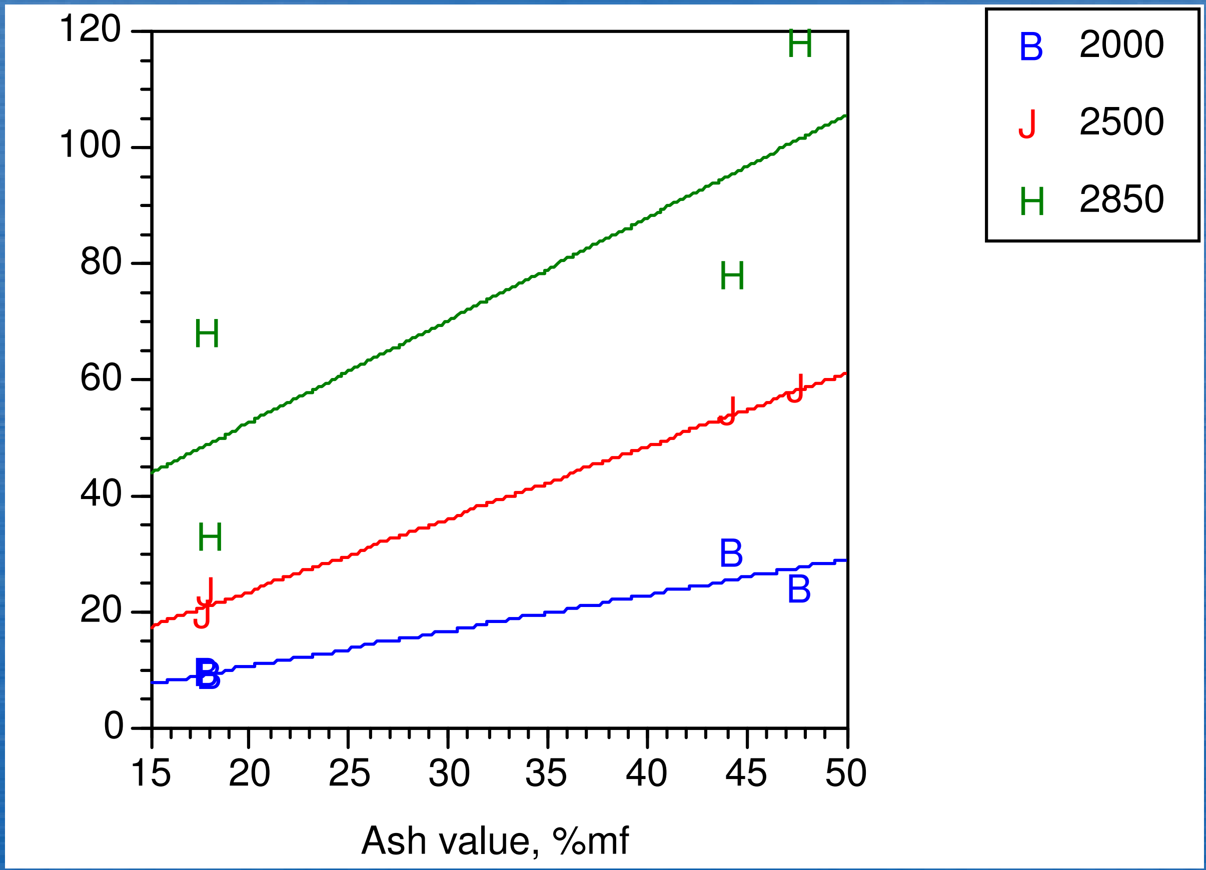
Not All Anthracites Are Created Equal…

- This suggests that there needs to be a simple criterion (or a few criteria) for selection of a "good" vs. "bad" anthracite.
- Previous work with added catalysts led us to speculate on the catalytic behavior of *in-situ* minerals.

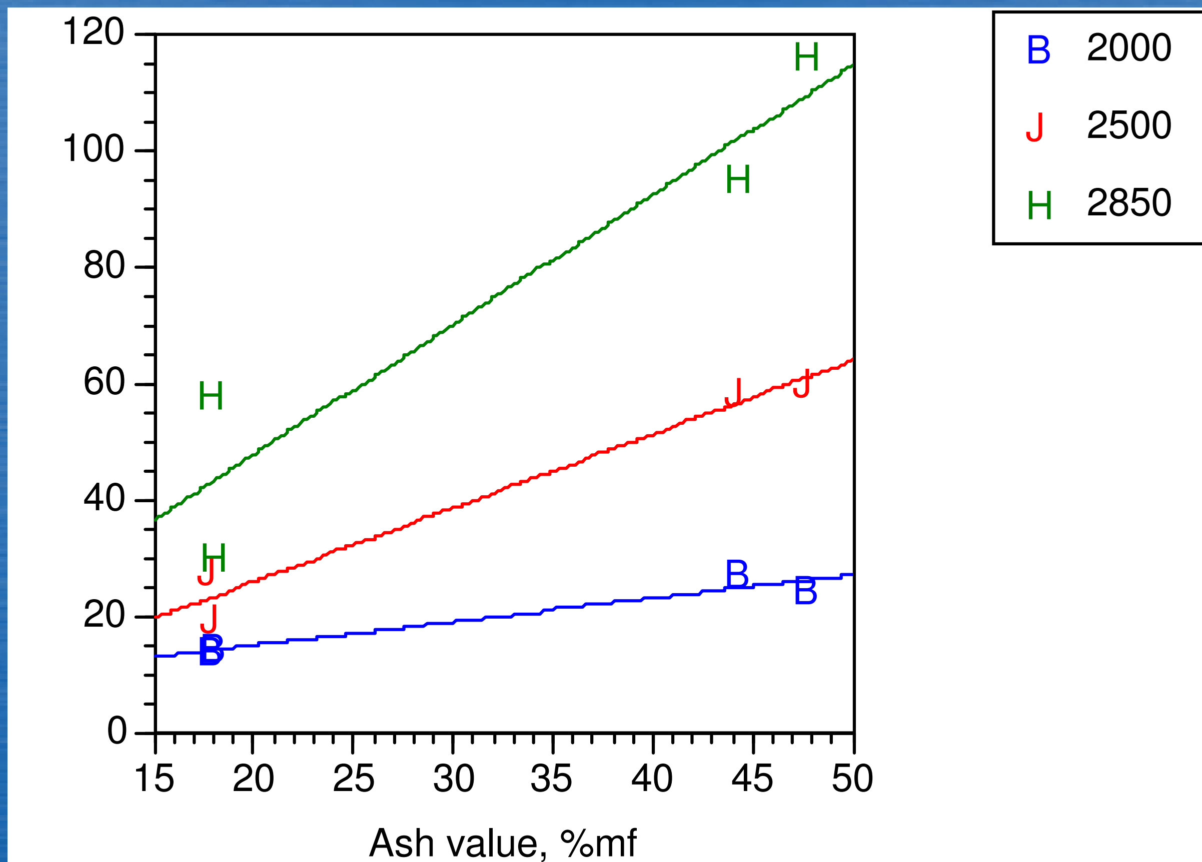
The Ash Value of Anthracites Affects d-Spacing Attained on Graphitization at Different Temperatures



The Ash Value of Anthracites Affects L_c Attained on Graphitization at Different Temperatures



The Ash Value of Anthracites Affects L_a Attained on Graphitization at Different Temperatures



Evaluation of Minerals as in-situ Catalysts for Graphitization

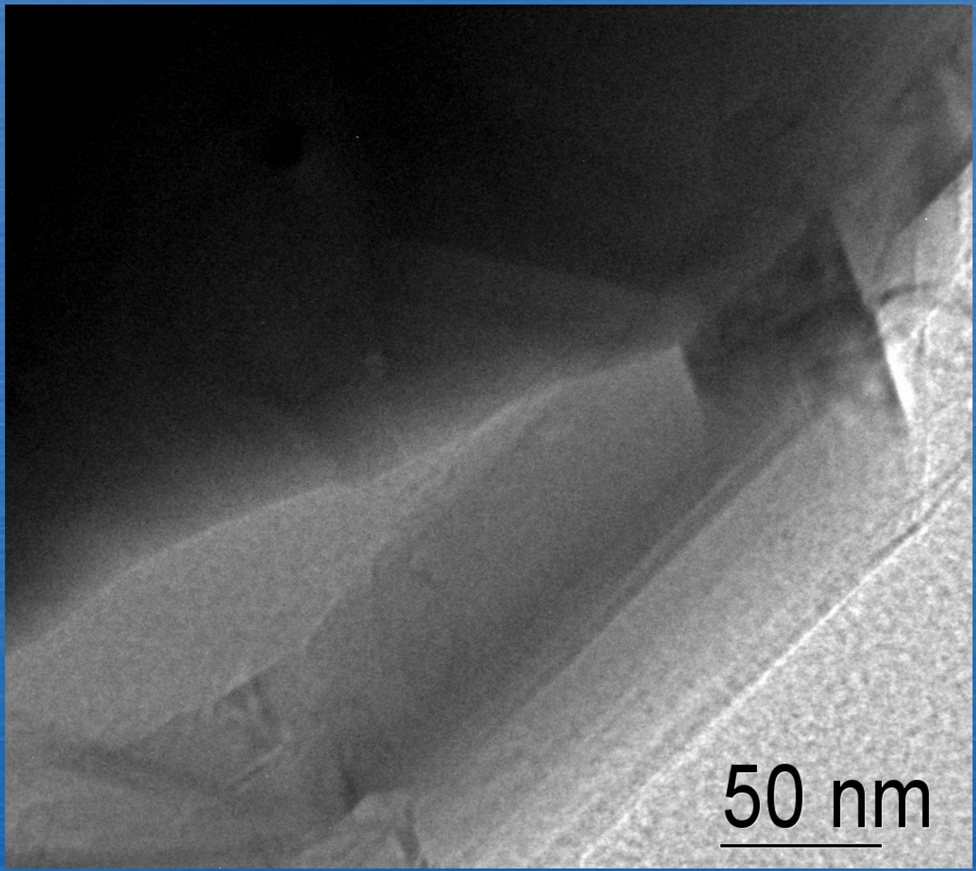
- Si, Fe, and Ca minerals showed particular effectiveness in graphitization.
- Demineralization of a "good" anthracite substantially reduced its graphitization.
- Adding minerals back to a demineralized anthracite restored good graphitization.
- Si, Fe, and Ca are all known to form carbides at high temperatures.

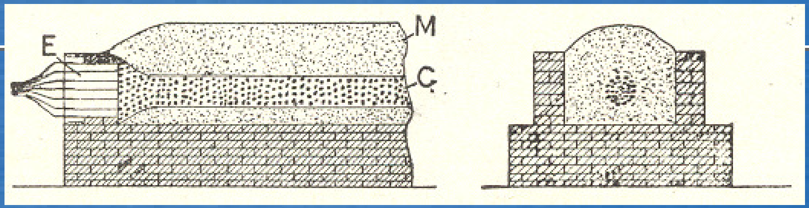
Proposed Mechanism for Silicon-catalyzed Graphitization via Carbide Intermediate

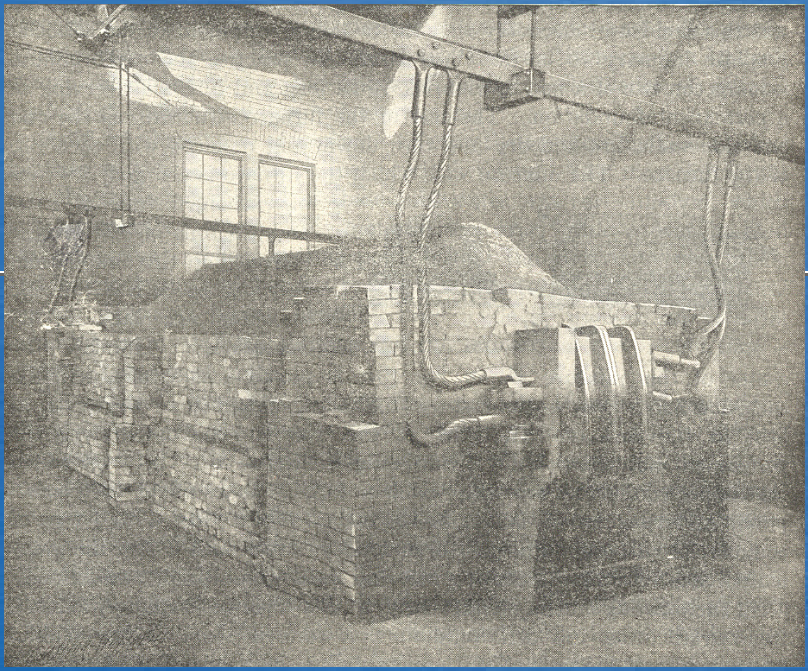
$$SiO_2 + 3\,C_{ng} \rightarrow SiC + 2\,CO$$

$$SiC \rightarrow Si\uparrow + C_g$$

TEM Observation of Silicon Carbide in Anthracite Heat-treated to Graphitization Temperatures







"The overheating of a carborundum furnace led to the discovery that by suitable decomposition of a carbide, graphite is left behind."

$$SiO_2 + 3\ C \rightarrow SiC + 2\ CO$$

$$SiC \rightarrow Si + C\ \text{(graphite)}$$

A. Rogers, Industrial Chemistry, van Nostrand, **1920**

Baldwin's Rule:

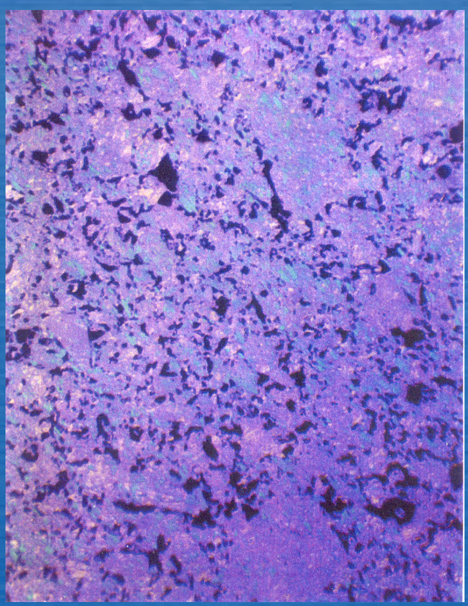
Six months of hard work in the laboratory will save you an hour in the library.

—Robert M. Baldwin
Colorado School of Mines

Properties of Industrially Graphitized Anthracites

	Control standards	*Graph. anthracites*
$d_{(002)}$, nm	0.3349–0.3354	0.3349–0.3357
L_c, nm	29.1–30.2	16.7–29.1
Density, g/cm^3	1.72–1.74	1.65–1.70
Resistivity x 10^{-4}	4.3–4.6	6.4–9.4
Flex. strength MPa	40.8–41.2	24.6–41.2
Hardness	72–76	80–97
CTE x 10^{-6}	4	5.0–5.2

Properties and Microstructure of Industrially Graphitized Anthracites



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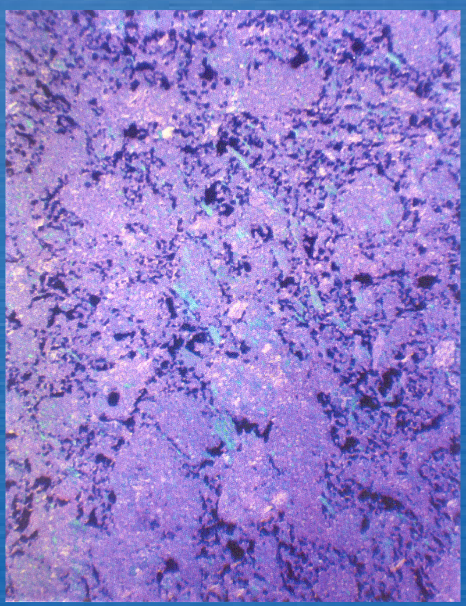
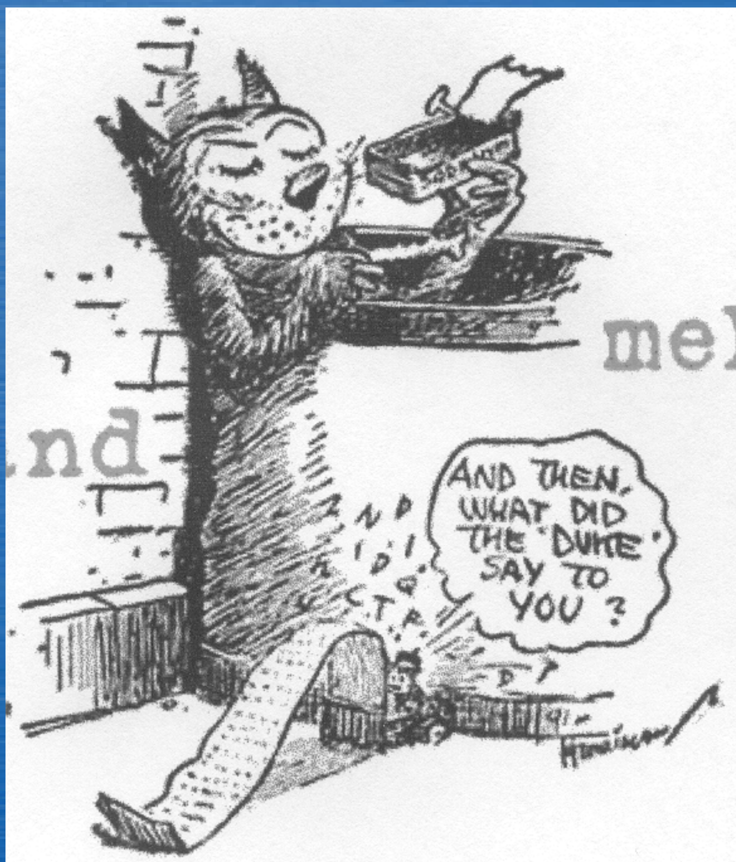
	Control	Anthracite
$d_{(002)}$, Å	3.349	3.354
L_c, Å	302	291
Resistivity, μΩ·m	0.00046	0.00046
Flex strength, MPa	40.8	42.6
Density, g/cm^3	1.74	1.70
Rockwell	76	97



Is Coal Dead?



"theres a dance or two
in the old dame yet"

—Don Marquis,
the song of mehitabel

Acknowledgements

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- John Andrésen, Joseph Atria, Frank Rusinko, Peter Pappano, and Shuming Zeng for their contributions.