# Behavior of Minerals During Anthracite Graphitization

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## Introduction

Anthracite coal was heated to three different temperatures to induce graphitization. The goal of the work was to determine how heating affected the mineral content and texture of the coal. This paper will focus on the various mineral transformations underwent during the heating process. The mineral transformations were measured using scanning electron microscopy and x-ray microanalysis.

Heating of the anthracite samples was conducted at Pennsylvania State University (1). Anthracite and heat-treated samples were analyzed by Microbeam Technologies Incorporated (MTI) to determine size, composition, and abundance of mineral and transformed mineral grains using computer-controlled scanning electron microscopy (CCSEM). In addition, morphological analysis was conducted to provide images and chemical compositions of selected features in the anthracite samples (2). The quantities of minerals and transformation products were determined at 2000°C, 2500°C, and 2600°C.

## Experimental

LCNN anthracite was heated to three different temperatures: 2000°C, 2500°C, and 2600°C to induce graphitization. The samples were heat-treated in a Centorr Vacuum Industry Series 45 furnace, accurate to ±10°C. Graphite crucibles containing 12 grams of sample under graphite lids were placed in the hot zone of the furnace. The environment of the hot zone was purged by pulling a vacuum, and then backfilling with ultra-high purity argon three times. Following this purge, the samples were heated to 2000, 2500, and 2600° C with a heating rate of 10°C/min and held at the maximum temperature for one hour (in vacuum). The heat-treated samples were prepared and analyzed to determine size, composition, and abundance of mineral grains using CCSEM.

Samples of the raw and heat-treated anthracite were prepared for scanning electron microscopy analysis by mixing two grams of sample material with three grams of melted carnauba wax. This mixture was poured into a small rubber mold and, after solidifying, was backed with epoxy. The epoxy is used to increase the strength of the resulting plug. Plugs were allowed to harden overnight, and polished to expose cross-sections of the particles. Polished plugs were cleaned and coated with carbon to improve conductivity in the electron microscope.

Prepared samples were analyzed to determine size, composition, and abundance of mineral grains using fully automated computer-controlled scanning electron microscopy. The CCSEM technique characterizes up to three thousand individual particles in a single sample. Elemental compositions are used to categorize individual mineral types.

MTI also performed scanning electron microscope (SEM) morphology analysis to obtain representative photographs of the samples and determine variations in inorganic content between the organic matrix and mineral matter. Backscattered electron imaging, which best shows compositional differences, was used to examine the minerals present in the samples.

## Results and Discussion

Table 1 shows the results of the CCSEM analyses for a raw anthracite and three heated samples. Mineral content for the raw coal was 6.8 wt%, and ranged from 1.1 wt% (at low temperature) to 0.6 wt% (at high temperature). This indicates significant loss of mineral phases from the coal due to decomposition and vaporization during heating. Figure 1 shows backscattered electron images of polished cross-sections of raw anthracite and heat-treated samples. The images show some changes in the shape of the minerals upon heating. Figure 1c shows void spaces where minerals may have been associated. These minerals likely volatilized during heating.

Mineral assemblages vary considerable between the raw and heated coals. Clays and aluminosilicates are abundant in the raw coal but absent from heated coals. This trend occurs for kaolinite, illite, and aluminosilicate. Calcium aluminosilicate, gypsum containing aluminosilicate (mixture of calcium, sulfur, and aluminosilicates), and unknown or amorphous material are most abundant in the sample heated to 2000°C. Pyrite, a sulfide mineral, is absent from the heated coal samples. Calcite-derived (or calcium oxide) and calcium-rich phase are important minerals in the heated coals, with the highest concentrations in the sample heated to 2500°C. Rutile ($TiO_2$), which is nearly absent in the raw coal sample and scarce in the 2000°C sample, is a dominant phase in the sample heated to 2500°C. Rutile and calcium oxide are stable at high temperatures and are not prone to volatilize during heating. Quartz and alumina are both present in the raw coal and the coal heated to 2000°C, but alumina is not present in the higher temperature samples, and quartz is not present in the 2600°C sample. Iron oxide increases in abundance as the temperature of treatment increases.

## Conclusions

Significant mineral transformations were found when comparing the mineral types and abundance in the raw and heated coals. Clay minerals including kaolinite, illite, and aluminosilicate were abundant in the raw coal but absent from heated coals. These materials interacted with other components to produce calcium aluminosilicate, gypsum-containing aluminosilicate, and unclassified materials. The unclassified materials are typically glassy amorphous phases. Pyrite, a sulfide mineral, was absent from the heated coal samples. As a result of the decomposition of pyrite, iron oxide increases in abundance as the temperature of treatment increases. Calcite-derived (or calcium oxide) and calcium-rich phases are important minerals in the heated coals with the highest concentrations in the sample heated to 2500°C. Rutile and calcium oxide are stable at high temperatures and are not prone to volatilize during heating.

## References

1. Pappano, P.J. "A mechanism of Pennsylvania anthracite graphitization involving carbide formation and decomposition." Ph.D. Dissertation. The Pennsylvania State University, University Park, PA. **2003**.
2. Laumb, M.L., Benson, S.A, and Laumb, J.D., Ash Behavior in Utility Boilers: A Decade of Fuel and Deposit Analysis, Proceedings of Engineering Foundation Conference, Production in the 21st Century: Impacts of Fuel Quality and Operations, October 28 - November 2, **2001**, Snowbird, Utah.

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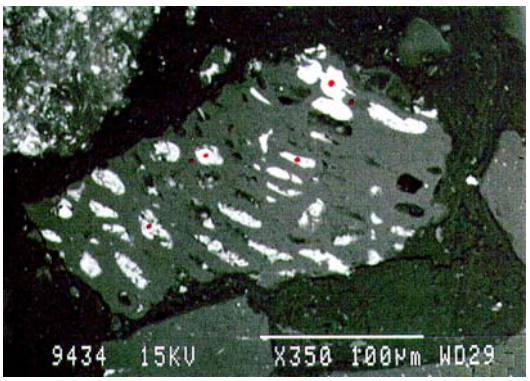
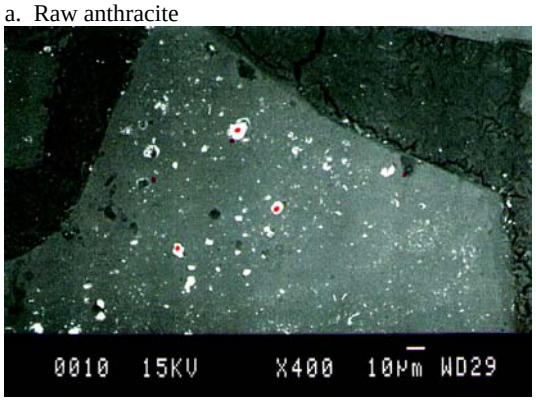
**Table 1. CCSEM analysis results for untreated LCNN anthracite and three heated LCNN anthracites. Results are expressed as weight percents normalized to 100% on a mineral basis.**

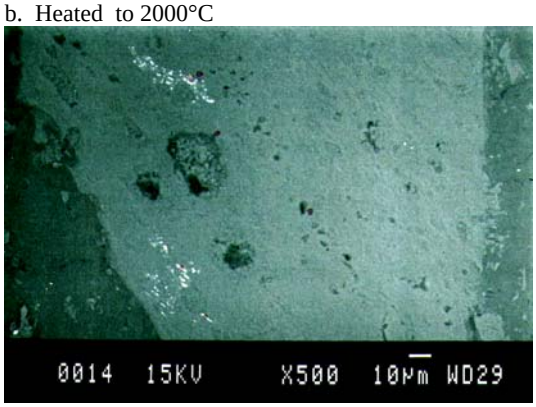
| Mineral/ phase | Raw | 2000°C | 2500°C | 2600°C |
|---|---|---|---|---|
| **Quartz** | 1.2 | 8 | 2.5 | 0.4 |
| **Iron oxide** | 0.5 | 1.1 | 1.5 | 2.8 |
| **Periclase** | 0 | 1.5 | 0 | 0 |
| **Rutile** | 0.8 | 9 | 42.7 | 38.5 |
| **Alumina** | 1.1 | 3.2 | 0 | 0 |
| **Calcite/calcite derived** | 1.6 | 8.2 | 12.3 | 9.2 |
| **Dolomite** | 1.4 | 0.1 | 0.4 | 0.1 |
| **Ankerite** | 0 | 0 | 0 | 0 |
| **Kaolinite** | 60.4 | 0.2 | 0.2 | 0 |
| **Montmorillonite** | 2 | 0.2 | 0 | 0.2 |
| **Illite** | 7.5 | 0 | 0.3 | 0 |
| **Fe Al-silicate** | 1.5 | 0 | 0 | 0 |
| **Ca Al-silicate** | 0.3 | 16.2 | 0.1 | 0.7 |
| **Na Al-silicate** | 0.5 | 0 | 0 | 0 |
| **Aluminosilicate** | 5.3 | 0.3 | 0 | 0 |
| **Mixed Al-silica** | 0.9 | 0.1 | 0.8 | 0 |
| **Fe silicate** | 0 | 0 | 0 | 0 |
| **Ca silicate** | 0 | 0.9 | 0.2 | 0 |
| **Ca aluminate** | 0 | 0.1 | 0 | 0 |
| **Pyrite** | 4.9 | 0 | 0 | 0 |
| **Pyrrhotite** | 0 | 0 | 0 | 0 |
| **Oxidized pyrrhotite** | 0.1 | 0.2 | 0 | 0 |
| **Gypsum** | 0.1 | 0.9 | 1.7 | 0.4 |
| **Barite** | 0 | 0 | 0 | 0 |
| **Apatite** | 0.5 | 0 | 0.6 | 0 |
| **Ca Al-P** | 0.1 | 0 | 0 | 0 |
| **KCL** | 0 | 0 | 0 | 0 |
| **Gypsum-Barite** | 0 | 0.8 | 0.1 | 0.2 |
| **Gypsum-Al-silic.** | 0.1 | 9.3 | 0.8 | 0 |
| **Si-rich** | 0.3 | 2.3 | 0.5 | 0.3 |
| **Ca-rich** | 0.8 | 6.1 | 8.5 | 5 |
| **Ca-Si-rich** | 0 | 0 | 0 | 0 |
| **Unknown/amorphous** | 8.1 | 31.6 | 26.9 | 42 |



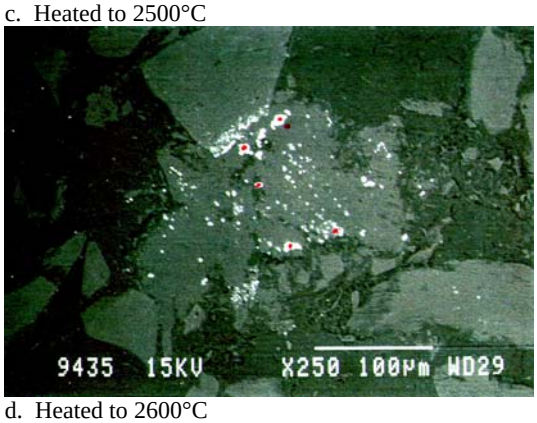
a. Raw anthracite



b. Heated to 2000°C



c. Heated to 2500°C



d. Heated to 2600°C

**Figure 1.** Backscattered electron images of polished cross-sections of raw coal and heat-treated samples.