# In-depth study on carbon speciation focussed on graphite

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## Summary

Quantifying and qualifying the presence and form of carbon in natural geological materials is essential to assessing value or determining potential harm to the analysis and metallurgical processing of other commodities. Early-stage resource evaluation is hampered by the lack of cost-effective, accurate tests to differentiate carbon forms and by confusion in terminology assigned to these forms.

Our study of carbon species focused on the transition zone between non-graphitic organic carbon and graphite using coal, petroleum coke, and graphite to potentially define a low-cost, accurate method for distinguishing between these forms. X-Ray diffraction (XRD) analysis established the presence of nanoscale graphite in the petroleum coke but only non-graphitic organic carbon in anthracitic coal. Graphite estimation by nitric acid extraction of organic carbon prior to Leco analysis gave correct estimation of graphite in the petroleum coke but erroneously identified graphite in the coal. Leco analysis of reference materials following pyrolysis pre-treatment at different temperatures identified a sweet-spot that minimized false positive and false negative errors in differentiating between organic carbon and graphite. It also identified an acute sensitivity in a narrow temperature range (550°C – 600°C) for the rapid oxidation of nanoscale graphite not observed with the coarser graphite tested. The contrast in oxidation rates between the nanoscale and coarser-crystalline graphite warrants further investigation to ascertain the potential for a robust, inexpensive graphite quality test.

## 1. Introduction

Carbon in a highly-organized aromatic arrangement as a single sheet (e.g. graphene, nanotubes) or stacked sheets (e.g., graphite) has remarkable properties. Its high electrical conductivity, tensile strength, flexibility and light weight (Geim and Novoselov, 2007) make it a strategic commodity for a growing list of applications including paper-thin Li-ion batteries (Hu et al., 2010). Conversely, carbon in gold ore can cause preg-robbing during hydrometallurgy (Helm et al., 2009) resulting in poor recoveries.

Several analytical methods can be employed to quantify graphite. X-ray diffraction analysis is a well-established method providing quantity and crystallinity (Franklin, 1951). Raman spectroscopy can quantify the degree of bulk graphitization in poor to well-ordered graphitic material (Beyssac et al., 2002a), and transmission electron microscopy (TEM) can provide detailed images of nanoscale graphite structures (Buseck and Huang, 1985). Although these methods provide accurate detailed information, they can be costly and time consuming if not conducted on a commercial lab scale, and may not provide information for non-graphitic organic carbon or inorganic carbon.

Commercial-scale carbon analysis has suffered from confusion in methodology and terminology, as noted by Girard and Klassen (2001), who examined seven published analytical methods. All methods, except for proton balance, use Leco analysis to determine total carbon, inorganic carbon (IC) and organic carbon (OC). Each method employs direct analysis of total carbon (TC) on a sample split. A second sample split is either analyzed directly to determine inorganic carbon or is pre-treated to selectively remove inorganic carbon or organic carbon. The missing component is then determined by difference using one of the following equations.

1) OC = TC – IC
2) IC = TC – OC

Girard and Klassen (2001) did not differentiate graphite from other carbon species, however they did note that, depending on the pre-treatment used, graphite would report either as organic or inorganic carbon. The transition between non-graphitic organic carbon and well-crystalized graphite is a diffuse zone of poorly to well-organized aromatically structured carbon atoms (Buseck and Beyssac, 2014) related to the degree of metamorphism (Beyssac et al., 2002b). We examined this zone to ascertain if the proportions of non-graphitic organic carbon and graphitized carbon can be accurately and precisely defined with a cost-effective Leco analysis. Carbon species are separated here into two groups: inorganic carbon (IC) comprising inorganic carbon-bearing minerals such as carbonates, and organic carbon (OC) that includes non-graphitized, partially graphitized and completely graphitized material of likely organic origin.

## 2. Methods

This study examined three carbon test materials comprising a medium-volatile coal from Kuzbass, Russia (Coal 2008-4), a calcined low-volatile petroleum coke (PC-8), and a ground-up high purity graphite crucible (Graphite) with visible granularity employed in whole rock digestions and analyses and supplied by SCP Science. Both the coal and petroleum coke were analyzed by XRD at the University of British Columbia in Vancouver, British Columbia to determine graphite content. Bureau Veritas Commodities Canada laboratory in Vancouver, British Columbia analyzed all three test materials for total carbon, inorganic carbon, and organic carbon in non-graphitized and graphitized form.

### 2.1. XRD analysis

The samples were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 10 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKα radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted beam Soller slits and a LynxEye-XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

### 2.2. Carbon species by Leco analysis

All carbon determinations were conducted on a Leco CS-230 carbon-sulphur analyser. In general, 0.1 g of sample material was combusted at 1350°C in the analyser's induction furnace. Evolved carbon was swept up by a flow of oxygen and converted to $CO_2$ and CO. The gases were passed through an infrared cell where the integration of the amount of infrared (IR) light absorption during sample ignition determined the quantity of total carbon in the sample. Samples reporting >40% carbon were re-analyzed using a 0.03 g sample.

#### 2.2.1. Total carbon analysis

Analysis of total carbon entails directly combusting a 0.1 g (or 0.03 g) sample split without any pre-treatment. All carbon-bearing compounds (inorganic, non-graphitic organic and graphitic) were decomposed thus giving the total carbon content of the sample.

#### 2.2.2. Inorganic carbon analysis

A 0.1 g (or 0.03 g) sample was reacted with perchloric acid in a closed vessel in a warm bath (70°C) for 1 hour to fully evolve $CO_2$ through decomposition of all carbonates. The $CO_2$ was swept up by a flow of oxygen into the CS230 analyser where the concentration of carbon was determined by integration of the amount of IR light absorbed.

#### 2.2.3. Graphitic carbon determination by nitric acid leach

A 0.1 g (or 0.03 g) sample was pre-treated by leaching with concentrated nitric acid ($HNO_3$) at 70°C for 1 hour to oxidize and decompose the non-graphitic organic carbon fraction. The residue was then leached with hydrofluoric acid and 15% HCl to remove inorganic carbon. The residue was washed several times with de-mineralized water to remove all acid, and oven dried. The residue was analyzed by Leco CS230 analyser to determine graphitic carbon.

#### 2.2.4. Graphitic carbon determination by pyrolysis

A 0.1 g sample was pre-treated by igniting at a specific temperature for 1 hour to remove organic carbon. The residue was leached with 15% HCl in filter crucibles at 70°C for 1 hour to remove inorganic carbon present as carbonates. The residue was then washed with de-mineralized water to remove all traces of acid, and oven dried. The residue was analyzed by Leco CS230 analyser to determine carbon present as graphite. Separate tests were conducted at 450°C, 475°C, 500°C, 525°C, 550°C, 575°C and 600°C.

### 2.3. Calibration and quality control

For all Leco analyses, the apparatus was calibrated using a pure calcium carbonate (calcite) and an analyte blank to establish the baseline. Analyses of the carbon reference materials were conducted on five replicate sample splits to fully evaluate precision. Accuracy was measured by inclusion of Geostats certified reference materials (CRMs) GGC-02 and GGC-06 (natural graphite from Eyre Peninsula, South Australia), and GGC-10 (flake graphite from Halls Creek, Western Australia) that were analyzed in duplicate or triplicate. Precision and accuracy of each test group is reported in the results below. Recommended values for the Geostats CRMs are listed in Table 1.

## 3. Results

### 3.1. XRD analysis

XRD analysis of the coal (Coal 2008-4) and petroleum coke (PC-8) carbon test materials are presented in Table 2. Coal 2008-4 contains abundant (95%) amorphous material comprising organic matter and 5% inorganic material consisting of carbonates (dolomite-ankerite, siderite), clay (kaolinite, illite) and quartz. Carbon reference material PC-8 is composed almost entirely of graphite (99.1%) and trace quartz, which is inferred to be a contaminant from the grinding pellets. The graphite in PC-8 is nanoscale (microcrystalline), given the extreme peak broadening.

These results correlate well with the total carbon and inorganic carbon contents reported by Leco analysis (Table 3) and the round-robin coal analyses results reported by Quality Associates International Ltd. for these materials (Table 4).

### 3.2. Graphitic carbon, nitric acid leach method analysis

The nitric-acid leach method reports high graphitic carbon concentrations for all three test materials. These results are acceptable for PC-8 (95% graphite) and the medium-grained graphite (101% graphite), but a graphite content of 69% reported for Coal 2008-4 is erroneous. Although the graphitic carbon results for Coal 2008-4 are inaccurate, they are nonetheless precise, with an RSD of 1.8% over the five splits tested. This suggests the presence of an organic phase readily attacked by

**Table 1.** Recommended values for graphite CRMs from Geostats.

| Element | Units | Certified Value |
|---|---|---|
| **GGC-02** | | |
| Graphitic Carbon | % | 27.04 |
| Total Carbon | % | 28.25 |
| Total Sulphur | % | 0.04 |
| **GGC-08** | | |
| Graphitic Carbon | % | 7.68 |
| Total Carbon | % | 8.16 |
| Total Sulphur | % | 0.05 |
| **GGC-10** | | |
| Graphitic Carbon | % | 4.79 |
| Total Carbon | % | 5.22 |
| Total Sulphur | % | 4.40 |

**Table 2.** XRD analysis of carbon reference materials Coal 2008-4 and PC-8.

| Mineral | Ideal Formula | Coal 2008-4 | PC-8 |
|---|---|---|---|
| Quartz | $SiO_2$ | 0.7 | 0.9 |
| Kaolinite | $Al_2Si_2O_5(OH)_4$ | 1 | |
| Illite | $K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$ | 2 | |
| Dolomite-Ankerite | $CaMg(CO_3)_2$-<br>$Ca(Fe^{2+},Mg,Mn)(CO_3)_2$ | 0.7 | |
| Siderite | $Fe^{2+}CO_3$ | 0.3 | |
| Amorphous | | 95 | |
| Graphite | C | | 99.1 |
| Total | | 100 | 100 |

**Table 3.** Total carbon and inorganic carbon by Leco analysis for Coal 2008-4 and PC-8.

| Carbon Species (Wt%) | Coal 2008-4 | PC-8 |
|---|---|---|
| Total Carbon | 84 | 94 |
| Inorganic Carbon | 0.1 | 0.0 |

**Table 4.** Constituents as reported by Quality Associates International for Coal 2008-4 and PC-8.

| Constituents (wt%) | Coal 2008-4 | PC-8 |
|---|---|---|
| Carbon | 84.71 | 96.54 |
| Hydrogen | 4.09 | 0.07 |
| Nitrogen | 2.22 | 0.81 |
| Sulphur | 0.37 | 2.70 |
| Ash | 4.86 | 0.13 |
| Moisture | 1.76 | 0.03 |

the nitric acid leach, and a nitric acid resistant, possibly poorly graphitized carbon phase. No further work was conducted using this method. However, follow-up work is warranted to determine if increasing the leaching time or temperature would improve the attack on the resistant carbon phase.

### 3.3. Carbon by pyrolysis

The Coal 2008-4, PC-8 and Graphite test materials define distinctly different trends (Fig. 1) in the reported graphite content following ignition pre-treatment at temperatures between at 450°C to 600°C. For Coal 2008-4, pyrolysis pre-treatment at 450°C was insufficient to remove all of the non-graphitic organic carbon, resulting in a significant residual amount of carbon (28%) reported as graphite. Successively higher temperatures removed more carbon; at 550°C essentially all the carbon was driven off leaving only a trace (0.3%) reported as graphite. The very short whiskers attest to good agreement between the five splits at each temperature. Precision was good, with RSD ranging from 2.9% at 450°C to 10.6% at 550°C where carbon concentrations were very low (15 times above the detection limit).

The nanoscale graphite in PC-8 remained relatively untouched by the ignition pre-treatment at temperatures up to 500°C, with 100% carbon reported. Minor graphite loss (4%) started to occur at 525°C. The loss accelerated with 10% loss at 550°C, 47% loss at 575°C and essentially complete destruction (97% loss) of the nanoscale graphite at 600°C. Variability between the five splits was low (RSD of 0.4% to 0.7%) from 450°C to 500°C, confirming stability in this temperature range. Variability increased in conjunction with carbon loss as seen by an RSD of 16.1% at 575°C.

The graphite test material was stable in the temperature range of 450°C to 575°C with 100% carbon reported. However, at a pre-treatment ignition temperature of 600°C, oxidation of the graphite resulted in a 15% loss of carbon. The loss is uniform among the five splits, with an RSD of 1.1%.

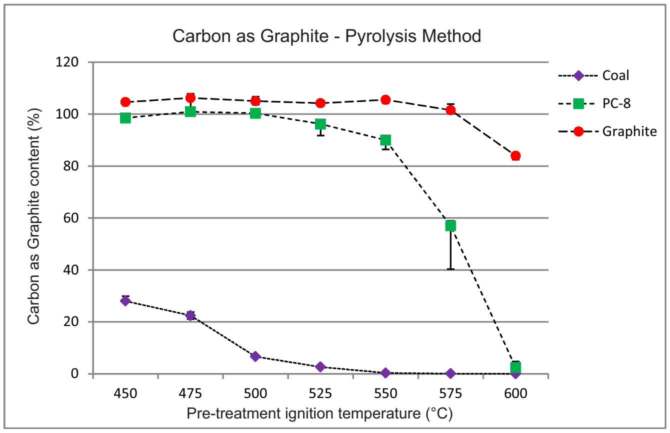

**Fig. 1.** Dot and whisker plot for carbon as graphite determined by pyrolysis pre-treatment followed by Leco analysis for three test materials (Coal 2008-4, PC-8 and Graphite). Dot and whiskers represent maximum value, median and minimum value of five splits analyzed for each ignition temperature.

Both GGC-06 and GGC-10 reported stable concentrations across the full temperature range (Fig. 2) coincident with their recommended values (RV). However, GGC-02 demonstrated successive losses across the entire temperature range, with accelerated loss at 575°C accompanied by greater variation among the triplicate splits.

## 4. Discussion

The pyrolysis method for identifying graphite in samples with mixed carbon species can minimize cases where graphite is falsely identified (false positive) and cases where graphite is present but undetected (false negative). Based on the test materials, this method appears to segregate non-graphitic organic carbon from graphite carbon. Pre-treatment by igniting the samples at a temperature between 500°C to 525°C minimizes both false negatives and false positives by preserving nanoscale and coarser graphite while driving off nearly all of the non-graphitic organic carbon. Kouketsu et al. (2014) conducted Raman analyses of carbonaceous materials to develop a geothermometer based on the degree of ‘graphitization’. Temperatures from 280°C to 650°C coincide with the transition from amorphous (non-graphitized) carbon to well-crystallized graphite. The persistence of carbon in Coal 2008-4 from 450°C to 525°C may relate to graphitization that, while insufficiently crystalline to be detected by XRD, increases resistance to combustion.

The behaviour of the nanoscale graphite in PC-8 relative to the coarser-grained Graphite test material between 550°C to 600°C indicates a rate of loss that is material dependent wherein the oxidation rate may be related to crystal size and shape. The high variability between sample splits of PC-8 at 575°C indicates acute sensitivity to boundary layer conditions in the ignition crucible, possibly caused by variable oxygen availability to convert graphite to $CO_2$, as has been observed in experiments by Xiaowei et al. (2004), and in work by Chi and Kim (2008) and Contescu, et al. (2008). Conversely, although the Graphite test material incurred 15% loss at 600°C, the oxidation rate was low enough to avoid fully consuming oxygen in the crucible micro-environment, thus giving a uniform loss among the five sample splits.

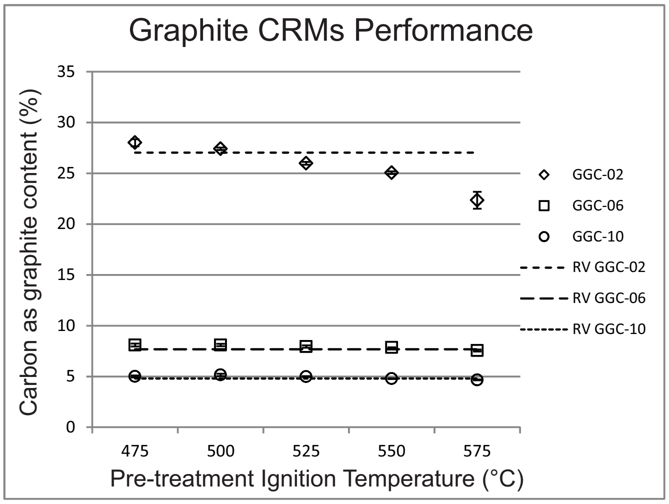

**Fig. 2.** Box and whisker plot for carbon as graphite by Leco analysis for Geostat CRMs. Box and whiskers represent minimum value, average and maximum value for 2 or 3 splits analyzed at each ignition temperature. Dashed lines represent recommended value (RV) for each CRM.

Behaviour of the Geostat CRMs to pre-treatment ignition temperatures may provide insight to the nature of the graphite in each CRM. GGC-06 and GGC-10 remain stable across the 475°C-575°C temperature range, much like the Graphite test material. However, GGC-02 demonstrated loss across the temperature range, with accelerated loss at 575°C much like the nanoscale graphite in PC-8. This loss suggests that GGC-02 may include a component of nanoscale graphite. The differences in behaviour between the CRMs may also be related to the presence or absence of imputities. Chi and Kim (2008) reported that cokes from different sources (pitch versus petroleum) contrasted in oxidation rates and that impurities likely have a significant influence on those rates.

## 5. Conclusions

Pyrolysis pre-treatment of samples at an ignition temperature between 500 and 525°C minimizes false positive and false negative errors in distinguishing between non-graphitic organic carbon and graphite. However, follow-up work is needed to define the effect of time in isothermic tests to determine if further improvement is achievable. The nature of the graphite may control the oxidation rate at different temperatures, as shown by the contrast between the nanoscale graphite in petroleum coke and the coarser grained graphite derived from the high purity graphite crucibles. Therefore, further work is also required to determine if graphite quality (crystallinity, particle size) can be quantified by quick and inexpensive Leco tests using pyrolysis pre-treatment at set temperatures and modeled against known reference materials.

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