APPLICATION OF A TGA METHOD TO ESTIMATE COAL, CARBONATE, AND NON-CARBONATE MINERAL FRACTIONS AS A PROXY FOR THE MAJOR SOURCES OF RESPIRABLE COAL MINE DUST

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
In
Mining Engineering

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October 15, 2021
Blacksburg, VA

Keywords: Thermogravimetric analysis (TGA), Dust sources, Respirable Coal Mine Dust (RCMD), Lung disease

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TECHNICAL ABSTRACT

Inhalation of respirable dust in coal mines is a serious occupational health hazard which can lead to the development of chronic and irreversible lung diseases, such as Coal Worker's Pneumoconiosis (CWP) and Progressive Massive fibrosis (PMF). After the passage of the Federal Coal Mine Health and Safety Act (CMHSA) in the late 1960's the prevalence of CWP among US coal miners decreased. However, since the late 1990's a resurgence of lung diseases has been reported, particularly in central Appalachia. On the other hand, dust monitoring data suggest that concentrations of respirable coal mine dust (RCMD) and crystalline silica have been on a downward trend. This contradiction has prompted keen interest in detailed characterization of RCMD to shed light on dust constituents-and their sources. Such information might help miners understand where and under what conditions specific sources contribute to RCMD, and how dust controls and monitoring could be enhanced to mitigate the exposure to respirable hazards.

Respirable dust particles generated in coal mines are generally associated with three primary sources: the coal strata that is mined and generates mostly coal particles that could contribute for lung diseases, the rock strata that is cut along with the coal and generates most of the respirable silica and silicates, and the rock dust products that are the main source of carbonates which could produce respiratory irritations.

Thermogravimetric Analysis (TGA) is one of many analytical tools that might be used for dust characterization. Its primary benefit is that it can be used to apportion the total sample mass into three mass fractions (i.e., coal, carbonates, non-carbonates) which should be roughly associated with the primary dust sources (i.e., coal strata, rock dust products, rock strata) in many coal mines.

This thesis consists of two main chapters: Chapter 1, outlines the research motivation, recaps the efforts to establish a standard TGA method for RCMD, and shows results of the validation experiments that were performed in the current work to enable application of the TGA method to a large set of RCMD and laboratory-generated dust samples. In Chapter 2, 46 lab-generated samples from primary dust source materials collected in 15 coal mines, and 129 respirable dust samples from 23 US coal mines are analyzed using the TGA method validated in Chapter 1. Results for both sets of samples are presented

and the mine samples are interpreted based on sampling location, mining method and region. Additionally, Chapter 3 summarizes recommendations for future work.

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GENERAL AUDIENCE ABSTRACT

The chronic exposure to dust generated in underground coal operations represents a serious health concern among coal miners that can lead to the development of lung diseases such as Coal Workers Pneumoconiosis (CWP or “black lung). Despite of dust compliance monitoring data that have shown that the concentrations of dust have been declining, since the late 1990’s the number of US coal miners diagnosed with lung diseases has been increasing, especially in central Appalachia. This contradiction has prompted keen interest in detailed characterization of respirable coal mine dust (RCMD) to shed light on dust constituents-and their sources. Such information might help miners understand where and under what conditions specific sources contribute to RCMD, and how dust controls and monitoring could be enhanced to mitigate the exposure to respirable hazards.

Thermogravimetric Analysis (TGA) has been proposed as an alternative approach for dust characterization. Its primary benefit is that it can be used to apportion the total sample mass into three mass fractions (i.e., coal, carbonates, non-carbonates) which should be roughly associated with the primary dust sources (i.e., coal strata, rock dust products, rock strata) in many coal mines.

This thesis consists of two main chapters: Chapter 1, outlines the research motivation, recaps the efforts to establish a standard TGA method for RCMD, and shows results of the validation experiments that were performed in the current work to enable application of the TGA method to a large set of RCMD and laboratory-generated dust samples. In Chapter 2, 46 lab-generated samples from primary dust source materials collected in 15 coal mines, and 129 respirable dust samples from 23 US coal mines are analyzed using the TGA method validated in Chapter 1. Results for both sets of samples are presented and the mine samples are interpreted based on sampling location, mining method and region. Additionally, Chapter 3 summarizes recommendations for future work.

ACKNOWLEDGMENTS

First, I would like to express my gratitude to my advisor, Dr. Emily Sarver for her continuous support and valuable guidance throughout the past two years. Her knowledge, commitment, kindness, and insightful feedback pushed me to work hard and pursue my objectives. I am and always will be very grateful to her for this incredible opportunity.

I would like to thank my committee members, Dr, Nino Ripepi and Dr, Setareh Ghaychi Afrouz for their support and valuable comments and recommendations. I would also like to extend special thanks to Dr. Çiğdem Keleş for all her help and support with TGA and data analysis.

I would like to acknowledge Eleftheria Agioutanti who with her kindness and TGA knowledge, patiently walked me through the TGA sample preparation process.

I would also like to thank the National Institute of Occupational Safety and Health (CDC/NIOSH) for supporting and sponsoring this project. Special thanks to the industry partners who graciously provided mine access and support for sampling collection.

I would like to thank Baxter Jones and Sydnie Wilson for their help with dust sample generation.

I would like to thank Nestor Santa, Jonathan Gonzalez, and Nishan Pokhrel for being great friends and research colleagues, for being supportive and helpful. Special thanks to all my friends in Blacksburg who with their uniqueness contributed to everlasting memories.

I would like to thank my mom for all the love and care, for being my driving force, for always being by my side, even in the most difficult moments. My dad for teaching me to work hard and follow my dreams. My sister for all the love, help, and for being my role model. My grandparents, Hernan and Marina for all the love and support throughout these years.

Finally, I would like to thank my husband for being my anchor, for all the love and support, for helping me go through difficult times, for never letting me down, and for always pushing me to see the beauty of life. Honestly, I would not be where I am today without him.

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CHAPTER 1 - RESEARCH MOTIVATION AND APPROACH

1. RESURGENCE OF OCCUPATIONAL LUNG DISEASE AMONG US COAL MINERS

The chronic exposure to respirable dust in coal mines can cause irreversible and debilitating occupational lung diseases such as Coal Workers' Pneumoconiosis (CWP, or "black lung") and silicosis (Antao et al., 2005; Joy, 2012; Suarthana et al., 2011). The diagnosis of lung diseases can vary from classic coal workers' pneumoconiosis (CWP) to progressive massive fibrosis (PMF) (Almberg et al., 2020) which is the most advanced and severe form of disease, and historically has been associated with respirable silica exposure (Hall et al., 2019a; Laney & Weissman, 2014). Numerous studies have shown that PMF may not be associated only to silica but also to mixed dust exposure, including silicates (e.g., Cohen et al., 2016; Jelic et al., 2017).

With the objective of protecting US miner's health, the exposure to respirable coal mine dust (RCMD) has been federally regulated since late 1960's with the passage of the 1969 Federal Coal Mine Health and Safety Act (CMHSA). CMHSA set personal exposure limits and mandated standard sampling and monitoring programs. Additionally, it created the Coal Workers' Health Surveillance Program (CWHSP) which offers voluntary health screenings.

Following the passage of the federal regulation, the prevalence of CWP among coal miners declined (NIOSH, 2008). However, since the late 1990's, health surveillance data have showed a resurgence in the number of miners affected by lung diseases (Blackley et al., 2016, 2018; Hall et al., 2019b; Reynolds et al., 2018). This unexpected uptick is even more perplexing due to the fact that the available dust monitoring data suggest that concentrations of crystalline silica (Agioutanti et al., 2020) and respirable dust (Doney et al., 2019) in coal mines across the US have mostly been on a downward trend.

The prevalence of CWP among US coal miners has been especially characterized by regional hotspots of severe and rapidly progressive forms of disease (Graber et al., 2017). Numerous studies indicate that the most significant hotspot is the central Appalachia region (i.e., including southwest VA, eastern KY and WV) where the resurgence has been particularly alarming since the most severe and progressive forms of disease have been reported (Almberg et al., 2018; Antao et al., 2005; Blackley et al., 2016; Graber et al., 2017; Reynolds et al., 2018) . In fact, in 2018 it was reported that the prevalence of CWP among long-tenured coal miners in central Appalachia exceeded 21% which was the highest level recorded over the past 25 years (Blackley et al., 2018).

2. RESPIRABLE COAL MINE DUST CHARACTERIZATION AND SOURCES

On the basis of the severity and the rapid progression of CWP in central Appalachia, multiple factors could come into play as potential contributors. In general, mines in this region tend to be relatively small in terms of labor force and production (Laney et al., 2012; Laney & Attfield, 2010) which could mean having fewer workers covering a wide range of roles, thus, they could be exposed to more time in dusty environments. On the other hand, in several studies it has been speculated that there is a tendency to exploit thin coal seams in this region (Johann-Essex et al., 2017; Pollock et al., 2010; Sarver et al., 2019). Thin seams require mining significant roof and/or floor rock along with the coal, which might generate an important amount of mineral dust (i.e., respirable silica) (Schatzel, 2009). Likewise, the development and use of more powerful mining equipment to easily cut through rock might have resulted in the increase of the exposure to the mineral fraction (i.e., silica and silicates) of the respirable dust (e.g., Brodny & Tutak, 2018; Cohen et al., 2016; Jelic et al., 2017).

The exposure to high concentrations of respirable silica alone does not seem to completely explain the resurgence of CWP. In fact, in coal mines there are generally considered to be three major sources of respirable dust: rock dust products (often made of calcium carbonate) that are applied to reduce explosibility hazards, the coal seam that is mined, and the roof and/or floor strata that is mined or drilled (NASEM, 2018; Sarver et al., 2019). Rock dusting activities in mines began more than a century ago but over the past decades this practice has increased (Harris et al., 2015). A recent joint survey by MSHA and NIOSH suggested that the use of more powerful technology in underground operations might be generating finer coal particles (Cashdollar et al., 2010) which require the application of more rock dust products that could be significantly contributing to RCMD (Harris et al., 2010, 2015; NASEM, 2018) . Although these products are not known to have associated toxicity, it is possible that they can cause some type of respiratory irritation (CDC, 1995; Khaliullin et al., 2019). The dust produced from the coal strata itself has been considered harmful and a potential contributor to the development of debilitating lung diseases (Beer et al., 2016). Also, it has been suggested that the composition of the coal could play an important role. For example, some preliminary studies have speculated that there is a link between the iron content in the coal and CWP (Huang, 2011; Huang et al., 1999, 2005; McCunney et al., 2009). The rock strata are expected to generate most of the respirable silica and silicates, which have been long considered a key contributing factor in this new era of PMF especially in central Appalachia (Antao et al., 2005; Johann-Essex et al., 2017; Laney & Attfield, 2010; Pollock et al., 2010; Schatzel, 2009).

To shed light on the resurgence of occupational diseases among coal miners and improve exposure monitoring and dust controls moving forward, there is a need to better characterize RCMD and enable dust source apportionment (NASEM, 2018). In fact, little is known in terms of dust characteristics (e.g., particle size, composition) because of routine dust monitoring that only requires total dust mass fraction (mg/m^3) and silica mass fraction (%). The dust source apportionment could help to characterize and understand the major dust sources in the mines. In fact, it could provide valuable information in terms of primary sources of dust in different locations. This might help mine operators determine where and what conditions influence the contribution of different dust sources to RCMD and how dust monitoring and controls may be improved considering the characteristics of the specific locations and/or mines.

2.1 Evolution of Thermogravimetric Analysis (TGA) for RCMD

While many analytical methods can potentially be used for RCMD characterization, they each have benefits and drawbacks (NASEM, 2018). Thermogravimetric analysis (TGA) has been proposed as a favorable method because it is inexpensive, straightforward and allows for a reliable fractionation of the RCMD sample into three main components, which should roughly correspond to three primary dust sources in many coal mines (Scaggs et al., 2015) Briefly, TGA tracks the weight change of a sample under controlled temperature conditions. In general, the coal and the carbonates (i.e., calcium carbonate) tend to lose weight under specific temperature ranges and the non-carbonates (i.e., silica and silicates) seem to show no reaction in this ranges of temperature. Thus, based on the sample weight changes with temperature, the mass fractions of coal, carbonates and non-carbonates can be estimated.

The first attempts to apply TGA to RCMD were by Scaggs et al. (2015). A direct-on-filter TGA approach was considered using samples that were collected on polyvinyl chloride (PVC) or mixed cellulose ester (MCE). However, experimental results showed that due to low masses of dust, the decomposition of the filter might yield inaccurate interpretations of the results. Further analysis showed that other filter media such as polytetrafluoroethylene (PTFE) and polycarbonate (PC) were also inappropriate for a direct-on-filter TGA method.

Thus, further work by Scaggs (2016) turned to a dust-only TGA method with the aim of analyzing a particular set of RCMD samples that had already been collected on PVC and MCE filters. Briefly, the dust was dislodged from the filter by sonication in deionized water; the water was evaporated; and the dust was resuspended in isopropyl alcohol and transferred to the TGA pans to be analyzed following a thermal routine that included specific temperatures to oxidize the coal and decompose the carbonates (Scaggs et al., 2015). Corrections for internal drift, filter residue and premature weight loss for the rock dust were also included.

Phillips et al. (2017) applied the dust-only TGA method by Scaggs (2016) to analyze the aforementioned set of 106 respirable coal mine dust samples. TGA- derived coal, carbonate and non-carbonate mass fractions for each sample were compared with replicate samples that were analyzed using scanning electron microscopy with energy dispersive X-ray (SEM-EDX). In general, the comparison showed a good agreement but, at the same time exposed the influence that the mass of the sample has on TGA results. The outcomes showed a better agreement as the mass increased. On the basis of this finding, Scaggs (2016) and Phillips et al. (2017) realized that the dust recovery from PVC and MCE filters was frequently low which could impact the accuracy of TGA results. Additionally, the fibrous nature of the filters may also interfere with the dust recovery that could not be representative of the entire sample.

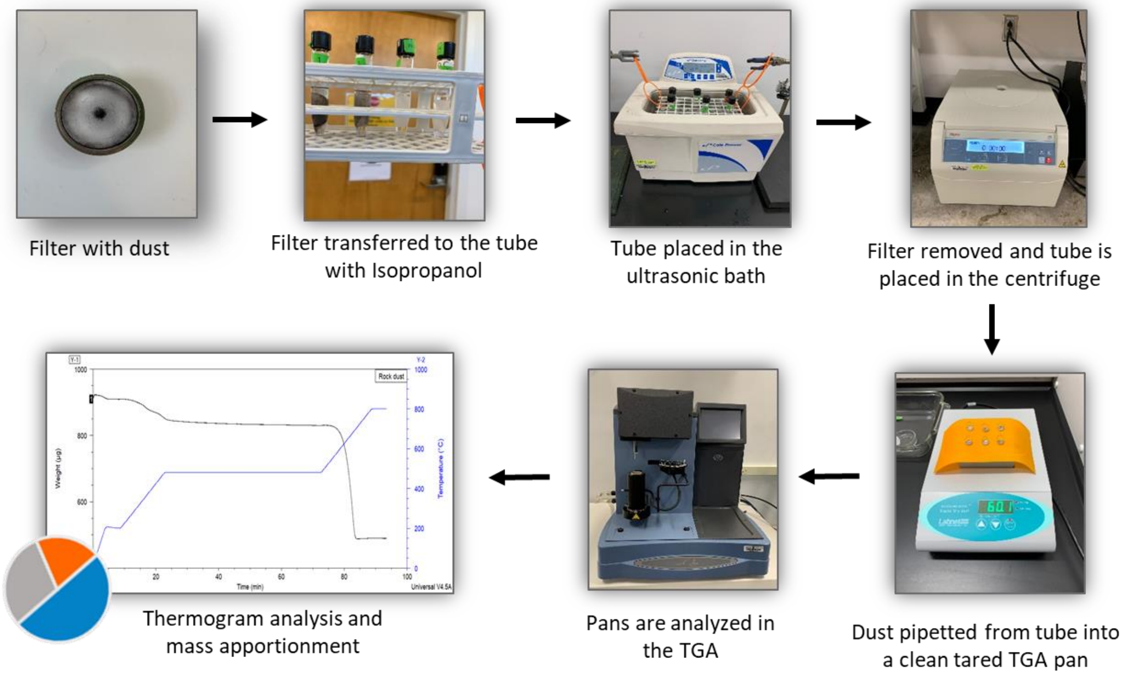
Following the lessons learned, Agioutanti et al. (2020) developed an improved dust-only TGA method for respirable coal mine dust. The aim of this method is still to estimate the mass fractions of coal, carbonate and non-carbonate minerals present in the samples, but it uses samples collected on smooth, non-fibrous polycarbonate (PC) filters that enable more efficient dust recovery and less TGA interference from the filter media. The sample preparation and TGA thermal ramping routine were also modified by Agioutanti et al. (2020).

3. APPLICATION OF TGA TO RCMD IN THIS THESIS

This section describes the improved dust-only TGA method proposed by Agioutanti et al. (2020) which will be used in this thesis for the analysis of lab-generated samples from primary bulk materials and RCMD samples from mines across the US. Some validation analysis and slight changes to the mass balance equations published by Agioutanti et al. (2020) are also discussed.

3.1 TGA Sample Preparation

The TGA sample preparation used here was based on the work of Agioutanti et al. (2020).Figure 1.1 shows the illustrative sample preparation procedure for TGA. First, each filter was carefully rolled dust-side in and placed into a 15 ml clean glass tube with conical bottom, then 5-10 ml of isopropyl alcohol were added to the tube to completely submerge the filter. The tube was placed in an ultrasonic bath for 3 minutes at 30℃ to dislodge the dust. Next, the filter was delicately removed from the tube. After that, the tube was centrifuged for 10 minutes at 2500 rpm to settle the dust. Using a volumetric pipette, the dust suspended in the isopropyl alcohol was pipetted from the glass tube into a clean-tared platinum TGA pan. The pan was placed in a fume hood for the isopropanol to totally evaporate. The last two steps were repeated until no dust could be seen in the tube by using a microscope. A small change was made to the method proposed by Agioutanti et al. (2020) which was to use a hot plate set at 60℃. The pan was placed on top of the hot plate allowing for evaporating faster the isopropanol and decreased the time needed between pipetting. Lastly, the pan with the dust inside was weighed using a microbalance (Sartorius MSE6.6S, Gottingen, Germany) and immediately taken to the TGA instrument to be analyzed. The measurements of the microbalance were recorded and used as a check for TGA derived data.


Filter with dust

Filter transferred to the tube with Isopropanol

Tube placed in the ultrasonic bath

Filter removed and tube is placed in the centrifuge

Dust pipetted from tube into a clean tared TGA pan

Pans are analyzed in the TGA

Thermogram analysis and mass apportionment

Figure 1.1 Illustrative TGA sample preparation procedure

3.2 TGA Instrument and Thermal Routine

As in the previous work by Agioutanti et al. (2020) and Phillips et al. (2017) the TGA method was carried out using a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE). The instrument utilizes a microbalance with 0.1 μg accuracy, and is equipped with an autosampler which permits to run up to 16 samples consecutively. For this work, the number of samples analyzed per run was limited to 8, due to the use of gas cylinders (i.e., air and nitrogen) that needed to be regularly replaced. Within each set, pans 2-7 were used for dust samples and the first and last pans (i.e., pan 1 and 8) were always run empty. Periodically, all 8 pans were run empty to check and correct the internal drift of the instrument.

The aim was to establish a thermal routine for the TGA method which helped to determine temperature regions of interest from which weight loss can be translated into mass fractions of coal, carbonate, and non-carbonate minerals. The thermal routine used in this work was established by Agioutanti et al. (2020) (see Table 1.1) who adapted it from Scaggs (2016). Briefly, three separate regions on which the weight loss occurs are expected to correspond to three separate dust constituents. First, volatiles, moisture and any residue from sample preparation should be lost between ambient and 200℃. Next, coal oxidation will happen between 200-480℃. Finally, decomposition of carbonates (i.e., assumed to be mostly $CaCO_3$) to CO_2 and CaO will occur between 480-800℃. The weight of the pan after the sample run will correspond to the non-carbonate minerals fraction and the CaO obtained from the decomposition of the carbonates.

Table 1.1 TGA thermal routine for respirable coal mine dust (Taken from Agioutanti et at. (2020)).

Region of interest	Thermal step	Temperature (℃)	Description of Sample mass
	Initiate routine in air	Ambient	Initial sample mass
"PC filter"	Ramp 50℃/min to 200℃, isotherm for 5 minutes	Ambient – 200 ℃	Mass loss due to moisture, volatiles, and residue (e.g., from the PC filter) associated with sample preparation
"Coal"	Ramp 20°C/min to 480°C, isotherm for 50 min	200 - 480°C	Mass loss due to coal decomposition, premature CO2 release and secondary PC filter residue oxidation
"CO_2"	Ramp 20°C/min to 800°C, isotherm for 5 min	480 - 800℃	Mass loss due to major CO2 release
	Cool in N_2 for 16 minutes	800℃ – Ambient	Final sample mass (recorded at beginning of step)

3.3 Mass Balance Equations and Corrections

In order to fractionate the mass of the samples into coal, carbonate and non-carbonate minerals based on TGA results, Agioutanti et al. (2020) developed a series of mass balance equations (see *Equations 1.1 to 1.10*). For that, 35 single-material (i.e., coal, rock dust and shale) samples were analyzed and made it possible to establish thermal characteristics of the materials and validate that each material behaved as expected (Figure 1.2 shows representative thermograms for single materials).

CO_2 correction

$$CO_{2\,(2)} = W_{480℃-800℃} \qquad \textit{(Equation 1.1)}$$

$$CO_{2\,(1)} = \frac{39.35\ x\ CO_{2\,(2)}}{269.39 + CO_{2\,(2)}} \qquad \textit{(Equation 1.2)}$$

$$CO_{2\,(Total)} = CO_{2\,(1)} + CO_{2\,(2)} \qquad \textit{(Equation 1.3)}$$

Filter correction

$$F_1 = W_{ambient-200℃} \qquad \textit{(Equation 1.4)}$$

$$F_2 = \frac{28.39\ x\ F_1}{3.24+F_1}\ ^{1} \qquad \textit{(Equation 1.5)}$$

$$F_3 = 5\ \mu g \qquad \textit{(Equation 1.6)}$$

Final mass estimation after all corrections (i.e., internal drift, filter, CO_2 premature release)

$$M_{CaO} = \frac{0.56\ x\ CO_{2\,(Total)}}{0.44} \qquad \textit{(Equation 1.7)}$$

$$M_{Coal\,(F)} = W_{200-480℃} - F_2 - CO_{2\,(1)} \qquad \textit{(Equation 1.8)}$$

$$M_{Carbonates\,(F)} = \frac{CO_{2\,(Total)}}{0.44} \qquad \textit{(Equation 1.9)}$$

$$M_{Non-carbonates\,(F)} = Total\ residue_{@800℃} - M_{CaO} - F_3 \qquad \textit{(Equation 1.10)}$$

Where:

$CO_{2\,(2)} = CO_2\ major\ release\ in\ the\ carbonates\ region\ of\ interest$

$CO_{2\,(1)} = premature\ CO_2\ release$

$F_1 = filter\ residue\ loss\ in\ the\ PC\ region, from\ ambient\ to\ 200℃$

$F_2 = filter\ residue\ loss\ in\ the\ coal\ region, between\ 200 - 800℃$

$F_3 = non\ oxidizable\ filter\ residue\ at\ the\ end\ of\ the\ TGA\ run$

$W_{ambient-200℃} = total\ weight\ loss\ between\ ambient\ and\ 200℃$

$W_{200-480℃} = total\ weight\ loss\ between\ 200 - 480℃$

$W_{480℃-800℃} = total\ weight\ loss\ from\ 480℃\ to\ 800℃$

$Total\ residue_{@800℃} = non\ oxidizable\ materials\ at\ the\ end\ of\ the\ TGA\ run$

$M_{Coal\,(F)} =\ coal\ mass\ fraction\ accounting\ for\ CO_2\ premature\ release\ and\ filter\ correction$

$M_{Carbonates\,(F)} = mass\ fraction\ of\ carbonates$

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[1] This equation was slightly modified from what was initially published by Agioutanti et al. (2020). The explanation is provided in what follows.

$$M_{Non-carbonates\ (F)} = non\ carbonates\ mass\ fraction\ with\ filter\ correction$$

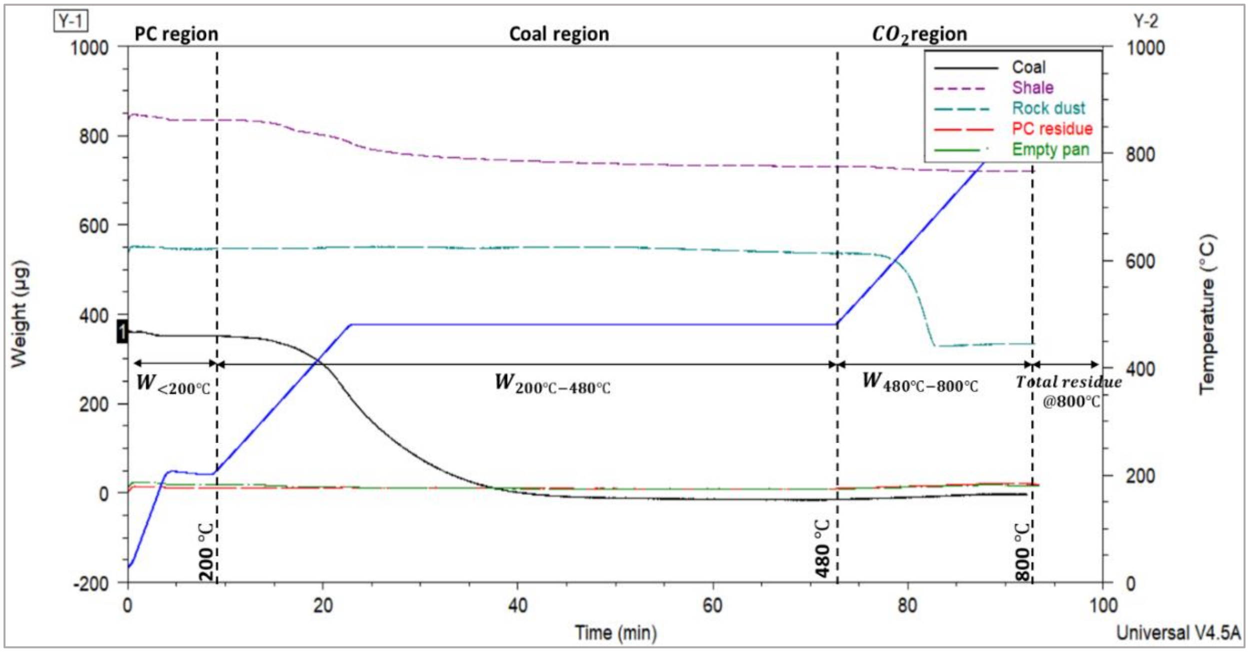

Figure 1.2 Representative thermograms for respirable dust generated from single materials (i.e., coal, shale, and rock dust), empty pans and blank PC filters.

Additionally, some corrections were considered by Agioutanti et al. (2020). As mentioned above, all 8 TGA pans were periodically run empty to correct for internal drift of the instrument. A correction for premature release of CO_2 from the carbonates in the region of coal was also made (*Equations 1.1-1.3*). Finally, corrections for filter and/or any other residue yielded by the dust recovery procedure were also applied (*Equations 1.4 and 1.5*). Briefly, the analysis of filter and any residue showed two weight losses in separate regions; an initial weight loss from ambient to 200℃ and a second weight loss in the coal region (200℃ - 480℃). Agioutanti et al. (2020) used a Langmuir relationship to reasonably predict the weight loss from 200℃ to 480℃ based on the weight loss from ambient to 200℃ .To validate the equations that were established for this correction, analysis on blank PC filters were carried out by replicating procedure established by Agioutanti et al. (2020). Results obtained from the replication of the experiment were compared to those obtained by Agioutanti et al. (2020). The comparison is shown in Figure 1.3.

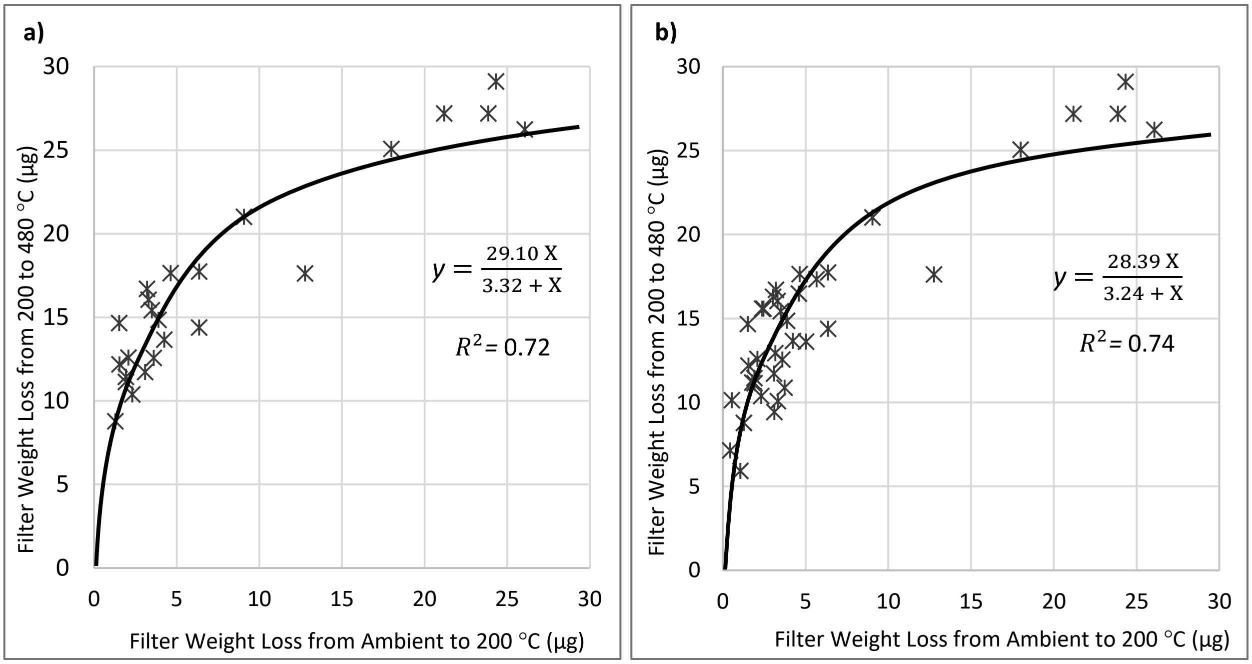

*Figure 1.3 Langmuir relationship between filter weight loss in the ambient-200℃ range and the filter weight loss in the 200℃ - 480℃ range. Plot **a)** is taken from Agioutanti et al. (2020), and shows the 24 samples that were analyzed to estimate the Langmuir relationship; in plot **b)** results from the 24 samples analyzed by Agioutanti et al. (2020) are combined with 14 samples that were recently prepared and analyzed for this work.*

Figure 1.3 shows that in general, the shape of the Langmuir relationship curve did not change between the two-validation analysis. Moreover, the equation and R^2 obtained from both tests were essentially the same. Thereby, to account for previous correction analysis and the validation efforts that were performed here, the combined equation (Figure 1.3 b) (i.e., Equation 1.5, which is slightly modified from Agioutanti et al. (2020)) for filter and/or residue correction was applied to all samples presented in this thesis.

After validating the use of the filter and/or residue correction, further tests were also considered. During the last phase of the experiments by Agioutanti et al. (2020) and to verify the improved TGA method, a set of 36 composite lab-generated samples (i.e., using respirable coal, shale, and rock dust) were analyzed. The mass of the single materials used for each sample was recorded and then compared to those obtained from TGA results after the application of the published equations. Preliminary results showed a good agreement between the expected mass (i.e., the recorded mass of single materials for each sample) and observed mass (i.e., TGA-derived mass after computations). Intending to confirm that by the application of the TGA method, most of the mass balance equations as proposed by Agioutanti et al. (2020) and the modified *Equation 1.5* it is possible to obtain similar results, a total of 18 composite samples were generated and analyzed in this work. Then, they were compared to the results obtained in the previous work. The comparison of both validation tests is shown in Figure 1.4.

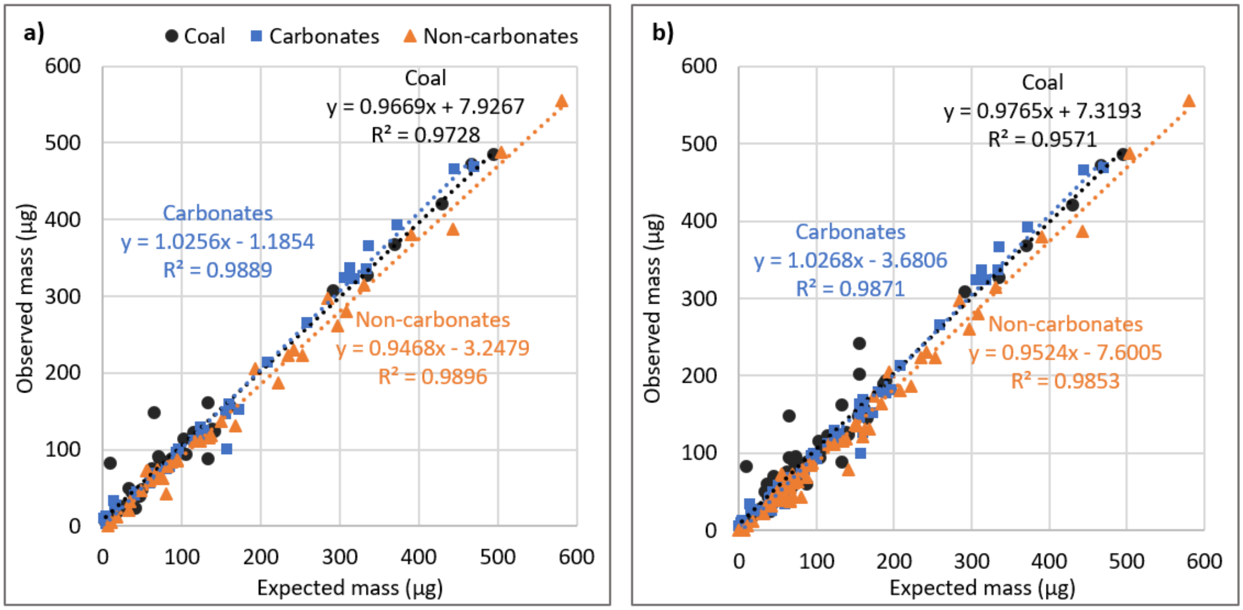

*Figure 1.4 Expected vs observed TGA results in lab-generated composite samples using respirable coal, shale and rock dust. The plot **a)** is taken from Agioutanti et al. (2020), and shows the 36 samples that were prepared and analyzed for validation of the method; in plot **b)** results from the 36 samples analyzed by Agioutanti et al. (2020) are combined with 18 additional samples that were recently prepared and analyzed for this work*

Figure 1.4 shows that the trendline equations for each respirable dust material as well as the R^2 values were essentially unchanged between the two validation experiments. Therefore, it was concluded that the TGA method, and equations proposed by Agioutanti et al. (2020) (with the slightly modified *Equation 1.5*) can be reliably applied.

3.4 RCMD Analysis Included in this Thesis

The above sample preparation, TGA and mass balance computations were used to obtain results on a total of 129 mine dust samples and 46 primary dust source material samples included in this thesis (formally presented in Chapter 2). The first 75 mine dust samples were previously analyzed by Agioutanti (2019) and the remaining 54 mine dust samples and all 46 source material samples were analyzed by the thesis author. It should be noted that the same TGA instrument and software (TA Universal Analysis 2000, version 4.5A) were used to analyze all the samples.

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CHAPTER 2 - THERMOGRAVIMETRIC ANALYSIS OF RESPIRABLE COAL MINE DUST SAMPLES AND RESPIRABLE DUST GENERATED FROM PRIMARY SOURCE MATERIALS

1. INTRODUCTION

Despite all efforts to protect miners' health and after more than thirty years of decline in the number of miners diagnosed with lung diseases, respirable coal mine dust (RCMD) still represents a serious occupational health concern (Antao et al., 2005; Blackley et al., 2016, 2018; Doney et al., 2019; Suarthana et al., 2011). In fact, health surveillance data have shown that the number of miners affected by lung disease has been on an upward trend since the late 1990's (Hall et al., 2019b; Reynolds et al., 2018). The diagnosis of lung diseases among coal miners can vary from classic coal workers' pneumoconiosis (CWP) to progressive massive fibrosis (PMF) which is the most severe form of disease(Almberg et al., 2020; Hall et al., 2019a; Laney & Weissman, 2014). Numerous studies have suggested the exposure to respirable silica and silicates as one of the primary causes of disease.(e.g., Cohen et al., 2016; Jelic et al., 2017).

This new era of CWP has been specially alarming in the central Appalachian region (i.e., including southwest VA, eastern KY and WV) where the most severe forms of diseases have been identified, even among young miners (Almberg et al., 2018; Antao et al., 2005; Blackley et al., 2016, 2018; Graber et al., 2017; Reynolds et al., 2018). Based on the severity and the rapid progression of such disease in central Appalachia, multiple factors could be considered as potential contributors. First, it has been speculated that coal seams in this region are particularly thin which requires mining rock strata along with the coal and might generate a significant amount of respirable silica (Johann-Essex et al., 2017; Pollock et al., 2010; Sarver et al., 2019). Second, mines in this region are generally small in terms of labor force and production which may require fewer workers covering a wide range of roles that could expose them to heavy dusty environments (Laney et al., 2012; Laney & Attfield, 2010). Third, the use of more powerful and mechanized equipment in underground operations to cut thought the rock might increase the exposure to respirable silica and silicates (Brodny & Tutak, 2018; Cohen et al., 2016; Jelic et al., 2017).

Although the exposure to the respirable mineral fraction of the dust (i.e., silica and silicates) has been pointed as the primary culprit for the resurgence of CWP, a recent report from the National Academies of Science, Engineering and Medicine (NASEM) has stated the need to better characterize RCMD components and enable dust source apportionment - so improved sampling and monitoring techniques can be developed (NASEM, 2018).

Overall, in coal mines there are considered to be three primary dust sources: (1) the coal seam that is mined and generates coal particles which are considered a potential contributor to the development of lung disease (Beer et al., 2016; Huang, 2011; Huang et al., 1999, 2005; McCunney et al., 2009) ; (2) the rock strata that is mined or drilled along with the coal, which is supposed to generate most of the respirable silica and silicates (Johann-Essex et al., 2017; Laney & Attfield, 2010; Pollock et al., 2010; Schatzel, 2009). (3) the rock dust products (often made of calcium carbonate) that are used to reduced explosibility hazards and could cause some type of respiratory irritation (CDC, 1995; Khaliullin et al., 2019). Therefore, dust source apportionment could provide valuable insights in terms of major dust sources in specific locations which might help mine operators identify where and under what conditions different dust sources contribute to RCMD, and how dust monitoring and controls could be targeted based on the specific characteristics of the mines and/or locations.

Thermogravimetric analysis (TGA) has been proposed as an approach to characterize RCMD and enable the apportionment of the dust sources. TGA is an inexpensive, quick and straightforward mass-based method that allows for the apportionment of the RCMD into three main dust components (i.e., coal, carbonates and non-carbonates) which could approximate the three major dust sources (i.e., coal strata, rock dust products, rock strata) in many mines(Scaggs et al., 2015). In general, TGA tracks the weight change of a sample under controlled temperature conditions. The coal and carbonates decompose at specific temperature ranges and the non-carbonates (i.e., silica and silicates) are inert at these temperatures which allows for the estimation of mass fractions of coal, carbonates and non-carbonates (Agioutanti et al., 2020; Phillips et al., 2017; Scaggs et al., 2015).

The purpose of this paper is to present TGA results for 46 lab-generated samples from primary dust source materials collected in 15 US coal mines, which are used as proof of concept to demonstrate that most of the mines have three major dust sources such as coal strata, rock dust products, rock strata. Additionally, TGA results for 129 respirable dust samples that were collected in 5 key locations in 23 US coal mines are reported and discussed based on sampling location, mine region, and mining method.

2. MATERIALS AND METHODS

2.1 Mine Details

In this study, field sampling was conducted in 23 underground US coal mines between Summer 2014 and Winter 2020. Fifteen mines were located in central Appalachia (MSHA districts 4,5,7, and 12), four in northern Appalachia (MSHA districts 2 and 3), two in the mid-western Illinois coal basin (MSHA district 8), and two located in the western coal basin (MSHA district 9). Table 2.1 shows key details for all 23 mines included in this study.

Table 2.1 Principal characteristics for 23 mines included in this study.

Mine No	MSHA District	Region [1]	Mining method [2]	Seam thickness (ft)	Total mining height (ft)	Primary rock strata
1	4	CA	CM	3-5	5	Sandstone
2	4	CA	CM	3-4	5.5	Sandstone
3	4	CA	CM	4.5	6	Shale/sandstone
4	4	CA	CM	2-4	4	Sandstone
5	2	NA	LW	6-8	8	Sandy shale/slate
7	12	CA	CM	5-6	6-7	Sandy shale/slate
8	12	CA	CM	4-4.5	6	Shale
10	7	CA	CM	3.33-3.75	5.83-6.25	Shale/sandstone
11	5	CA	CM	2.5	4-4.33	Shale
12	5	CA	CM	2.5-5	6.25-6.67	Shale/sandstone
13	5	CA	LW	5-5.83	5.83-6.67	Sandstone/shale
14	5	CA	CM	2.08-3.33	5-6.25	Shale
15	4	CA	CM	3-3.83	6.5	Shale
16	3	NA	CM	9	7	Shale
17	3	NA	LW	5-5.83	6.67-7.5	Shale
18	3	NA	CM	2.33-2.67	5-5.83	Shale
19	8	MW	CM	5.83-6.67	6.25-7.5	Shale/limestone
20	8	MW	CM	5.83-6.25	5.83-6.67	Shale/limestone
21	12	CA	CM	2.5-3.33	6.5	Shale/sandstone
22	12	CA	CM	2.5	4.58	Shale
23	9	W	LW	14	14	Shale
24	9	W	LW	6	7-8	Shale/sandstone
25	12	CA	CM	3	8	Shale/sandstone

[1] CA: central Appalachia, NA: northern Appalachia, MW: mid-western Illinois coal basin, W: western coal basin

[2] LW: longwall, CM: continuous miner

2.2 Mine Dust Sampling

Table 2.2 shows the respirable mine dust samples included in this study, which were collected in five key locations: intake (in the fresh airways, upstream of any bolting or mining activities), return (in the exhaust airway, including downwind of ventilation tubing exhaust where present), production area (just downwind of an active continuous miner, or on the longwall face), roof bolter (just downwind of an active roof bolter), and feeder (adjacent to the feeder breaker, or along the main conveyor belt). A general schematic representation of these locations is shown in the Appendix, Figure A.1). An effort was made to sample each location in each mine, however this was not always possible (e.g., based on activities at the mine during sampling or limited time during the mine visit). Moreover, in some mines, multiple samples were collected in some of the locations during different sampling events (e.g., on different shifts or days during the mine visit). In total 112 sampling events were carried out, which represent 101 unique sampling locations (mine x location).

Table 2.2 Number and location of RCMD samples and primary dust source materials included in this study.

Mine number	RCMD samples						Dust source materials				
	Sampling locations[1]					Total sets	Material[2]				Total sets
	I	R	P	B	F		RD	C	RS		
									RR	BD	
1	1	1	1	1	1	5					
2	1	1	1	1	1	5					
3	1	1	1	1	1	5					
4	1	1	-	1	1	4					
5	2	2	1	1	2	8					
7	1	1	1	1	1	5					
8	1	2	2	1	1	7					
10	1	1	1	2	2	7	-	-	1	1	2
11	-	1	1	1	1	4	1	-	1	-	2
12	1	1	-	1	1	4	1	1	1	-	3
13	2	1	1	1	1	6	1	1	-	1	3
14	1	-	1	1	1	4	1	1	1	1	4
15	1	1	1	1	1	5	1	1	1	-	3
16	-	1	1	1	1	4	1	1	-	1	3
17	2	2	1	1	-	6	1	1	-	1	3
18	1	1	1	1	1	5	1	1	1	1	4
19	1	2	1	1	1	6	1	1	1	1	4
20	1	1	1	1	2	6	1	-	-	1	2
21	1	1	1	1	1	5	-	1	1	1	3
22	1	-	1	-	1	3	1	1	1	1	4
23	3	1	-	-	-	4	1	1	1	1	4
24	3	2	-	-	1	6	1	-	-	1	2
25	1	4	8	1	1	15	-	-	-	-	-
Total	28	29	27	21	24	**129**	13	11	10	12	**46**

[1] I: intake, R: return, P: production, B: bolter, F: feeder

[2] RD: rock dust, C: coal, RS: rock strata (i.e., bolter dust (BD) and/or run-of-mine rock (RR))

All mine dust samples were collected by the research group members using standard equipment and materials obtained from Zefon International (Ocala, FL). Sampling equipment included Escort ELF pumps at a flow rate of 2 L/min equipped with 10 mm Dorr-Oliver cyclones. The cyclone discards particles larger than 10 µm and yields a d_{50} of about 3.5 µm, consistent with requirements for compliance sampling in US coal mines. Respirable dust was collected directly onto polycarbonate (PC) filters (37-mm, track-etched with nominal 0.4-µm pore size), which were housed in two-piece styrene cassettes.

2.3 Primary Dust Source Materials

In addition to the respirable dust samples, from 15 of the mines, a total of 46 bulk samples of primary dust source materials were collected including: run-of-mine (ROM) material, which was pulled from the production belt and later separated into coal and rock; material taken directly from the dust collection system of the roof bolter; and samples of rock dust products, taken from the duster bin or new product sacks. These materials were used to represent the coal (C), rock strata (RS, from the run-of-mine (ROM) rock and roof bolter dust), and rock dust (RD) product sources contributing to the respirable dust fraction during mine sampling. Table 2.2 shows the source materials available for each mine.

It should be noted that, since the bulk dust source materials were collected directly in the mining operation, they were expected to include some impurities. Specifically, coal materials were expected to contain a fraction of non-carbonate minerals, the rock strata materials should contain some coal and perhaps carbonates, and the rock dust products should contain small fractions of non-carbonate minerals.

Samples of respirable dust were generated from each of the 46 primary dust source materials in the laboratory under controlled conditions. The roof bolter dust and rock dust products did not require pre-processing since they were already a powder. However, the ROM coal and rock materials were pulverized and sieved to -230 mesh (-63µm) in the laboratory prior dust sample generation. For each material, a small mass of the bulk powder was loaded into a sealed enclosure and was made airborne by applying compressed air pulses during sample collection. The aforementioned sampling equipment (pump and cyclone) was used to collect the respirable-sized dust onto the same PC filters used for the mine dust sampling. During sample collection, the target weight was about 800 -1500 µg to make it significant for the TGA experiments. Sample mass was estimated by weighing the filter before and after dust loading using a microbalance (Sartorius MSE6.6S, Gottingen, Germany).

2.4 Dust Sample Analysis

TGA samples were prepared and analyzed using the method proposed by Agioutanti et al. (2020) that is described in Chapter 1. Briefly, each PC filter was placed inside a 15 ml clean glass tube and submerged in 5-10 ml of isopropyl alcohol (IPA). The tube was placed in an ultrasonic bath at 30℃ for 3 minutes. Next, the filter was carefully removed and the tube was centrifuged to settle the dust. After that, the dust suspended in Isopropanol was pipetted into a clean tared TGA pan. When no dust could be seen in the tube and the evaporation of the Isopropyl alcohol was completed, the pan with the dust inside was weighed using a microbalance to determine the amount of dust. Finally, the pan was taken to the TGA to be analyzed.

In general, the dust masses recovered from mine samples were lower than the masses from the bulk materials. This occurred because the bulk materials were collected in the laboratory under controlled conditions and with specific target weights (i.e., 800-1500 µg).

For each sample, the TGA output was a thermogram; representative thermograms for several mine dust samples and dust samples generated from dust source materials are shown in Figure 2.1 and Figure 2.2, respectively. In the thermograms, the weight loss obtained in each specific temperature region was recorded and the coal (200-480℃), carbonate (480-800℃), and non-carbonate mineral (at 800℃) fractions were estimated using most of the mass balance equations as proposed by Agioutanti et al. (2020) and the modified Equation 1.5 that are presented in chapter 1.

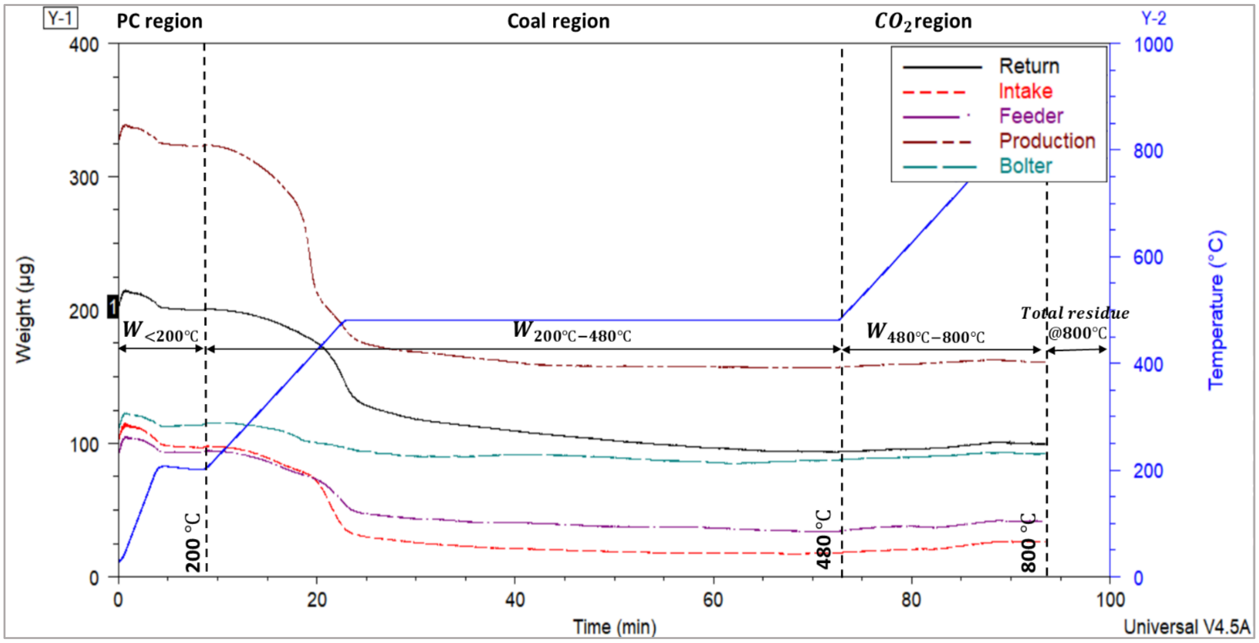

Figure 2.1 Representative thermograms of RCMD samples collected in the 5 key locations (i.e., return, intake, feeder, production, bolter) from mine 1.

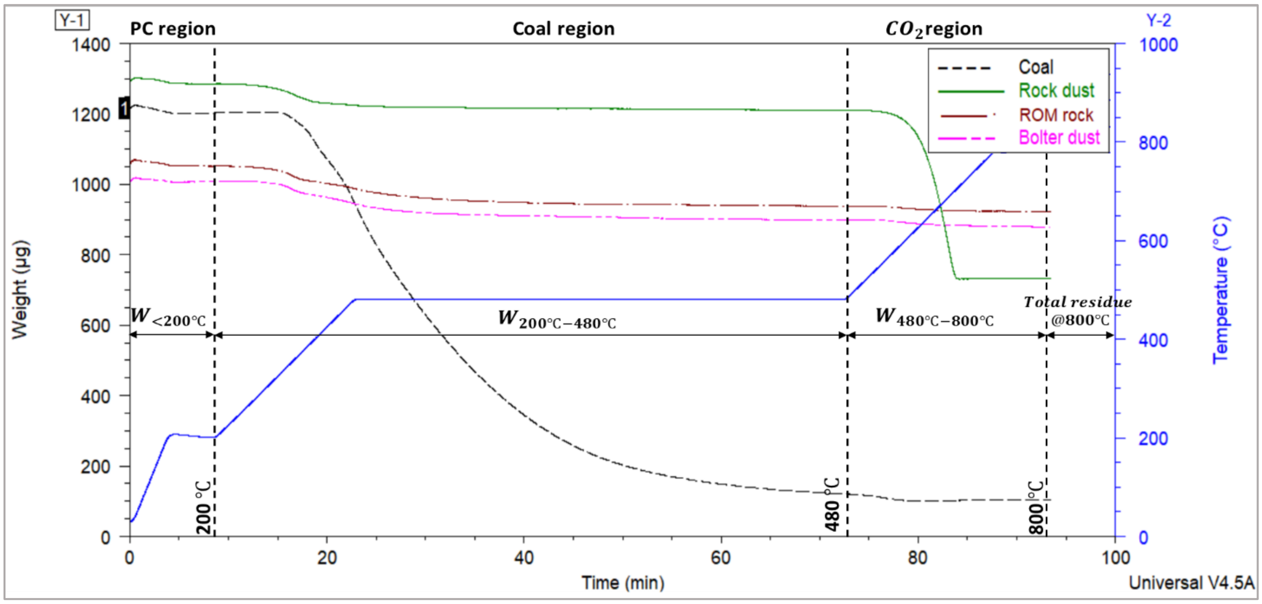

Figure 2.2 Representative thermograms of the primary dust source materials (i.e., coal, rock dust, ROM rock, bolter dust) from mine 14.

2.5 Data Analysis

For the mine dust samples, results were grouped based on sampling location, mine region and mining method to evaluate trends. In cases where multiple samples were collected in a single location for a given mine, the TGA results for these samples were averaged to yield a single set of results for each unique location. This was done to avoid biasing analysis toward mines with multiple samples. Thus, the 129 individual mine dust samples shown in Table A.2 were reduced to represent 101 unique locations.

To statistically test for significant differences in terms of mass fraction (coal, carbonate, non-carbonate), the mine dust sample results were grouped as follows: sampling location (I, R, P, B, F), mine region (central Appalachia, outside of central Appalachia), and mining method (continuous miner, longwall). One-way analysis variance (ANOVA) was conducted to the aim of comparing between group means. The null hypothesis was defined as no significant difference between means, and decisions were made using a confidence level of 90% (i.e., $\alpha = 0.1$), meaning that a p-value < 0.1 indicates a significant difference between means. For this analysis, the following assumptions were checked: population distribution is approximately normal, and residuals have constant variance. In some cases, the distribution of the residuals was not normal and logarithmic transformations were applied to the data.

The statistical analysis of the mine dust samples was performed in two iterations. First, all sample results were included regardless of the dust sample mass recovered for TGA. Then, the analysis was repeated only for samples with recovered dust mass > 55 µg (n = 69). This threshold was established based on the work by Agioutanti et al. (2020) which showed that accuracy of the TGA method decreases with particularly small sample masses. The 55µg threshold was chosen to limit the influence of small samples on the analysis, while preserving relatively many results (i.e., 75%).

3. RESULTS AND DISCUSSION

3.1 Dust Source Materials

TGA results for the samples generated from dust source materials were used as proof of concept, i.e., to demonstrate whether material compositions followed expectations. Figure 2.3 shows the TGA results for all 46 respirable dust samples generated from the bulk source materials (i.e., ROM coal, ROM rock, roof bolter dust, and rock dust products), and the data are tabulated in Table A.1 in the appendix. Additionally, representative thermograms for all samples are shown in the appendix, from Figure A.2 to Figure A.5.

As expected, the respirable samples generated from all 13 rock dust products represented in this study showed high fractions of carbonates. On average, the carbonate mass fraction in these samples was > 90% (± 3%), and most of the balance was attributed to non-carbonate minerals.

Results for the 11 samples generated from raw coal showed that the coal mass fraction was on average 76% (± 10%). For 7 of these samples, the non-coal fraction was dominated by non-carbonate minerals. This is consistent with expectations of small fractions of impurity from the rock layers surrounding the coal seam and could be explained by multiple contributing factors. One factor could be the nature of the formation of the rock and coal layers that makes it difficult to completely separate them. Another likely factor is the size of the non-coal components when the coal is pulverized which might be concentrated in the finer size fraction.

For the other four coal materials (mines 13, 15, 21, and 22), results showed a relatively high fraction of carbonates (> 20% on average). However, after an examination of the thermograms for these four samples (Figure A.3 in the appendix) it was evident that the coal was not completely oxidized in the expected region (200-480℃); instead there was still coal to be oxidized in the "CO_2 region" (480-800℃). Thus, the TGA misclassified a fraction of the coal as carbonates. This finding was somewhat unexpected and a possible contributing factor is the temperature of oxidation for the coal. It could be that those 4 samples have low volatility and different properties – so they required higher temperatures for combustion as mentioned by Kök (2005) Replicate samples of all 11 coal materials were also analyzed by two other analytical methods (i.e., scanning electron microscopy with energy dispersive X-ray, SEM-EDX, and Fourier transform infrared spectroscopy, FT-IR) and both showed low carbonates compared to the TGA (Pokhrel et al., 2021).

Results for what is termed rock strata are divided into two groups, ROM rock and bolter dust with 10 and 12 samples analyzed, respectively. Results of the ROM rock samples included in this analysis showed that the mass of the sample was primarily dominated by the presence of non-carbonate minerals (> 75% on average (± 12%)). A fraction of impurities, mostly coal was also identified. Such results were also consistent with expectations, and may be explained by the nature of the geological formation of the strata that make perfect separation between coal and rock layers difficult. Moreover, the samples were generated from raw rock that was hand-picked from the ROM material along with the coal.

As expected, 10 out of 12 bolter dust samples showed that the non-carbonate mass fraction was dominant (> 80% on average (± 5%)). Thus, the remaining 20% was coal and carbonates. Even though both the ROM rock and the bolter samples showed coal impurities (Figure 2.3), the coal impurity was lower in the bolter samples. It could be explained by the fact that in most of the mines the roof bolting activity involves primarily drilling into the rock. It should be mentioned that the bolter dust results for mines 19 and 20 were quite different, containing very high carbonate content (60% and 83%, respectively) rather than non-carbonate minerals. This is explained by the fact that the rock strata in those mines is described as a thin layer of shale directly above the coal seam, with much thicker limestone above the shale (see Table 2.1).

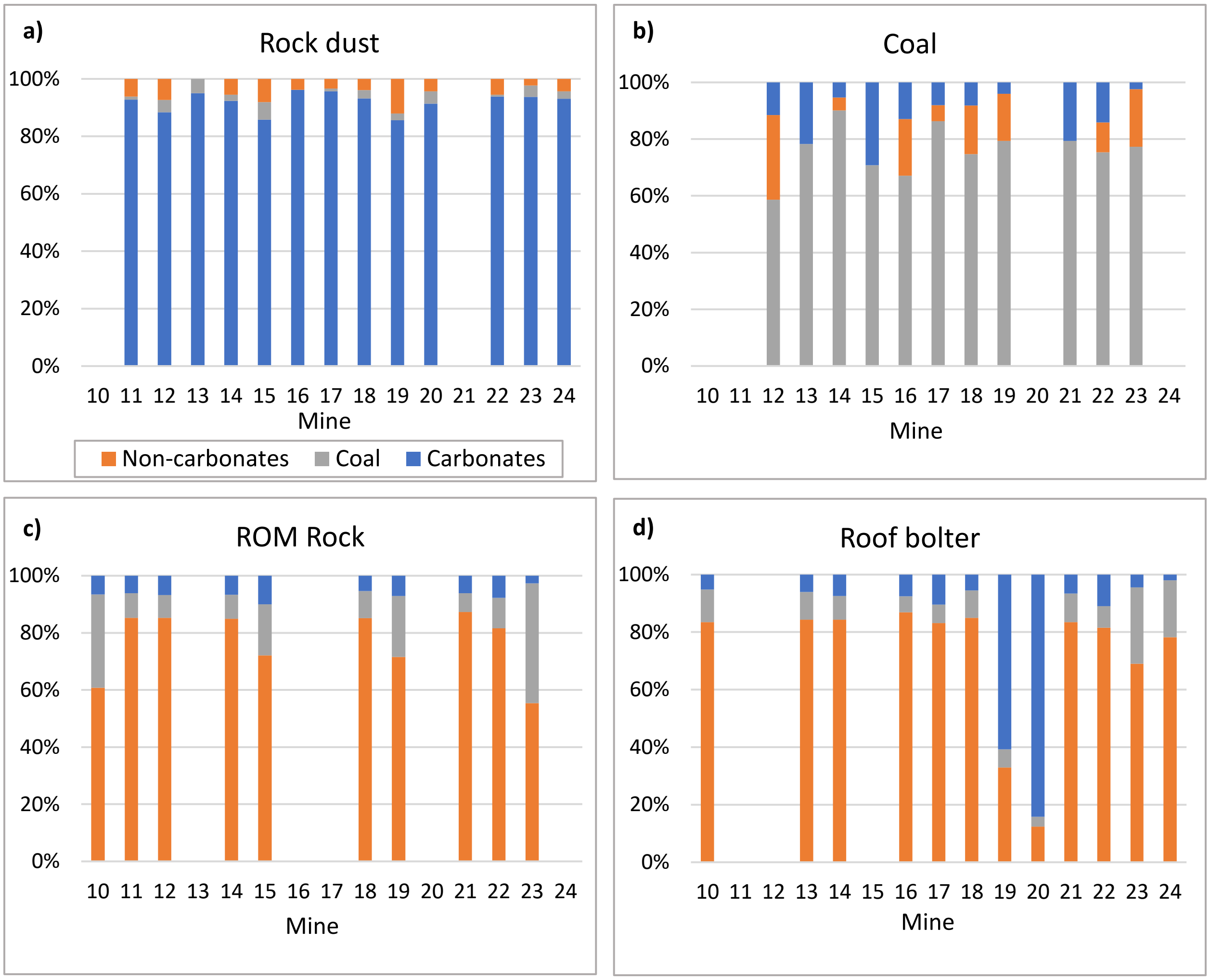

Figure 2.3 TGA-derived results for all 46 dust source materials by mine. ***a)*** *rock dust,* ***b)*** *coal,* ***c)*** *ROM rock, and* ***d)*** *bolter*

Although the materials analyzed above were not completely pure, it was always the case that the component which was expected to represent the largest mass fraction of the sample was certainly dominating. That is, for rock dust samples the carbonate mass fraction was dominant, for coal samples the coal fraction was the largest one, and for ROM rock and bolter dust samples the non-carbonate mass fraction was the most significant. This demonstrates that the TGA approach to source dust apportionment is reliable.

Overall, the results obtained from the characterization of the dust source materials support the notion that the TGA-derived mass fractions can be used to assess major respirable dust sources for most of the mines included in this study. Namely, coal should primarily be associated with the coal seam being mined, carbonates should be associated with the application of rock dust products to the mine surfaces, and non-carbonate minerals should be associated with the rock strata being mined along with the coal seam or drilled during roof bolting activities.

3.2 Respirable Coal Mine Dust Samples

Table A.2 (Appendix A) summarizes the TGA results for all 129 mine dust samples. For the presentation of results and statistical analyses presented below, the sample number was reduced in three steps: (1) Based on the predominance of limestone rock strata in mines 19 and 20, which might confound efforts to reliably apportion carbonate to its source, results from respirable dust samples collected in these mines were excluded. (2) As previously described, in instances where multiple samples were analyzed from a particular location in the same mine, the results were averaged to yield a single mine x location result. (3) Samples with recovered dust mass <55 μg were excluded. The first two steps reduced n = 129 to n = 91 for an initial iteration of statistical analysis (results are presented from Figure A.6 to Figure A.8 and from Table A.3 to Table A.5 in the appendix); and the last step reduced to n = 69.

Figure 2.4 shows the mass fractions of coal, carbonate and non-carbonate by sampling location following all three data reductions (i.e., total n = 69). From the figure, a few key observations can be made. First, the feeder (F) and intake (I) samples seemed to have the highest coal fractions. Second, return (R) samples showed the highest mass fraction of carbonates. Third, production (P) and bolter (B) samples presented the highest fractions of non-carbonates.

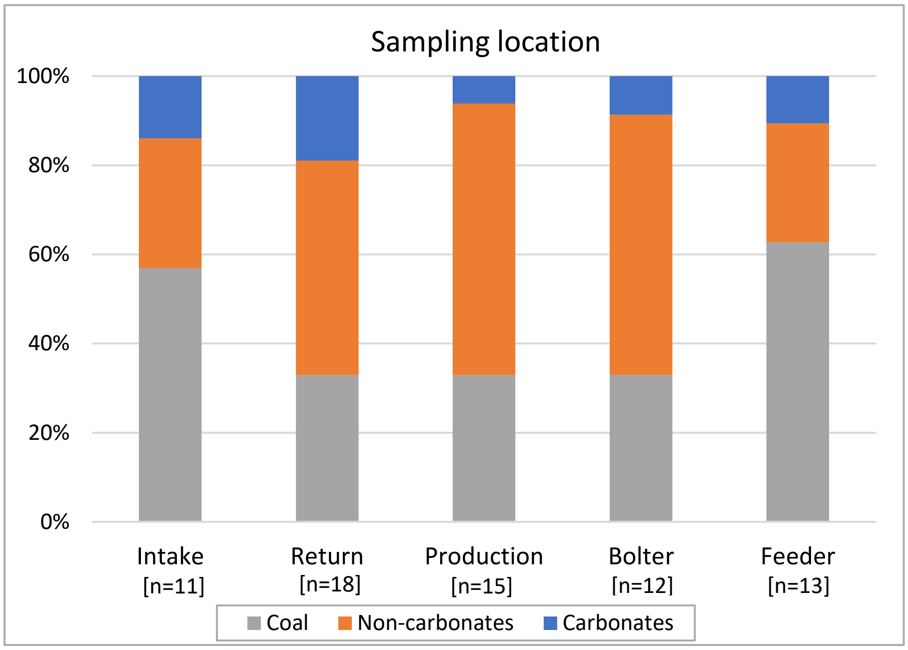

Figure 2.4 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location.

TGA results of F samples were consistent with expectations and findings by Phillips et al. (2017) based on TGA to estimate coal and non-coal mass fractions in dust samples collected in 8 mines in central Appalachia, and Johann-Essex et al. (2017) based on particle mineralogy distributions. Near the feeder, raw coal is being crushed and dropped onto a conveyor belt, these activities might generate or make airborne coal dust. This suggests the coal strata itself as the primary dust source. Regarding I samples, again the results were consistent with expectations. Although this location is supposed to carry the fresh air, and dust concentrations are generally quite low, multiple contributing factors could help to explain the presence of coal. In general, samples from this location exhibited the lowest mass (9 out of 11 were < 200 μg),which as previously mentioned might interfere with the accuracy of the TGA mass fractionation. Another possible factor is the presence of diesel particulates in the samples which could be misclassified as coal by the TGA (21 out of 23 mines were using diesel equipment). In fact, a study by Sarver et al. (2019) suggested that I samples collected in different underground coal mines, were generally dominated by diesel particulates on the basis of particle number fraction. Notably, the samples from mines 19 and 20 collected in these locations (F and I) did not show similar trends. For F samples, the mass fractions of coal and noncarbonates were dominant, however, the difference between them was not significant enough to consider the coal seam as the primary source. Regarding I samples the mass fractions of carbonates and non-carbonates were the most significant and the coal < 10%. As previously discussed, for these two mines is not possible to presume a specific source of the carbonates.

The relatively high carbonate mass fractions observed in R samples are consistent with the previous TGA results by Phillips et al. (2017) on which samples from central Appalachia were analyzed. Results suggested that rock dust products contribute significantly to the RCMD concentrations in return airways compare to other locations. It seems reasonable since the return receives dust transported from all other locations in the mines where rock dusting activities are probably carried out, also, it is possible that in these locations intensive rock dusting activities take place. Additionally, the non-carbonates seemed to notably contribute to RCMD, which could be attributed to the mineral dust that is generated in production areas where a lot of rock could be cut along with the coal, and eventually might be transported to the return. Such findings are similar to those presented by Johann-Essex et al. (2017) based on particle size and mineralogy distribution. Results for R samples collected in mines 19 and 20 showed similar results regarding non-carbonates (especially in mine 20). However, the mass fractions of carbonates were comparatively low < 12%.

The highest non-carbonate fractions were seen in the B and P locations, which is also consistent with expectations since a lot of rock could be mined and drilled during mining and bolting activities. Similar results were presented by Johann-Essex et al. (2017) based on particle mineralogy distribution. Thus, it is likely that a primary source of RCMD is the rock strata. On the other hand, samples from these locations appeared to have relatively low coal mass fractions. This is expected for B samples since bolting activities primary drill into roof rock, but it is somewhat surprising for P samples that were collected near active production. Nevertheless, Phillips et al. (2017) presented similar findings for samples collected in production areas of 8 underground coal mines in central Appalachia. B and P samples from mine 20 showed similar results (high non-carbonates, low coal). Nevertheless, samples from mine 19 showed the opposite, high coal and low non-carbonates.

Results of the ANOVA and Turkey-Kramer HSD performed to identify statistical differences between the sampling locations in terms of mass fractions (i.e., coal, carbonate and non-carbonate) are presented in Table 2.3. In general, these results confirm the ideas discussed above: F and I locations had higher fractions of coal than the rest of locations, the highest carbonate fraction was identified in R samples, and P and B locations had the highest non-carbonate fraction and low coal mass fractions. The same statistical analysis was done for n=91. The results are presented in the appendix (Table A.3). In general, the results were similar to those obtained for n=69, except for the carbonate fraction on which a significant difference between sampling locations was not identified.

Table 2.3 Summary statistics comparing fractions of coal, carbonates and non-carbonates by sampling location

All unique locations (n=69)			
Dust constituent	Overall P-value	Specific P-value Tukey-Kramer HSD	Mean difference (%)
Coal	< 0.0001	0.0008	F > R
		0.0029	F > B
		0.0015	F > P
		0.0176	I > R
		0.0386	I > B
		0.0264	I > P
Carbonates	0.0381	0.0289	R > P
Non-carbonates	0.0002	0.0016	P > F
		0.0066	B > F
		0.0065	P > I
		0.0206	B > I
		0.0730	R > F

I = intake, R = return, P = production, F = feeder, B = bolter

In addition to investigating differences in TGA results with respect to sampling locations, results were analyzed with respect to mine region and mining method. For the regional analysis, mines were grouped as either being in central Appalachia or elsewhere (i.e., northern Appalachia, mid-western Illinois coal basin or western coal basin).Figure 2.5 shows the mass fractions of coal, carbonates and non-carbonates by mine region and sampling location (again, total n = 69). The ANOVA results comparing the fractions of coal, carbonates and non-carbonates between sampling locations by mine region are presented in Table 2.4.

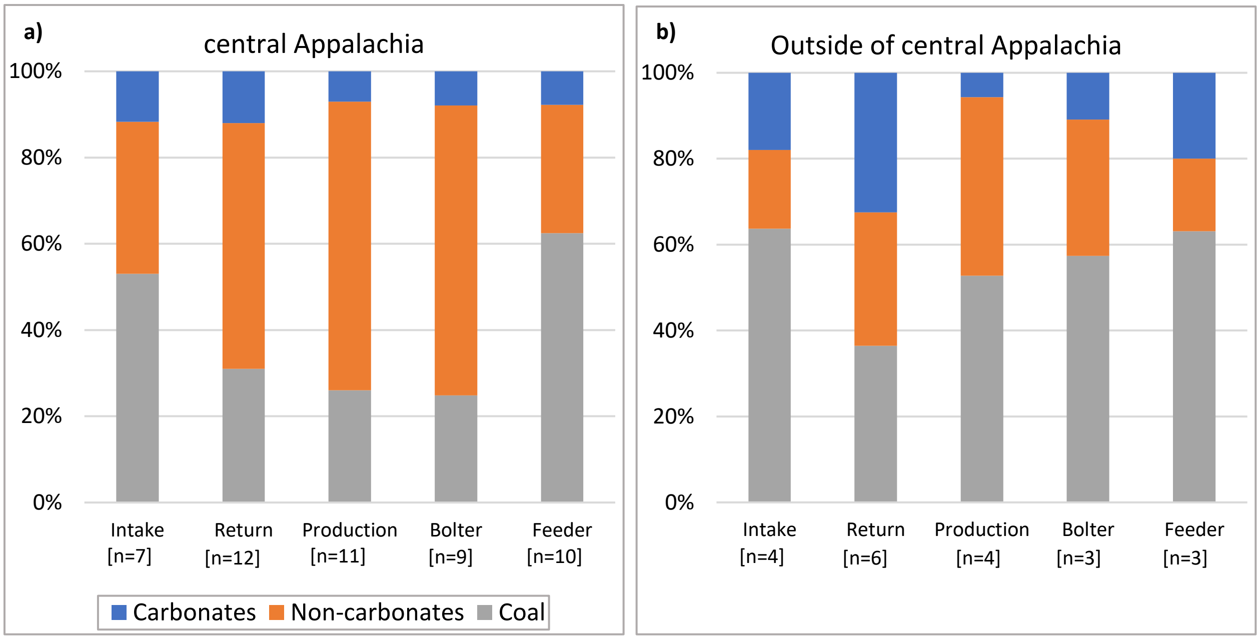

*Figure 2.5 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location for mines **a)** in central Appalachia and **b)** outside of central Appalachia*

Table 2.4 Summary statistics for comparison of mean mass fractions of coal carbonates and non-carbonates between sampling locations by mine region

central Appalachia vs outside of central Appalachia										
	Intake (n=11)		Return (n=18)		Production (n=15)		Bolter (n=12)		Feeder (n=13)	
	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference
Coal	0.4731	-	0.5357	-	0.0361	CA < O	0.0074	CA < O	0.9541	
Carbonates	0.3952	-	0.0112	CA < O	0.9636	-	0.4025	-	0.0506	CA < O
Non-carbonates	0.2520	-	0.0302	CA > O	0.0190	CA > O	0.0089	CA > O	0.3679	

CA= central Appalachia, O= outside of central Appalachia

In general, samples from central Appalachia showed higher fractions of non-carbonates than the samples from outside of central Appalachia, where fractions of coal and carbonates are relatively higher (see Figure 2.5). Such results are consistent with expectations since it has been speculated that thin-seams mining in central Appalachian generates more dust sourced from the rock strata surrounding the coal seam, which should typically be dominated by non-carbonate minerals such as silicates and silica (Johann-Essex et al., 2017; Pollock et al., 2010; Sarver et al., 2019; Schatzel, 2009). Moreover, these results are generally supported by observations during mine dust sampling. The relative height of rock being mined with the coal tended to be higher in central Appalachia (see Table 2.1) and, anecdotally, rock dusting activities were often more prevalent in the mines outside of central Appalachia.

Overall, samples from mine 19 showed high coal, whereas samples collected in mine 20 showed high non-carbonates. For both mines the mass fraction of carbonates was consistently low, except for I samples. In this sampling location the carbonates represented 49% for mine 19 and 63% for mine 20. Such results are not consistent with expectations since these two mines are located outside of central Appalachia where the coal is expected to represent a significant mass fraction of the RCMD, and the carbonates are supposed to contribute significantly to RCMD given the geology of the roof rock in these two mines.

Table 2.4 shows ANOVA results for comparison of data presented in Figure 2.5. As discussed above, central Appalachian samples tend to show higher fractions of non-carbonates which is specifically evidenced in P, B, and R locations. This makes sense with expectations since in the two first locations is where the cutting and drilling of rock takes place. For the R locations, it could be explained by the fact that dust produced in all other areas of the mine should be transported to the return airways-so dust from the rock strata might be produced in the P and B locations and transported to the R. Accordingly, it could be said that the primary source of RCMD in these locations in central Appalachia is the rock strata. Regarding samples from outside of central Appalachia, P and B locations presented higher fractions of coal as expected. The coal seams are thicker and are supposed to be the main source of dust; it is also likely that roof bolting not only involves drilling into the roof rock but also into some coal. Moreover, F and R samples outside of central Appalachia presented higher fractions of carbonates that again may be explained by the application of more rock dust products that contribute significantly to the RCMD. Table A.4 in the appendix presents the same statistical analysis for n=91. Overall, the results were similar to those obtained for n=69. However, for the B samples, there was no significant difference for the coal fraction, and for the F samples significant difference concerning the carbonate fraction was not identified.

To analyze the TGA results with respect to mining method, samples were grouped as either originating from a continuous miner or longwall operation. Figure 2.6 shows the mass fractions of coal, carbonate and non-carbonate minerals in different sampling locations by mining method (again, total n = 69). Also, the ANOVA results comparing the coal, carbonate and non-carbonate mass fractions between locations and by mining method are presented in Table 2.5.

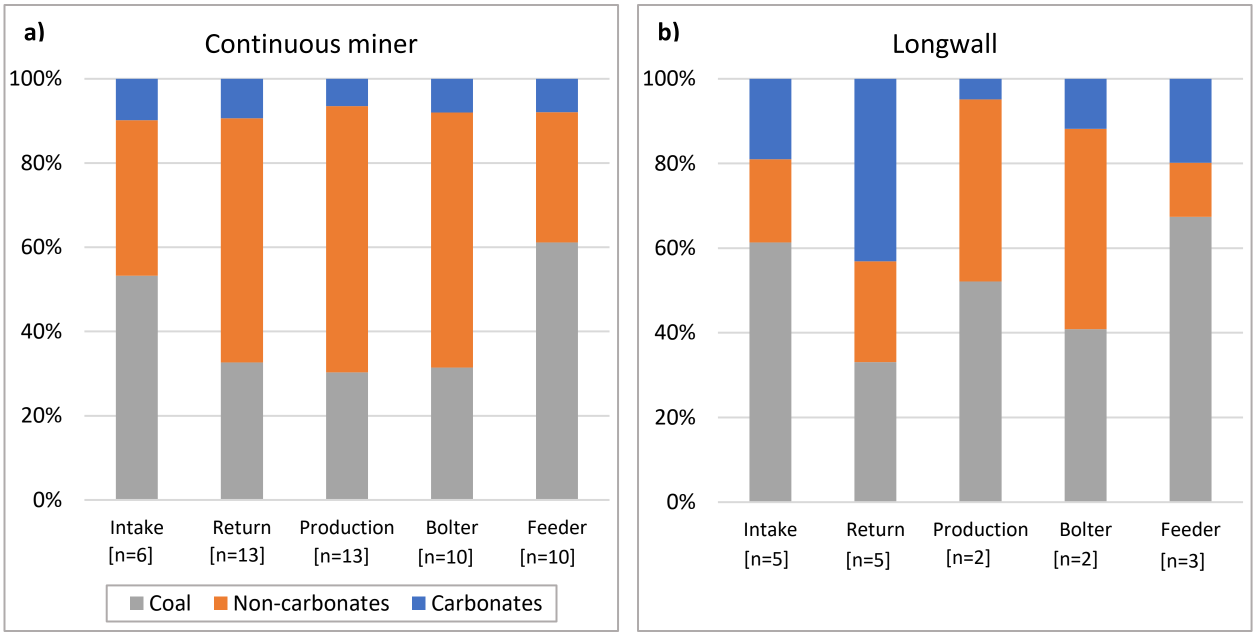

Figure 2.6 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location per mining method ***a)*** *continuous miner and* ***b)*** *longwall.*

Table 2.5 Summary statistics for comparison of mean mass fractions of coal carbonates and non-carbonates between sampling locations by mining method.

continuous miner vs longwall										
	Intake (n=11)		Return (n=18)		Production (n=15)		Bolter (n=12)		Feeder (n=13)	
	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference
Coal	0.5694	-	0.9113	-	0.1643	-	0.5676	-	0.6534	-
Carbonates	0.1861	-	< 0.0001	CM < LW	0.8755	-	0.3521	-	0.0609	CM < LW
Non-carbonates	0.2242	-	0.0042	CM > LW	0.2182	-	0.4719	-	0.1989	-

CM= continuous miner, LW= longwall

These outcomes were generally similar to those obtained when comparing by mine region since the majority of the mines (14 out of 15) in central Appalachia are continuous miner operations, and most of the mines outside of central Appalachia are longwall operations (4 out of 6). It is noteworthy that the major statistical differences (see Table 2.5) were found in the R and F locations. In continuous miner operations the rock strata dust contribution (i.e., primary source of non-carbonates) to RCMD appeared to be the most significant in R locations whereas, for the longwall operations, the fraction of carbonates that might be primarily sourced from the rock dust seemed to represent an important fraction to RCMD in the F and R locations. Moreover, although the difference between group means for P locations was not sufficient to identify statistically significant differences, it is notable that in continuous miner operations the primary source of dust in this location might be the rock strata that contributes significant non-carbonates to RCMD, while, for the longwall operations the coal strata (i.e., primary source of coal) seemed to be the main source of RCMD. The same statistical analysis was done for n=91 (Table A.5 in the appendix). The results were generally similar to those obtained for n=69, except for the B samples on which a significant difference for the carbonate fraction was observed.

Although mines 19 and 20 are both continuous miner operations, where the mass fractions of non-carbonates were consistently high, TGA results for mine 19 showed that the mass fractions of coal were in general high, except for the I location (non-carbonates were dominant). On the contrary, mine 20 showed high fractions of non-carbonates and notably the obtained fractions of carbonates were not consistent with expectations given the geology of the roof strata.

Overall, results on mine dust samples showed high mass fractions of non-carbonates, suggesting that the rock strata contribute significant respirable dust in many locations. To gain further insight, a comparison was made between the dust mass fractions and observed strata heights for samples collected in the P location (n = 16, excluding samples from mines 19 and 20). In this location, dust is expected to be dominated by the particles being generated by coal and/or rock cutting. Thus, a direct comparison can be made between the coal/(coal + non-carbonates) in the respirable dust and the coal seam thickness/total mining height (Figure 2.7). Additionally, TGA - results for the samples generated from bulk coal (presented in section 3.1) showed that the coal strata itself has impurities (20-30% of the total sample weight) that are mostly attributed to non-carbonates. In light of this, the same comparison was recreated to account for impurities in the coal seam and is also showed in Figure 2.7; a multiplier of 0.75 was used to approximate the portion of the coal seam thickness that actually contributes coal to the respirable dust concentration.

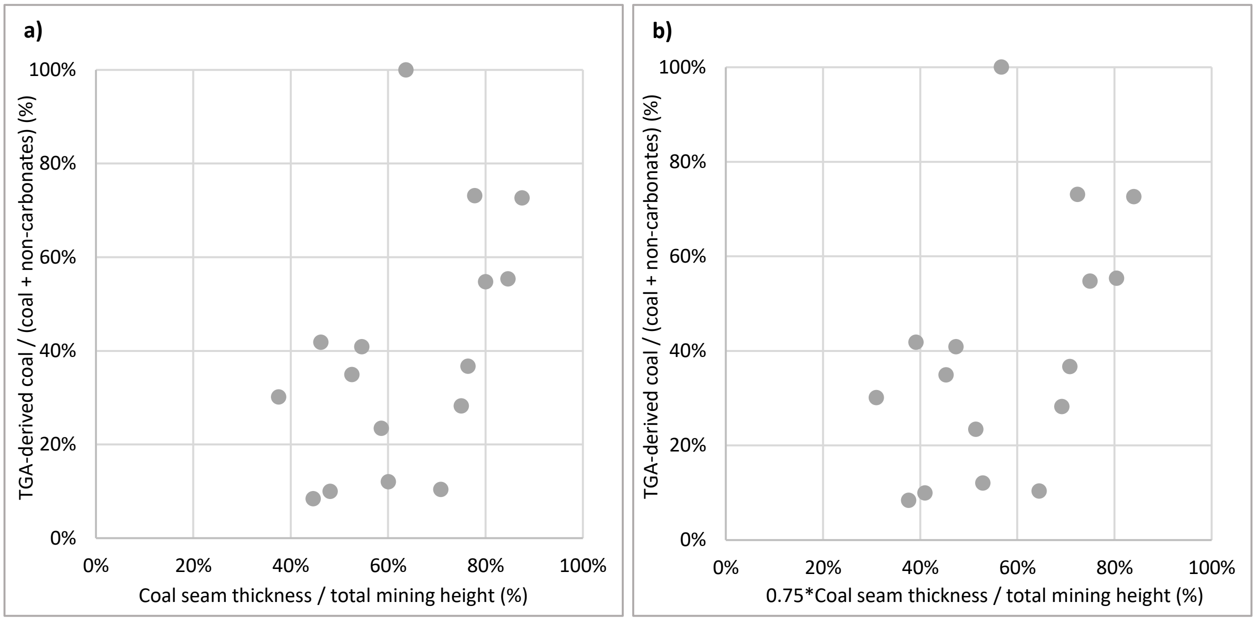

*Figure 2.7 Ratio of coal seam thickness to total mining height versus the ratio of TGA-derived coal to total dust from the strata (coal + non-carbonates) for P samples (excluding those from mines 19 and 20). In **a)** considering only the observed strata heights **b)** accounting for the impurities on the coal strata (0.75 of the total coal strata height)*

Figure 2.7 revealed that in general, even with this more conservative analysis, the P samples still tended to show an inordinate abundance of non-carbonate minerals. Thereby, it is likely that the major contributor to the RCMD in P locations is the rock strata (i.e., the primary source of non-carbonates) rather than the coal. Multiple contributing factors could explain this. One possible factor could be the fact that most of the mines presented here are located in central Appalachia (13 of 16) and as mentioned above the mines in this region tend to have thinner coal seams. Another likely factor may be the mechanical properties of the strata that could produce more dust from the rock than from the coal. Also, it could be that dust controls simply work better for coal.

4. CONCLUSIONS

TGA was done on primary dust source materials from 15 mines, and RCMD samples collected in 23 US coal mines. Overall, results on the respirable dust samples generated from primary source materials were consistent with expectations and suggested that in most mines the 3 major mass fractions of dust (i.e., coal, carbonates, non-carbonates) can be roughly associated with the 3 primary dust sources (i.e., coal strata, rock dust product, rock strata).

Analysis on RCMD samples showed variations between sampling location, and also between mine regions and mining methods. Outstandingly, TGA results seem to confirm the general trend that has been previously indicated by SEM-EDX data based on particle mineralogy distribution: the mine strata produce an inordinate amount of mineral dust and less coal dust in the respirable size. This information may have important health implications, and should be of interest for dust control and monitoring enhancement.

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CHAPTER 3 - CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The TGA is a useful analytical tool which through a comprehensive thermal ramping routine allows for the apportionment of respirable dust into three major mass fractions (i.e., coal, carbonates, and non-carbonates) which could serve as a proxy for the major sources (i.e., coal strata, rock dust, rock strata) of RCMD. Such estimations could provide valuable information in terms of dust source apportionment in specific mining locations and/or conditions, and shed some light on how dust control and monitoring could be improved.

TGA data on respirable dust samples generated from dust source materials may not only demonstrate the reliability of the TGA mass apportionment but also might indicate that indeed in most mines there are three major dust sources (i.e., rock dust, coal seam, rock strata) that contribute to the RCMD.

Comparison made based on sampling location showed that overall F and I samples exhibited the highest coal mass fraction. For F samples it is attributed to activities of crushing and transportation of coal. For I it could be explained by the implications that the mass of the sample and the presence of diesel particulates could have on the results. R locations showed the highest fractions of carbonates attributed to rock dusting activities that take place in the mine. Finally, P and B samples showed the highest non-carbonate mass fraction which might be explained by the mining and drilling of the rock strata. In fact, a comparison between the ratio of coal seam thickness to total mining height and the ratio of TGA-estimated coal to the total mine strata showed that the fraction of non-carbonates likely sourced from the rock strata was tremendously high in P locations.

In general, regional and mining method comparisons showed similar trends. Mines in central Appalachia or continuous miner operations showed higher fractions of non-carbonates (especially in R, B and P locations) likely attributed to the tendency to mine thinner coal seams and more rock that is surrounding the coal strata in this region. Mines outside of central Appalachia or longwall operations indicated higher mass fractions of coal and carbonates (particularly in R and P locations) which makes sense due to the fact that these mines are characterized by thicker coal seams and more intensive rock dusting activities.

From this research some lessons have been learned, which could be critical moving forward with RCMD characterization and dust source apportionment using TGA:

- Results on primary dust source material for two mines included in this work showed that the rock strata were dominated by carbonates instead of non-carbonates as happened with the rest of the mines. These results serve as a reminder that multiple sources of similar dust components can complicate source apportionment efforts. Thus, some knowledge of the primary dust sources in any particular sampling environment is critical to interpretation of dust characterization.

- Coal materials from different mines could have different volatilities and properties which might directly impact the time required for complete oxidation. Coal materials with low volatility require either higher temperatures or more time for oxidation, compared to the time and temperature established in the TGA thermal ramping routine. Incomplete oxidation of the coal in the expected temperature region yields inaccurate mass apportionment meaning that a fraction of coal is misclassified as carbonate.
- TGA is a mass-based method which means that samples with significantly small masses, decrease the accuracy of the dust mass fractionation, and results might be excluded from further analysis.
- Although the TGA method is quick and straightforward, it requires an exhaustive sample preparation on which contamination is pretty easily. TGA samples should be carefully handled, and any tool or space involved in the sample preparation process must be properly cleaned up before analysis.

Future work might include the collection and analysis of more RCMD samples. Preferably, from longwall operations or mines located outside of central Appalachia. This, to increase the database used to evaluate possible trends based on mining method or region. Also, sampling collection times in mines could be increased so sample masses will no longer be a barrier to the accuracy and interpretation of TGA results.

TGA is used to approximate major mass fractions of dust to primary dust sources. However, there is a need to further investigate the implications that silica and silicates have on miner’s health. The non-carbonate mass fraction estimated for TGA is expected to contain mostly particles generated from the rock strata which has long been speculated to be primarily related to respirable silica and silicates. That said, future work might include an approach to depict a more specific composition of the non-carbonate mass fraction through the analysis of replicate samples by SEM-EDX and FT-IR that enable a more specific dust characterization.

APPENDIX A- ADDITIONAL FIGURES AND TABLES

A.1 SCHEMATIC REPRESENTATION OF THE KEY SAMPLING LOCATIONS

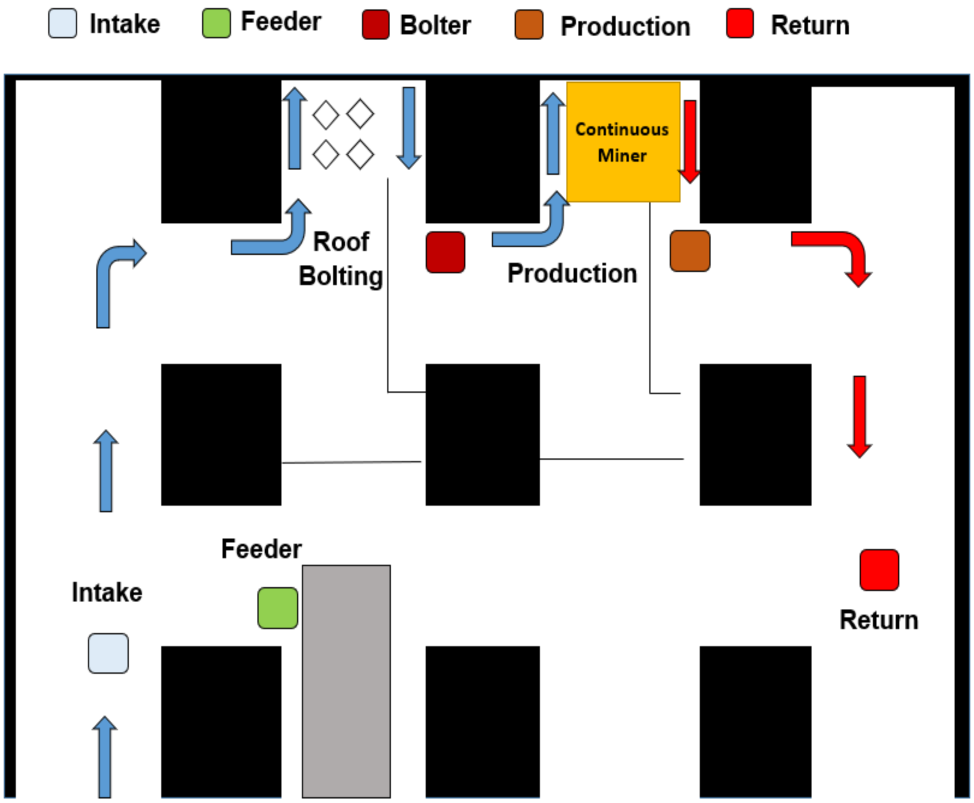

Figure A.1 Schematic representation of the 5 key sampling location in a continuous miner operation.

A.2 SAMPLES GENERATED FROM PRIMARY DUST SOURCE MATERIALS

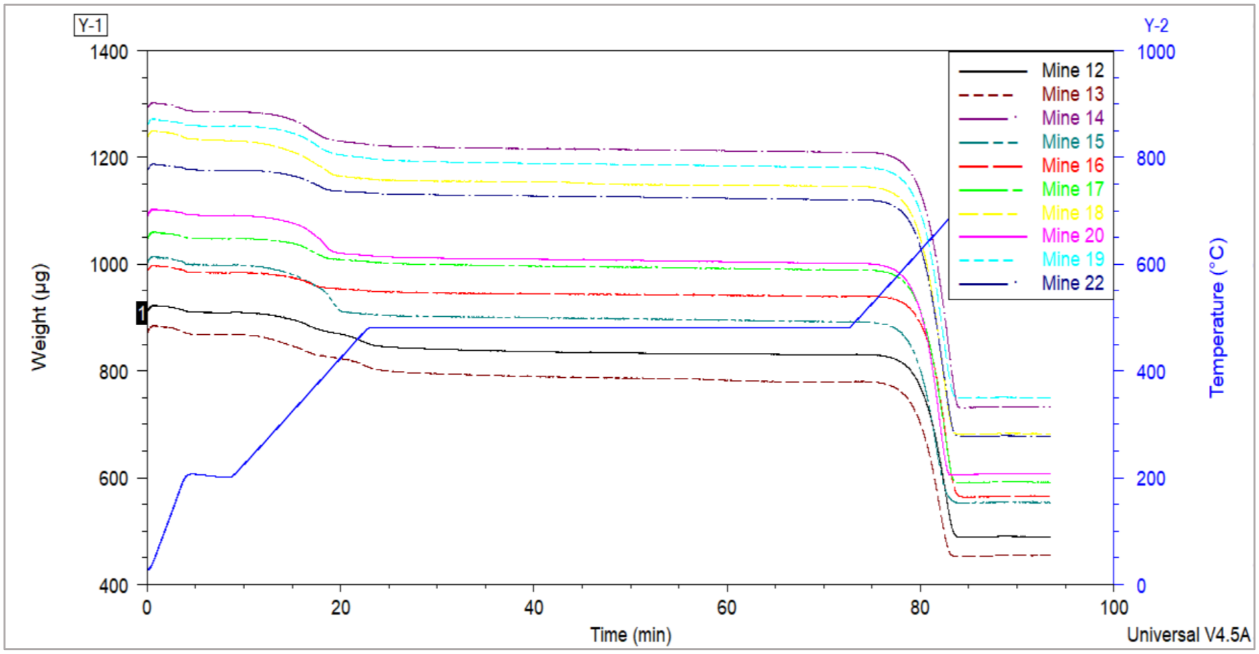

Figure A.2 Thermograms of single dust source material (Rock dust products).

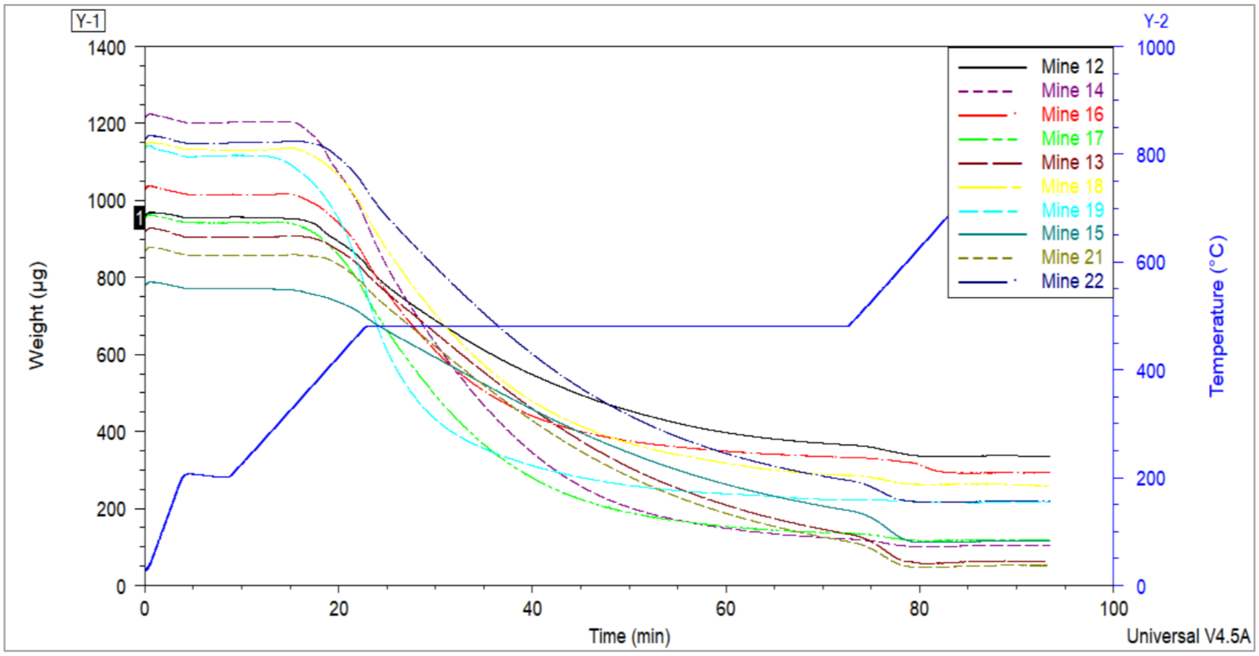

Figure A.3 Thermograms of single dust source material (Coal).

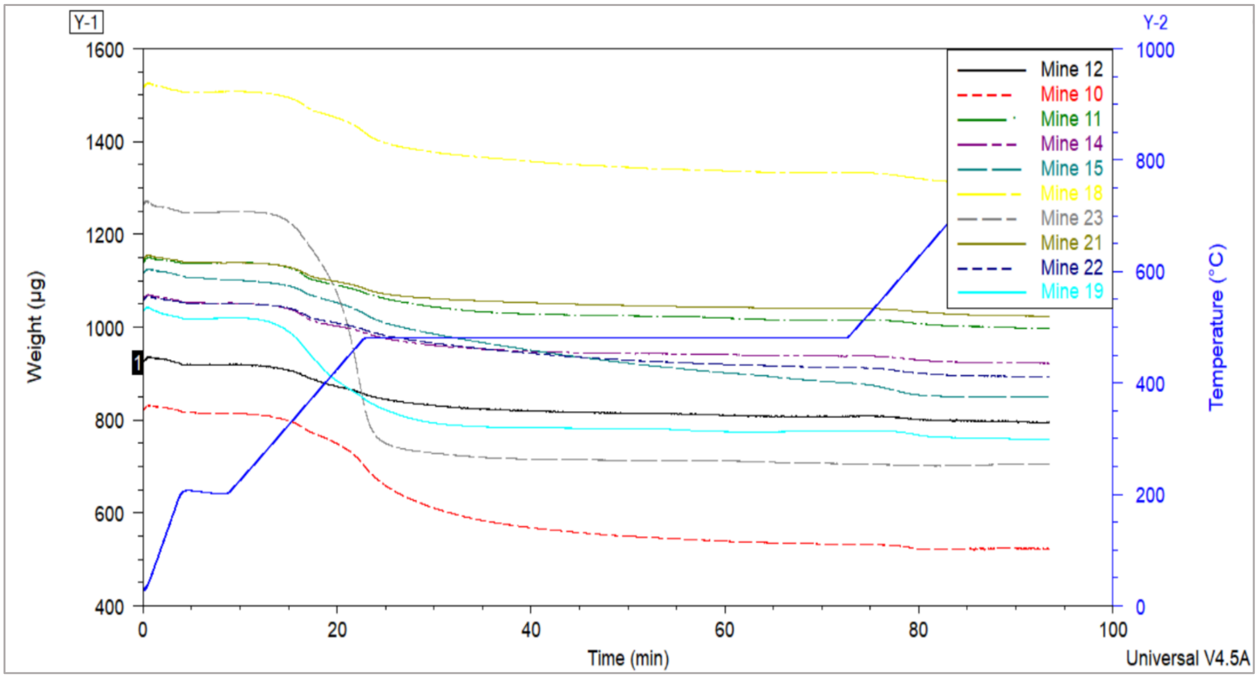

Figure A.4 Thermograms of single dust source material (ROM rock).

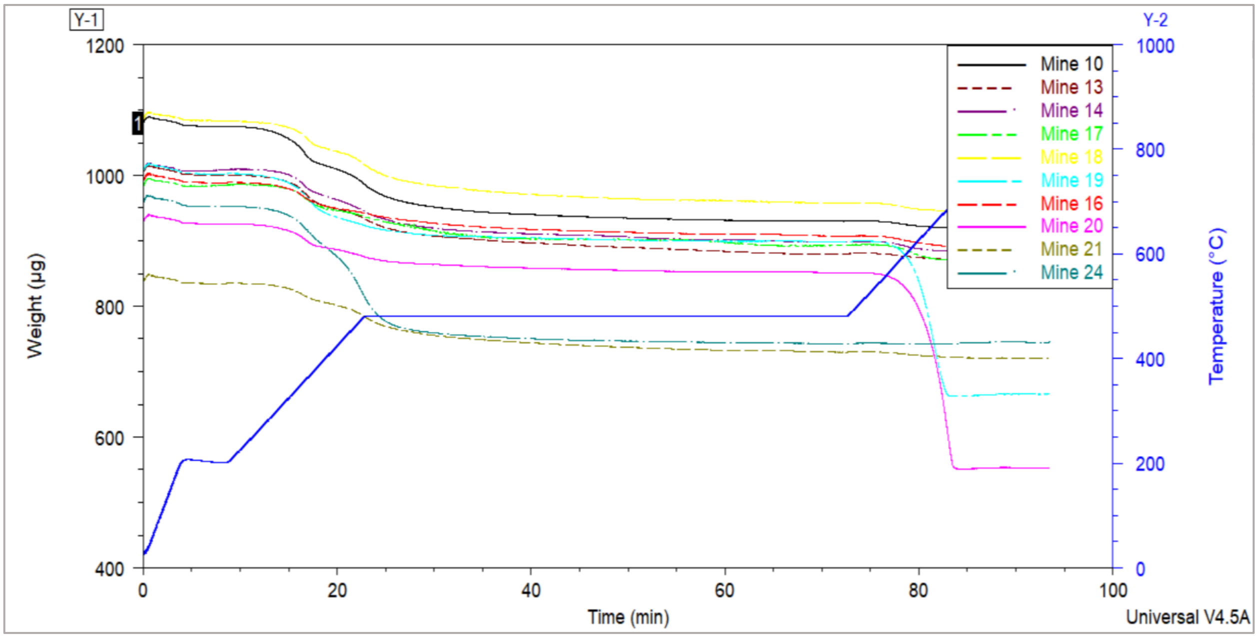

Figure A.5 Thermograms of single dust source material (Bolter dust).

Table A.1 TGA results for all 46 respirable dust samples generated from the source materials (i.e., coal, ROM rock, roof bolter dust, and rock dust products

Mine No	Material	Coal (%)	Carbonate (%)	Non-carbonate (%)
10	ROM rock	33%	7%	61%
10	Bolter dust	11%	5%	83%
11	Rock dust	1%	93%	6%
11	ROM rock	9%	6%	85%

12	Rock dust	4%	88%	7%
12	Coal	59%	12%	30%
12	ROM rock	8%	7%	85%
13	Rock dust	5%	95%	0%
13	Coal	78%	22%	0%
13	Bolter dust	10%	6%	84%
14	Rock dust	2%	92%	6%
14	Coal	90%	5%	5%
14	ROM rock	8%	7%	85%
14	Bolter dust	8%	7%	84%
15	Rock dust	6%	86%	8%
15	Coal	71%	29%	0%
15	ROM rock	18%	10%	72%
16	Rock dust	0%	96%	4%
16	Coal	67%	13%	20%
16	Bolter dust	6%	8%	87%
17	Rock dust	1%	96%	3%
17	Coal	86%	8%	6%
17	Bolter dust	6%	10%	83%
18	Rock dust	3%	93%	4%
18	Coal	75%	8%	17%
18	ROM rock	10%	5%	85%
18	Bolter dust	9%	6%	85%
19	Rock dust	2%	86%	12%
19	Coal	79%	4%	17%
19	ROM rock	21%	7%	72%
19	Bolter dust	6%	61%	33%
20	Rock dust	4%	91%	4%
20	Bolter dust	3%	84%	12%
21	Coal	79%	21%	0%
21	ROM rock	7%	6%	87%
21	Bolter dust	10%	7%	83%
22	Rock dust	1%	94%	6%
22	Coal	75%	14%	10%
22	ROM rock	11%	8%	82%
22	Bolter dust	8%	11%	82%
23	Rock dust	4%	94%	2%
23	Coal	77%	2%	20%
23	ROM rock	42%	3%	55%
23	Bolter dust	27%	4%	69%
24	Rock dust	3%	93%	4%
24	Bolter dust	20%	2%	78%

A.3 ADDITIONAL STATISTICAL ANALYSIS ON MINE DUST SAMPLES

Table A.2 TGA results on all 129 RCMD samples collected in 5 key locations (i.e., intake, return, feeder, bolter, production)

Mine No	Region	Mining method	Location	Code	Coal (%)	Carbonate (%)	Non-carbonates (%)
1	CA	CM	Return	R	48%	8%	44%
1	CA	CM	Intake	I	87%	13%	0%
1	CA	CM	Feeder	F	71%	17%	12%
1	CA	CM	Production	P	51%	7%	42%
1	CA	CM	Bolter	B	7%	13%	81%
2	CA	CM	Return	R	16%	4%	79%
2	CA	CM	Intake	I	38%	11%	50%
2	CA	CM	Feeder	F	86%	14%	0%
2	CA	CM	Production	P	20%	80%	0%
2	CA	CM	Bolter	B	10%	4%	86%
3	CA	CM	Return	R	30%	6%	64%
3	CA	CM	Intake	I	90%	10%	0%
3	CA	CM	Feeder	F	79%	21%	0%
3	CA	CM	Production	P	27%	6%	68%
3	CA	CM	Bolter	B	87%	10%	3%
4	CA	CM	Return	R	87%	13%	0%
4	CA	CM	Intake	I	96%	0%	4%
4	CA	CM	Feeder	F	97%	2%	1%
4	CA	CM	Bolter	B	44%	22%	34%
5	NA	LW	Return	R	19%	66%	15%
5	NA	LW	Return	R	56%	16%	29%
5	NA	LW	Intake	I	79%	11%	10%
5	NA	LW	Intake	I	76%	9%	15%
5	NA	LW	Feeder	F	65%	29%	5%
5	NA	LW	Feeder	F	42%	54%	4%
5	NA	LW	Production	P	68%	6%	26%
5	NA	LW	Bolter	B	68%	18%	14%
7	CA	CM	Return	R	57%	11%	32%
7	CA	CM	Intake	I	93%	7%	0%
7	CA	CM	Feeder	F	44%	13%	43%
7	CA	CM	Production	P	49%	11%	40%
7	CA	CM	Bolter	B	37%	16%	47%
8	CA	CM	Return	R	56%	4%	40%
8	CA	CM	Intake	I	74%	9%	16%
8	CA	CM	Feeder	F	79%	6%	16%
8	CA	CM	Production	P	5%	3%	92%
8	CA	CM	Production	P	15%	4%	81%
8	CA	CM	Bolter	B	27%	0%	73%
8	CA	CM	Return	R	9%	72%	19%
10	CA	CM	Bolter	B	25%	4%	71%
10	CA	CM	Bolter	B	27%	5%	68%
10	CA	CM	Feeder	F	42%	3%	55%
10	CA	CM	Feeder	F	44%	16%	40%

10	CA	CM	Intake	I	85%	2%	14%
10	CA	CM	Production	P	23%	3%	74%
10	CA	CM	Return	R	62%	3%	35%
11	CA	CM	Bolter	B	37%	9%	54%
11	CA	CM	Feeder	F	54%	7%	39%
11	CA	CM	Production	P	11%	5%	84%
11	CA	CM	Return	R	12%	6%	82%
12	CA	CM	Bolter	B	55%	13%	32%
12	CA	CM	Feeder	F	76%	5%	19%
12	CA	CM	Intake	I	29%	5%	66%
12	CA	CM	Return	R	21%	7%	72%
13	CA	LW	Bolter	B	14%	6%	81%
13	CA	LW	Feeder	F	78%	8%	14%
13	CA	LW	Intake	I	41%	33%	26%
13	CA	LW	Intake	I	63%	13%	24%
13	CA	LW	Return	R	8%	70%	22%
13	CA	LW	Return	R	74%	4%	22%
14	CA	CM	Bolter	B	34%	11%	55%
14	CA	CM	Feeder	F	28%	5%	67%
14	CA	CM	Intake	I	67%	9%	24%
14	CA	CM	Production	P	9%	5%	86%
15	CA	CM	Bolter	B	31%	10%	59%
15	CA	CM	Feeder	F	51%	22%	28%
15	CA	CM	Intake	I	76%	0%	24%
15	CA	CM	Production	P	33%	7%	60%
15	CA	CM	Return	R	17%	6%	77%
16	NA	CM	Bolter	B	72%	5%	23%
16	NA	CM	Feeder	F	65%	9%	26%
16	NA	CM	Production	P	68%	7%	25%
16	NA	CM	Return	R	62%	9%	28%
17	NA	LW	Bolter	B	47%	37%	16%
17	NA	LW	Intake	I	62%	6%	32%
17	NA	LW	Intake	I	93%	4%	3%
17	NA	LW	Production	P	35%	5%	60%
17	NA	LW	Return	R	35%	3%	61%
17	NA	LW	Return	R	31%	58%	11%
18	NA	CM	Bolter	B	32%	10%	59%
18	NA	CM	Feeder	F	71%	6%	22%
18	NA	CM	Intake	I	68%	12%	20%
18	NA	CM	Production	P	40%	5%	55%
18	NA	CM	Return	R	29%	9%	62%
19	MW	CM	Bolter	B	57%	9%	34%
19	MW	CM	Feeder	F	48%	6%	46%
19	MW	CM	Intake	I	0%	49%	51%

19	MW	CM	Production	P	50%	16%	34%
19	MW	CM	Return	R	45%	20%	35%
19	MW	CM	Return	R	47%	5%	48%
20	MW	CM	Bolter	B	32%	21%	47%
20	MW	CM	Feeder	F	34%	34%	32%
20	MW	CM	Feeder	F	37%	21%	42%
20	MW	CM	Intake	I	6%	63%	31%
20	MW	CM	Production	P	32%	8%	60%
20	MW	CM	Return	R	33%	11%	56%
21	CA	CM	Bolter	B	61%	16%	23%
21	CA	CM	Feeder	F	16%	3%	81%
21	CA	CM	Intake	I	20%	15%	65%
21	CA	CM	Production	P	8%	4%	88%
21	CA	CM	Return	R	9%	4%	87%
22	CA	CM	Feeder	F	62%	5%	33%
22	CA	CM	Intake	I	33%	49%	19%
22	CA	CM	Production	P	34%	16%	50%
23	W	LW	Intake	I	70%	18%	11%
23	W	LW	Intake	I	36%	64%	0%
23	W	LW	Intake	I	40%	50%	9%
23	W	LW	Return	R	29%	62%	9%
24	W	LW	Feeder	F	71%	10%	19%
24	W	LW	Intake	I	31%	3%	66%
24	W	LW	Intake	I	69%	16%	15%
24	W	LW	Intake	I	53%	20%	28%
24	W	LW	Return	R	42%	15%	43%
24	W	LW	Return	R	12%	71%	17%
25	CA	CM	Intake	I	77%	1%	22%
25	CA	CM	Bolter	B	39%	6%	55%
25	CA	CM	Feeder	F	40%	8%	51%
25	CA	CM	Production	P	18%	7%	74%
25	CA	CM	Production	P	57%	6%	37%
25	CA	CM	Return	R	22%	6%	72%
25	CA	CM	Production	P	27%	10%	63%
25	CA	CM	Production	P	42%	1%	57%
25	CA	CM	Return	R	23%	6%	71%
25	CA	CM	Production	P	14%	5%	81%
25	CA	CM	Production	P	43%	8%	49%
25	CA	CM	Production	P	14%	8%	78%
25	CA	CM	Production	P	29%	1%	70%
25	CA	CM	Return	R	53%	20%	27%
25	CA	CM	Return	R	18%	6%	75%

A.3.1 By Sampling Location

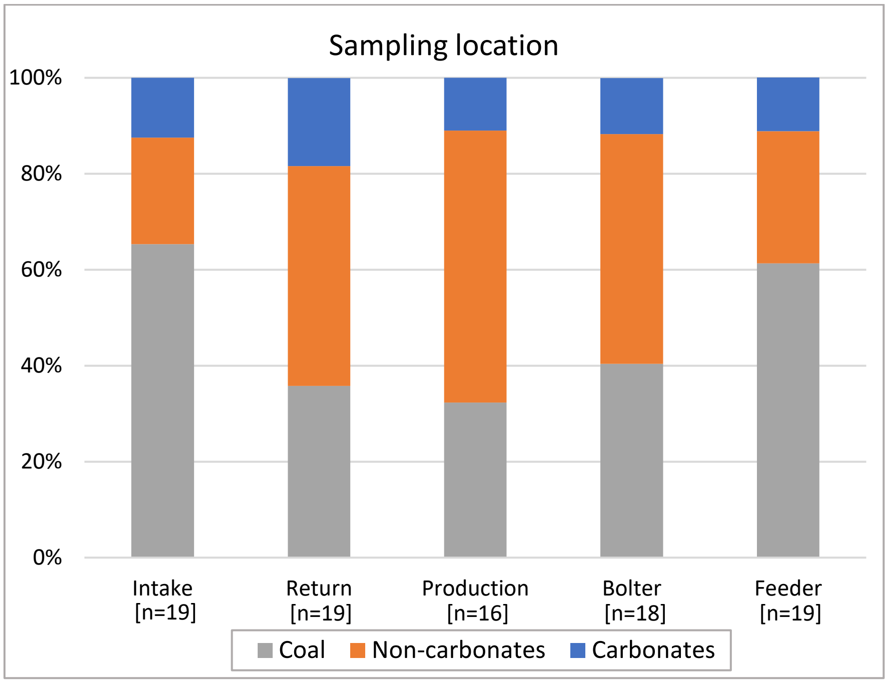

Figure A.6 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location.

Table A.3 Summary statistics comparing fractions of coal, carbonates and non-carbonates by sampling location

All unique locations (n=91)			
Dust constituent	Overall P-value	Specific P-value Tukey-Kramer HSD	Mean difference (%)
Coal	< 0.0001	0.0001	I > P
		0.0004	I > R
		0.0009	F > P
		0.0028	F > R
		0.0048	I > B
		0.0261	F > B
Carbonates	0.3045	-	-
Non-carbonates	< 0.0001	0.0005	P > I
		0.0045	P > F
		0.0125	B > I
		0.0245	R > I
		0.0775	B > F

I = intake, R = return, P = production, F = feeder, B = bolter

A.3.2 By Mine Region

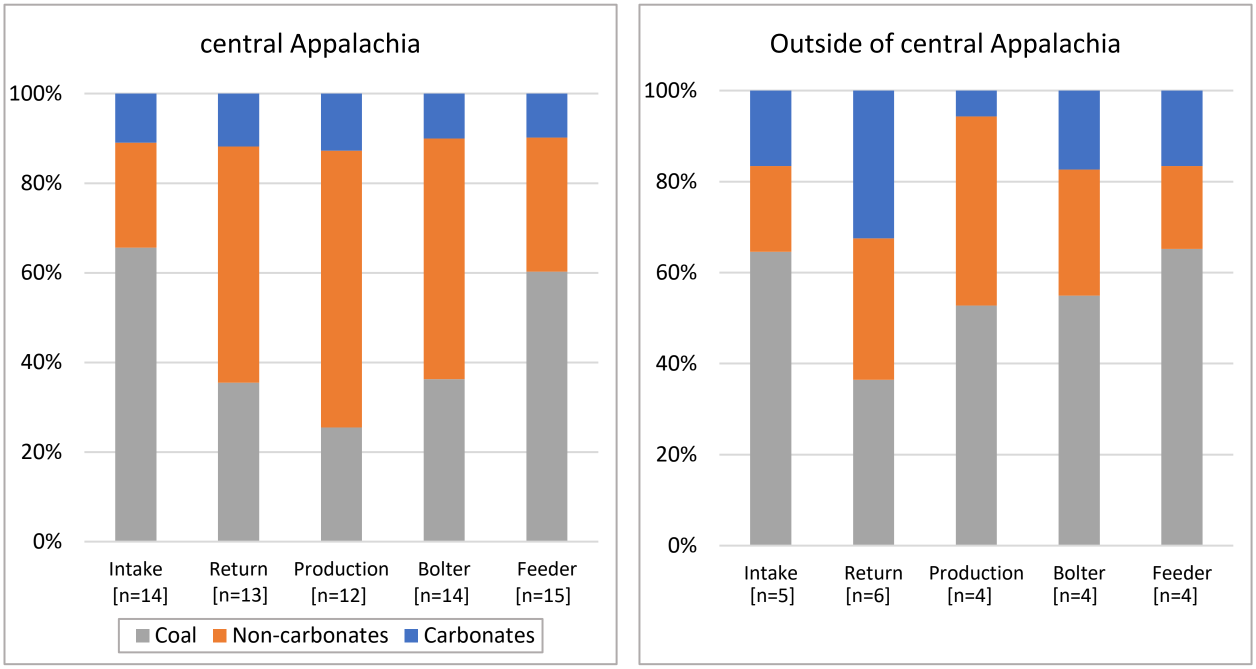

*Figure A.7 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location for mines **a)** in central Appalachia and **b)** outside of central Appalachia.*

Table A.4 Summary statistics for comparison of mean mass fractions of coal carbonates and non-carbonates between sampling locations by mine region.

	central Appalachia vs outside of central Appalachia									
	Intake (n=19)		Return (n=19)		Production (n=16)		Bolter (n=18)		Feeder (n=19)	
	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference
Coal	0.9253	-	0.9323	-	0.0086	CA < O	0.1384	-	0.6846	
Carbonates	0.4550	-	0.0106	CA < O	0.6249	-	0.1206	-	0.2945	-
Non-carbonates	0.3932	-	0.0991	CA > O	0.0190	CA > O	0.0727	CA > O	0.3577	

CA= central Appalachia, O= outside of central Appalachia

A.3.3 By Mining Method

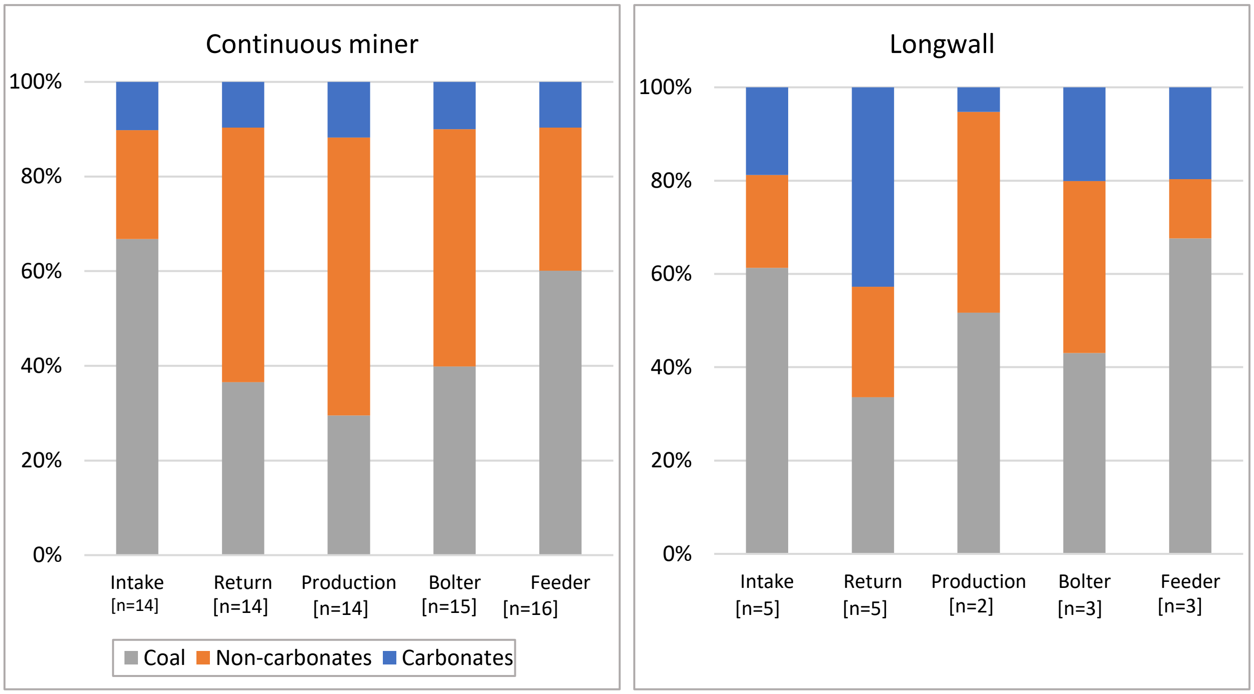

*Figure A.8 Average TGA results for the respirable mine dust samples (excluding those from mines 19 and 20) presented by sampling location per mining method **a)** continuous miner and **b)** longwall.*

Table A.5 Summary statistics for comparison of mean mass fractions of coal carbonates and non-carbonates between sampling locations by mining method.

	continuous miner vs longwall									
	Intake (n=19)		Return (n=19)		Production (n=16)		Bolter (n=18)		Feeder (n=19)	
	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference	P-value	Mean difference
Coal	0.6582	-	0.7888	-	0.1367	-	0.8306	-	0.5796	-
Carbonates	0.2682	-	< 0.0001	CM < LW	0.6962	-	0.0475	CM < LW	0.0747	CM < LW
Non-carbonates	0.4874	-	0.0241	CM > LW	0.4307	-	0.4280	-	0.2236	-

CM= continuous miner, LW= longwall