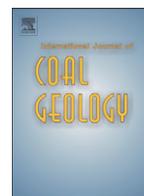




Contents lists available at SciVerse ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

A provenance study of mineral matter in coal from Appalachian Basin coal mining regions and implications regarding the respirable health of underground coal workers: A geochemical and Nd isotope investigation

Steven J. Schatzel ^{a,*}, Brian W. Stewart ^b

^a National Institute for Occupational Safety and Health, Office of Mine Safety and Health Research, PO Box 18070, Cochrans Mill Road, Pittsburgh, PA 15236, United States

^b Department of Geology and Planetary Science, 4107 O'Hara Street, University of Pittsburgh, Pittsburgh, PA 15260, United States

ARTICLE INFO

Article history:

Received 12 August 2011

Received in revised form 13 January 2012

Accepted 23 January 2012

Available online xxxx

Keywords:

Coal mining

Silicosis

Coal mineralogy

Neodymium isotopes

Geochemistry

ABSTRACT

This study presents geochemical data produced from the analysis of coal and adjacent rock samples retrieved from coal mining regions in the U.S. to examine mineral matter provenance. Study sites included the Northern Appalachian Basin, where the units of interest were the Lower Kittanning Coal bed, the overlying Columbiana Shale, and the underlying paleosol (Allegheny Formation). Additional study sites were located in the Central Appalachian Basin, where sampling was conducted on strata associated with multiple coal beds of Middle and Lower Pennsylvanian age. The Central Appalachian Basin rock and coal samples were much lower in overall mineral matter and contained very little carbonate (calcite and siderite) or pyrite mineralogy, which was common at the Northern Appalachian Basin sites. Elemental analysis of rock samples indicated a trend of enrichment in Ca, Mg, Mn, Na, and K cations in the immediate overburden compared to the underlying rock in the Central Appalachian Basin. A similar trend was observed in coal related strata from the Northern Appalachian Basin which was attributed to epigenetic marine incursions. Rare earth element (REE) concentrations were determined in the samples, and showed Eu and Ce anomalies when normalized by chondritic values. The total REE content of the overburden is generally less than that of the underlying rock units. Neodymium isotopic analysis of the Lower Kittanning coal, overburden, and paleosol from the Northern Basin indicate partial resetting of the Sm–Nd system close to the time of deposition. The data indicate a common Appalachian source for the clastic mineral matter in the overburden, underclay, and coal mineral matter. The geochemical findings of this study may provide a viable method for distinguishing respirable dust sources in both Appalachian Basins. There are potential applications for this research to aid in the respiratory health of underground coal miners.

Published by Elsevier B.V.

1. Introduction

Silicosis and coal workers pneumoconiosis (CWP) occur in underground coal mine workers in the U.S. as the result of inhaled mine dusts. The potential harm of these dusts to human lung tissue is significantly influenced by the geochemistry and mineralogy of the respirable material. A key issue in controlling exposure of mine workers to ambient dust is identifying the source(s) and specific components of dust in the mining environment. We present mineralogical, geochemical and neodymium (Nd) isotope data as indicators of mineral matter provenance in two Appalachian coal basins of the U.S. Although Nd isotopic methods have been shown to be an important tool in provenance studies of sedimentary rock, very little has been research has been done to utilize this investigative approach in coal studies.

This paper follows on earlier work by Schatzel and Stewart (2003) and Schatzel (2009) which focused on mineral matter origins and rare earth element (REE) sources in coal and associated rocks. The 2003 study focused on a single bituminous coal bed in the Northern Appalachian Basin and five sampling sites distributed over hundreds of kilometers in western Pennsylvania. This research was conducted due to concern about respirable dust hazards experienced by underground coal miners. One new finding from this study was the correlation between REE some major elements. The total rare earth element concentrations (TREE) were found to be more strongly related to Si concentrations than any other elemental component for the coal and rock samples. The 2009 study focused on geochemical methods for identifying sources of respirable quartz and silica dust in underground coal mines. Since the sources of respirable silica dust are thought to be the rock strata immediately above and below the mined coal bed, the 2009 study was concerned primarily with the composition of the rock units and respirable dust and less on the analysis of coal samples. The study was conducted in the Central Appalachian Basin, near the intersection of the Kentucky, West Virginia, and

* Corresponding author.

E-mail addresses: zia6@cdc.gov (S.J. Schatzel), bstewart@pitt.edu (B.W. Stewart).

Virginia borders. One finding from the study included the identification of a group of cation concentrations in the parent rock that were present in similar distributions within the mineral fraction in the produced respirable dust.

Despite advances in engineering controls for enhanced dust reduction during underground coal mining, particularly on continuous mining sections, and regulatory changes reducing the allowable respirable silica dust concentrations in air, incidence rates for coal worker's pneumoconiosis (CWP) and silicosis are not improving. In fact, data show that incidence rates for both diseases are in fact increasing in important segments of the work force since 2000 (Laney et al., 2010). Although this is a geochemical study, not an analysis of compromised worker health, mineral and chemical components present in respirable mine dusts have been shown to yield a significant influence on the inflammatory processes that result in silicosis (Cecala et al., 2012). Potential applications of this research for the enhanced capture of respirable dust and reduced dust exposures are reviewed.

2. Background

2.1. Major mineral groups in coal

Mineral matter in coal makes up a highly diverse range of materials. The primary motivations for analyzing coal-bound mineral matter have been coal utilization (Harvey and Ruch, 1986; Mackowsky, 1968; Stach et al., 1982), environmental (Gluskoter et al., 1977; Ward, 2002), and health interests (Finkelman, 1993; Palmer and Lyons, 1996). The most common minerals and mineral groups in coal seams are quartz, clays, feldspars, sulfides, and carbonates. These major groups were also present at one or both of the coal basins included in this study, and therefore are relevant to the study findings. Of the clay minerals, kaolinite is quite common (Gluskoter, 1967; Rao and Gluskoter, 1973), as is illite–smectite. Siderite, calcite, and dolomite are commonly observed carbonate minerals. Pyrite is the most commonly found sulfide mineral (Gluskoter et al., 1977).

Clastic mineral material is expected to potentially yield information about source rock origins. Clays (primarily illite and kaolinite) and quartz are common clastic minerals in coal, and in some cases can account for nearly all of the mineral matter present (Stach et al., 1982). Eolian transport appears to be a significant means of introducing quartz grains to the coal-forming mire. Detrital aluminosilicates may be introduced by aqueous or eolian transport modes. Tonsteins are known in many coal beds and represent another clastic mineral source, probably of volcanic origin.

Syngenetic quartz is also present in coal seams. Quartz dissolution has been reported from mire-type environments under reducing conditions (Bennett et al., 1988). Syngenetic quartz and clay may appear as cell and pore infillings (Ward, 2002), or as coatings or overgrowths on clastic mineral grains.

Most of the iron present in coal mineral matter is in the form of syngenetic and epigenetic iron disulfides. Finely dispersed pyrite in coal generally has syngenetic or early epigenetic origins. Organically combined sulfur is also common in coal. Iron is also present in coal beds in the form of siderite, which is usually present in coal as small (1–2-mm) nodules often associated with vitrinite and clay layers (Stach et al., 1982). Siderite is thought to form syngenetically or during early diagenesis. Larger nodules of siderite are found in many coal units and have been known to contain uncompact plant cell structures.

Epigenetic mineralization in general includes fracture and cleat infillings of material (Hower et al., 2001). Clastic dikes are well-reported in the literature in the Appalachian Basin, and generally consist of clays forming continuous veins through cleats, fractures, and fault planes. Quartz is also formed epigenetically in coal seams. Following coal deposition, mobilized silica can enter fracture voids or pore

spaces within the coal horizon. This material can then crystallize to form epigenetic quartz (Vassilev and Vassileva, 1996).

Sulfides make up a significant portion of the epigenetic mineral fraction in coal. Pyrite is the dominant sulfide found in coal beds as a fracture or cleat infill. Carbonates are found as epigenetic minerals in the form of veins or cleat fillings in coal (Stach et al., 1982). Common epigenetic carbonates can include calcite, ankerite, siderite, and dolomite. The calcium for mineral authigenesis is thought to be derived from groundwater (Cecil et al., 1978). Thus, we would expect more calcium carbonate minerals to be found in coals produced from topogenous mires than in coals produced by ombrogenous mires (Cecil et al., 1985; McCabe, 1993).

Phosphate minerals can contain significant amounts of the REE present in coal (Willett et al., 2000). Apatite is typically the most common of the phosphate minerals occurring in coals. Other reported forms of phosphate mineralization include aluminophosphates (Crowley et al., 1993; Finkelman and Stanton, 1978; Rao and Walsh, 1997, 1999; Ward et al., 1996). Phosphate minerals are present as cell and pore fillings, in concentrated layers within coal units, and aluminophosphates are known to be associated with tonsteins (Bohor and Triplehorn, 1993; Hill, 1988).

2.2. Rare earth elements in shale and coal

The rare earth elements (REE), defined as elements with atomic number 57 (La) through 71 (Lu), are present at the parts per million (ppm) level in most rocks, and have long been used in petrogenetic studies of igneous rocks (see Hanson, 1980, for a review). All of the rare earth elements readily form 3+ ions under earth surface conditions; in addition, Ce^{4+} can be stable in an oxidizing, low-temperature environment, and Eu^{2+} is stable under certain reducing conditions at high (magmatic) temperatures. This constancy in valence state, when combined with the systematic decrease in ionic radius with increasing atomic number, makes the REE a coherent group of trace elements for tracking petrogenetic sources and processes. The high charge/radius ratio of the REE means that these elements are relatively immobile during weathering, erosion, and deposition at the Earth's surface, and thus can be useful for identifying clastic sediment sources.

Rare earth elements in coal appear to consist of a primary fraction which is associated with clastic and syngenetic mineral matter (Finkelman, 1982; Palmer et al., 1990; Schatzel and Stewart, 2003). Another portion of the REE can be externally derived or mobilized when primary mineral matter is destroyed or modified, and may be retained in the coal bed but redistributed and incorporated into other mineral components (authigenic minerals). There still exists some disagreement about the proportion of primary and redistributed or authigenic REE in coal (Finkelman, 1982; Mariano, 1989; McLennan, 1989; Ruppert et al., 1993). Although REE are not considered to be highly mobile in low-temperature environments, some researchers have suggested possible mechanisms for mobilizing REE in coal (Eskenszy, 1987, 1999). Low pH water in the coal-forming mire can partially or completely dissolve a portion of the REE-bearing mineralogy. The mobilized REE in solution may crystallize in authigenic minerals forming in the coal bed. Minerals containing REE in coal are often present in both primary and authigenic forms which can make it difficult to distinguish between primary and secondary REE. The fine-grained nature of some REE-bearing minerals can also make chemical investigations of specific mineral fractions very challenging.

In addition to their retention in fine-grained phosphates (Finkelman, 1982; Willett et al., 2000), REE could also be bound to the surfaces of clay minerals, and may be retained in highly resistant REE-rich trace minerals such as zircon. Although little work has been done on REE in sulfides, pyrite and marcasite could contribute significantly to the overall REE budget in coal (e.g., Worrall and Pearson,

2001; Yang and Zhou, 2001; Zhang et al., 2000). Rare earth element concentrations are generally low in calcium carbonates (Sholkovitz and Shen, 1995; Vance and Burton, 1999; Zhong and Mucci, 1995), but little is known about REE associations with siderite (FeCO_3). Selective leaching and particle segregation studies of coals suggest that a portion of the REE may be associated with the organic fraction of coal (Palmer et al., 1990; Willett et al., 2000).

2.3. Nd isotopes as provenance indicators for sedimentary rock and coal

The Sm–Nd system has proven useful for studies of sedimentary rocks because the parent samarium (Sm) and daughter Nd, both rare earth elements, are generally not significantly fractionated by Earth-surface processes, and isotopic values can be determined as an indicator of the crustal formation age in the sediment source area (Patchett et al., 1999). The isotope ^{147}Sm undergoes alpha decay to ^{143}Nd (a radiogenic isotope of Nd) producing differences in $^{143}\text{Nd}/^{144}\text{Nd}$ among minerals over time, based on the starting Sm/Nd ratio and the amount of time that passes. The half-life of ^{147}Sm decay to ^{143}Nd is about 106 billion years.

Most of the Sm and Nd in clastic sedimentary rocks are associated with silicate and certain accessory minerals. Consequently, the Sm–Nd system has been used as a provenance tool to identify the sources of clastic material to sedimentary rocks (Bock et al., 1994, 1998; Linn et al., 1991; Miller et al., 1986; Nelson and DePaolo, 1988).

2.4. Respirable coal dust

Evidence has been forwarded showing that the source of respirable silica dust in coal mines is not the mined seam but rather the adjacent rock units (Dodgson et al., 1971; Hicks and Nagelschmidt, 1943; Ramani et al., 1987). Despite the advances in mining and health technologies, the incidence of CWP has actually been increasing in U.S. mines, according to recent statistics (Colinet et al., 2010). Increased exposure to respirable silica dust is thought to be a contributing factor in the observed CWP trends (Laney et al., 2010). Studies have also shown that variations in pneumoconiosis incidence rates are produced by a variety of factors, apparently not just the quantity of respirable silica dust in ventilation air (Robock and Bauer, 1990).

There are multiple mechanisms by which respirable mine dusts can challenge the health of underground workers, and they all are influenced by the composition of the dust. For example, respirable silica has also been recognized as a human carcinogen (IARC, 1997). Quartz particles of submicron size have been documented in a bituminous coal seam and linked to increased cancer rates in rural residences of China (Dai et al., 2008). Some mine dust particles have been determined to be layered or coated with clay, while clean, crystalline silicate forms have been found to be more damaging to human lungs than other types of silica mineral dust known to occur in this environment (Chen et al., 2005; Colinet et al., 2010; Dodgson et al., 1971; Harrison et al., 2005; Robock and Bauer, 1990). Research has shown the potential role of coal iron content in contributing to the occurrence of silicosis and coal worker pneumoconiosis in coal mine workers (Huang et al., 2005). The same authors have also suggested that increased carbonate content of the dust may diminish the toxic effects of bio-available iron. Unfortunately these trends have been demonstrated utilizing coal bed compositional data, not data on the rock strata adjacent to the mined seam where the respirable dust fraction is generated.

The current engineering controls that are used to dilute or suppress all coal dust produced during continuous miner operations are also the primary methods used to address respirable coal and silica dust. These controls include water sprays on the miner cutting head, scrubbers on a continuous miner chassis, and ventilation air which may be either blowing or exhausting on a continuous miner section (Taylor et al., 2010). Water spray control methods include

spray fans which influence nearby air movement and wet cutting heads that produce large volumes of dispersed water in the cutter head-coal face area.

3. Methodology

3.1. Northern Appalachian Basin field study

3.1.1. Site selection

The Lower Kittanning Coal bed is a late-middle Pennsylvanian age unit which ranges in rank from low volatile bituminous (Ogle) to high volatile A–B bituminous (West Freedom) in samples from the study sites. The unit has been extensively mined in the Commonwealth of Pennsylvania. Samples sites were surface mines or pits for drift mines operating in the Lower Kittanning Coal bed. The Lower Kittanning Coal is also very laterally extensive, which allows for the investigation of geochemical and other variations over an east-west range of about 170 km. The sites were chosen to represent coals with overburdens interpreted to have formed from various depositional environments, from fresh water to marine (Cecil et al., 1985; Rimmer and Davis, 1986; Williams and Bragonier, 1974).

A total of five study sites were selected (Fig. 1). They were chosen to encompass the three depositional regimes described for the overlying lithologies (overburden) by Williams (1957). The depositional environments for the overburden are interpreted as marine (West Freedom site), brackish (Clearfield, Enon Valley and Homer City sites), and non-marine (Ogle site). All sites were located at active coal mine operations.

3.1.2. Coal and rock sampling procedure

At each site, a complete section of Lower Kittanning Coal was selected and the exposed coal on the face was removed to depth of at least 2.5 cm. Using a handheld rock saw, two vertical slots spaced about 10 to 15 cm apart were cut in the coal, the underlying clay, and the shale overburden to form the channel. The section was then measured and the coal lithotypes described. After description was complete, the sample sizes and breaks were configured to ensure a high degree of homogeneity of the coal lithotypes in each sample of the Lower Kittanning Coal. Samples were then removed with the aid of hand tools, placed in plastic sample bags, labeled, and returned to the National Institute for Occupational Safety and Health, Office of Mine Safety and Health Research (NIOSH/OMSHR) in Pittsburgh for sample processing. The sampling scheme for the Northern Appalachian Basin is shown in Fig. 2.

3.2. Central Appalachian Basin field study

3.2.1. Study sites

The study area encompasses parts of western Virginia, southern West Virginia, and eastern Kentucky (Fig. 3). The coal beds include a range in rank from high volatile A bituminous in Kentucky and West Virginia to medium volatile bituminous in Virginia. All mines are drift room-and-pillar operations. The sampling scheme for the Central Appalachian basin samples is shown in Fig. 4. Multiple locations within the mine were sampled with rock samples being retrieved primarily from above and below the mined coal bed. Field sampling techniques and analytical methods for the Central Appalachian Basin portion of the study are discussed in Schatzel (2009).

3.3. Analytical methods

3.3.1. Northern Appalachian Basin samples

Sample preparation methods for the Northern Appalachian Basin sample suite were discussed in Schatzel and Stewart (2003). The original set of major cation concentrations did not include Mn, which is an important analyte in this study; consequently the samples were

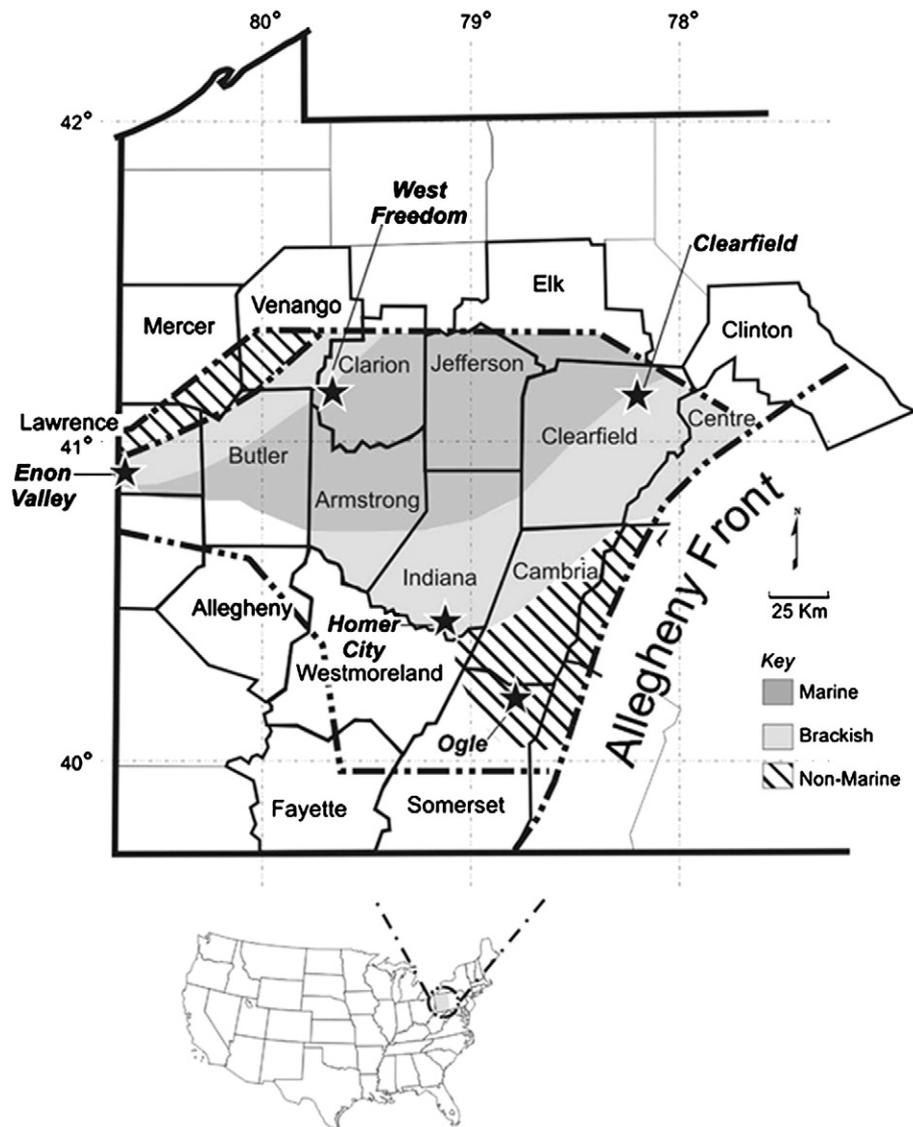


Fig. 1. Lower Kittanning Coal study sites (modified from Rimmer and Davis, 1986). Sample site key: cfd, Clearfield; evy, Enon Valley; hcy, Homer City; ogl, Ogle; and wfm, West Freedom (from Schatzel and Stewart, 2003).

re-run and new values were determined. The new data were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis following whole rock Li metaborate and Li tetraborate fusion conducted by Actlabs commercial laboratory, Ontario, Canada. Following the fusion, samples were dissolved in a solution of 5% nitric acid and analyzed at Actlabs on a Thermo Jarrell-Ash ENVIRO II ICP or a Varian Vista 735 ICP. Rock sample crushing and splitting procedures were unchanged compared to those of Schatzel and Stewart (2003). Analyses also performed on these samples included organic matter petrography, and instrumental neutron activation analysis (INAA) (Schatzel and Stewart, 2003).

For Nd isotope analysis, coal ash and crushed rock samples were digested with acid using a variation of the method described by Yokoyama et al. (1999). All sample digestions were performed under clean laboratory conditions at the University of Pittsburgh, using ultrapure reagents. Samples underwent mixed acid digestions in concentrated, heated HF and HClO₄ in Teflon® Savillex® vials. After the sample residues were heated to dryness, the samples were fluxed in concentrated, heated HClO₄. Dried sample residues were dissolved in 6 M HCl and evaporated to dryness, then dissolved in 4 M HNO₃. Following centrifuging and the removal of any undissolved

material (thought to be fluoride complexes; Yokoyama et al., 1999), the sample solutions were aliquoted for spiking. Predetermined amounts of a mixed, ultrapure spike consisting of ¹⁴⁷Sm and ¹⁵⁰Nd were added to the aliquoted samples. Spiked samples were evaporated to dryness, redissolved in 1.5 M HCl, centrifuged, and introduced to a set of cation exchange columns. The REE fraction from the cation exchange columns was dried down and the residue was dissolved in 0.18 N HNO₃, and introduced to a set of REE columns containing LnSpec® chromatographic resin for separation of Nd and Sm. Total procedural blanks were <1 ng for Nd and Sm.

The isotopic analyses were performed on a Finnigan MAT 262 thermal ionization mass spectrometer (TIMS) with one fixed and seven movable cups. For Nd, the concentration and isotopic composition were determined simultaneously on the spiked sample. About 150 ng of Nd and 100 ng of Sm were dissolved in 1 N HCl and loaded onto double Re filaments. On many of the sample turrets, the La Jolla Nd standard was run as an internal analytical standard. The Faraday cups were set to measure masses 142, 143, 144, 145, 146, and 150 simultaneously in static mode. At least 100 ratios were measured, with the ¹⁴⁴Nd beam intensity of 0.4–2.5 V. Interference from Sm (¹⁴⁴Sm, ¹⁵⁰Sm) was monitored at mass 149. Mass fractionation was corrected

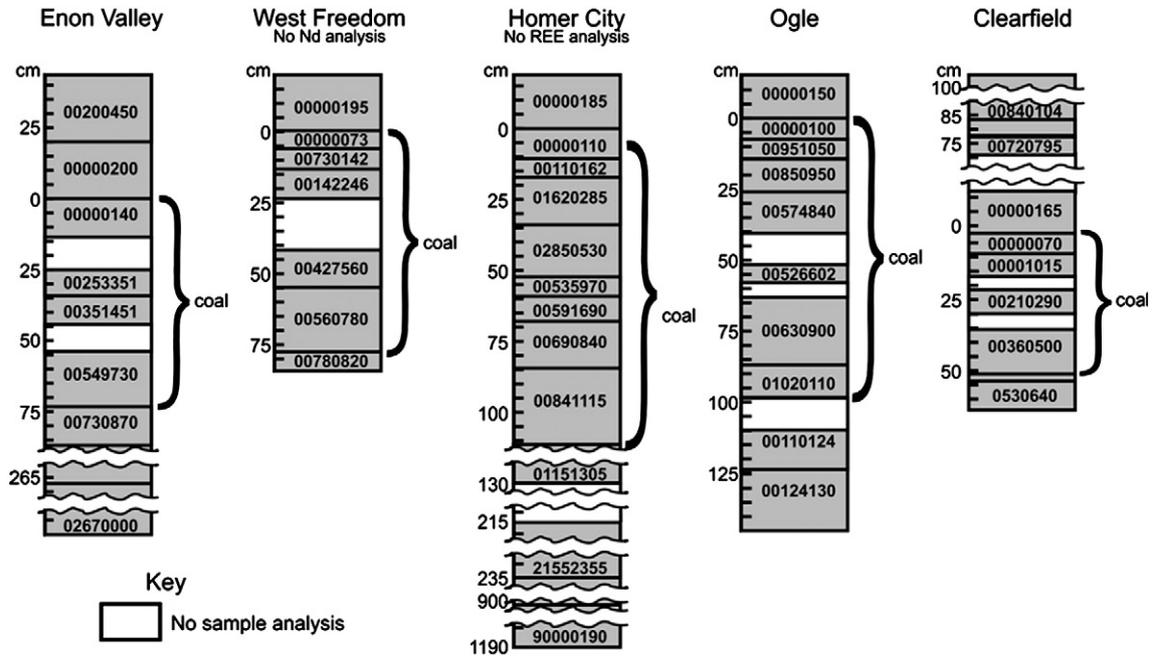


Fig. 2. Field sampling configuration at Northern Appalachian Basin sites.

using $^{146}\text{Nd}/^{144}\text{Nd} = 0.724134$ with an exponential law. Our calculated value for $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}$ is 0.511847. Estimated external reproducibility is ± 0.000015 .

3.3.2. Central Appalachian Basin samples

Samples from the Central Appalachian Basin underwent a suite of analyses, including organic matter petrography, X-ray diffraction (XRD), X-ray fluorescence (XRF), ICP-AES, inductively coupled plasma-mass spectrometry (ICP-MS), and (INAA). The methodologies used are discussed in Schatzel (2009).

4. Results and discussion

4.1. Mineralogical analysis

No XRD-based mineralogical data are available from the Northern Appalachian Basin samples. The Northern Appalachian Basin samples included shale and sandy shale overburden, and a clay-rich paleosol underlying the mined coal bed. Mineralogy descriptions for the Northern Appalachian Basin are based on petrography, hand sample descriptions, and observations from sampling sites. Fine pyrite was

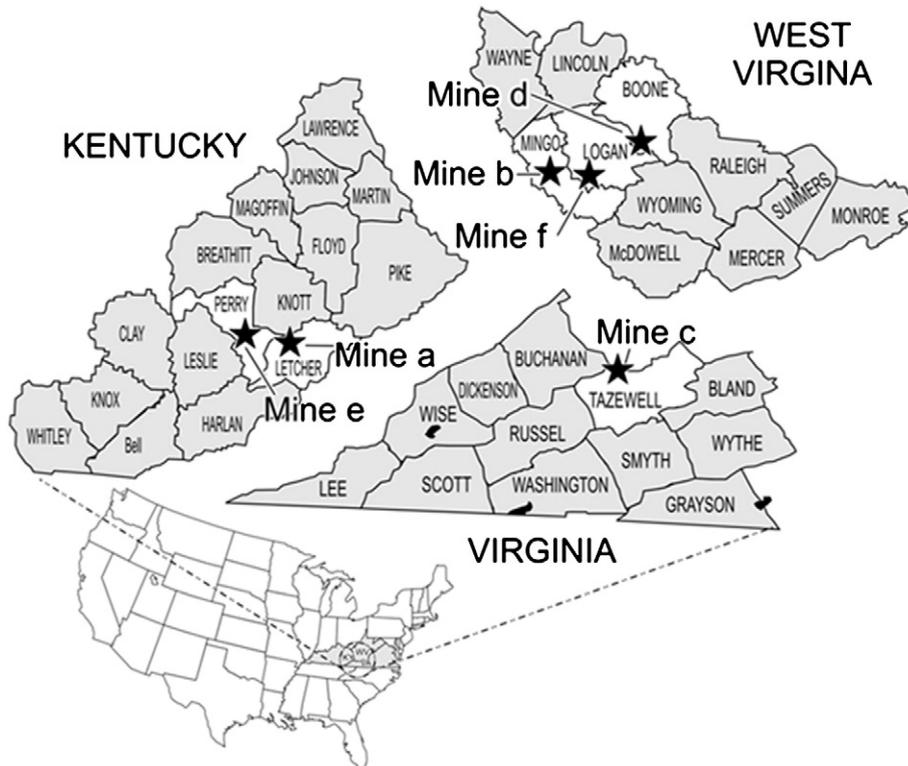


Fig. 3. The location of mine sites included in the Central Appalachian Basin study (from Schatzel, 2009).

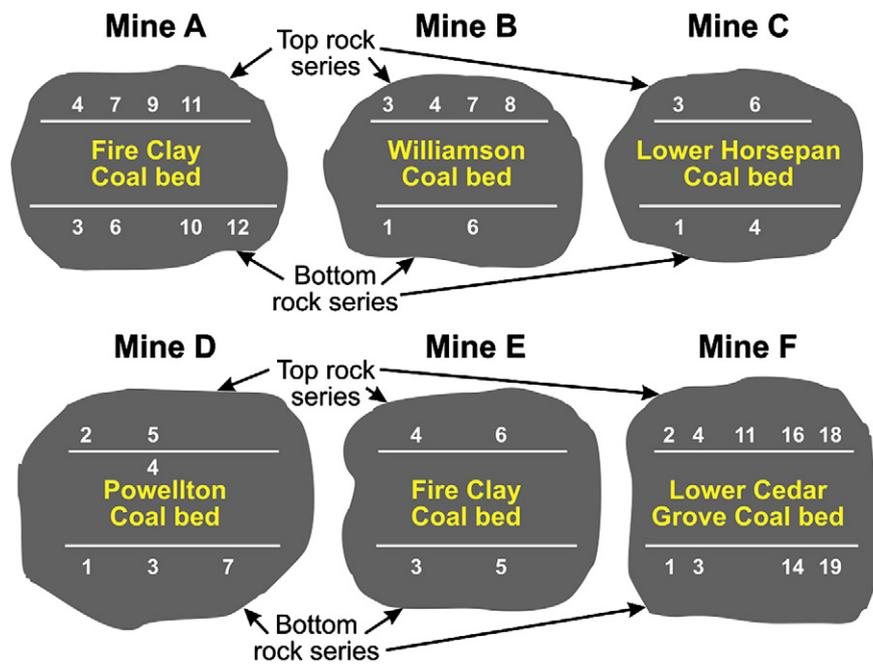


Fig. 4. Field sampling configuration at Central Appalachian Basin sites. Figure shows samples retrieved from mine sites A through F. Samples above or below the coal bed were designated as rock samples (Table 4). Samples vertically aligned above and below the coal bed represent sample pairs that were retrieved from the same location with the mine.

visible and abundant in many of the coal samples. Calcite mineralogy was evident in the coal, and siderite nodules were observed above and below the mined coal unit and often graded into partings within the coal bed.

The Central Appalachian Basin strata included in this study are dominated by sandstones and siliclastic rocks above and sometimes below the coal beds. X-ray diffraction (XRD) data for Central Appalachian Basin rock samples are shown in Table 1. Comparisons between the mineralogical data, cation compositions, and the REE distributions were made for an indication of provenance from different fractions of the rock composition. The data show that potential respirable silica dust sources exist in the overburden and underlying strata in the form of quartz and clay minerals. The most abundant minerals for most samples were quartz, kaolinite and illite, and most also contained plagioclase (indicated as albite) and chlorite. Phosphates and zircon fell below detection limits in all samples, as did hematite,

calcite and ankerite. No carbonates were observed petrographically or in hand samples. Iron sulfides were rarely observed petrographically and in the hand sample specimens. Mineral matter observed in the samples included quartz, feldspar, and clays. Other minerals containing REE that were not detected by XRD are expected to be present in the samples. The coal bed at Mines A and E (Fire Clay Coal bed) contained a persistent tonstein, which can show very elevated REE concentrations compared to the host coal unit.

Typically important carrier minerals for Nd, Sm, and other REE are the clay minerals, phosphates, and zircon (Condie, 1991; Gromet et al., 1984). Some REE may be associated with organic matter which was removed by low-temperature ashing. Prior research on REE associations with elemental groups, as determined by ICP-AES, showed total rare earth element (TREE) concentrations correlated best to Si content ($r^2 = 0.84$), followed by total ash values ($r^2 = 0.83$) and Al ($r^2 = 0.78$) (Schatzel and Stewart, 2003). In the Central Appalachian

Table 1
X-ray diffraction results.^{a,b,c}

Mine	Sample number	Quartz Concentration, %	Kaolinite	Illite	Albite	Chlorite	Pyrite	Siderite	Organic
A	arock10bot	44	8	17	19	11	bd ^d	bd ^d	2
A	arock11top	30	6	36	12	16	bd ^d	bd ^d	1
A	arock4top	27	4	43	9	18	bd ^d	bd ^d	0
C	crock1bot	16	0	62	14	4	bd ^d	bd ^d	5
C	crock3top	23	0	49	17	10	bd ^d	bd ^d	1
C	crock6top	38	0	19	5	1	19	18	1
D	drock3bot	59	2	29	5	bd ^d	bd ^d	bd ^d	6
D	drock5top	50	7	34	6	4	bd ^d	bd ^d	0
D	drock6bot	26	15	48	11	bd ^d	bd ^d	bd ^d	1
E	erock5bot	28	57		13	1	bd ^d	bd ^d	0
E	erock7coal	1	95	bd ^d	3				
E	erock6top	37	4	40	9	10	bd ^d	bd ^d	0
F	frock1bot	33	63		bd ^d	bd ^d	bd ^d	bd ^d	4
F	frock2top	37	4	33	10	16	bd ^d	bd ^d	0
F	frock6top	31	4	43	10	12	bd ^d	bd ^d	0

^a Analyses did not detect any hematite, calcite, ankerite, or bassinite in the samples.

^b Laboratory theoretical detection limits (%) for the analytes were: quartz, 0.1; kaolinite, 0.1; illite, 0.2; albite, 0.2; chlorite, 0.3; pyrite, 0.2; siderite, 0.1; organic matter, 0.1.

^c Modified from Schatzel, 2009.

^d Below detection.

samples, silicate minerals were the only potential sources of REE detected by XRD, and were also the most abundant minerals. The coal parting sample (erock7coal) is composed almost entirely of kaolinite, making it a potential source of silica but not quartz. Other trace minerals with relatively high REE concentrations may be present below detection limits.

The XRD data also yield some implications regarding the major cation analysis. Of the minerals shown in Table 1, the only potential sources of Mg, Na, and K are chlorite, plagioclase feldspar, and illite, respectively. Siderite is present in one sample as a potential source of Ca, but no other Ca mineralogy was detected besides plagioclase feldspar. It is likely that Mn-bearing minerals are present below conventional XRD detection limits in the Central Appalachian Basin.

4.2. Major cation analysis

Prior research on the Central Appalachian Basin (Schatzel, 2009) showed that Ca, Mg, Mn, Na, and K were enriched in the strata immediately overlying the mined coal bed, compared to the strata underlying the mined unit. This geochemical trend was used to identify the sources of respirable silica dust in coal mine continuous miner operations. At four of five sites with a complete set of geochemical data, the sampled respirable dust was measurably closer in Ca, Mg, Mn, Na, and K concentration to the overlying rock than to strata beneath the mined seam.

Major element concentrations for Northern Appalachian Basin samples are shown in Table 2. From this dataset, alkali, alkaline earth, and Mn concentration data were reviewed and plotted together to assess the relationship observed in the Central Appalachian Basin samples (Fig. 5). As no dust samples were available from these mine sites, no comparisons can be made to the respirable dust fraction. However, major element data can be analyzed to evaluate the potential for the same geochemical trends that were present in the Central Appalachian Basin rocks. In the Central Appalachian Basin, rock sampling was conducted at a minimum of two sampling sites within a mine where samples of the overburden and the underlying rock unit

were analyzed (a minimum of four samples). Only one site was sampled at each mine in the Northern Appalachian Basin.

Concentrations of Ca, Mg, and Mn from the Clearfield mine site (Fig. 5a) show relative enrichment in the overburden while Na and K concentrations are very similar for both overlying and underlying rock units. Additional discussion of Northern Appalachian Basin sample cation compositions is given in Schatzel and Stewart (2003). Calcite and other carbonates present in the Lower Kittanning Coal most likely produced the high Ca concentrations in the coal ash. Calcite mineralization was observed in the many of the coal and rock samples from the Northern Appalachian Basin.

At the Enon Valley mine site (Fig. 5b), Mg, Mn, and K are clearly enriched in the overburden compared to the underlying rock unit. Lower Kittanning Coal ash data show a similar pattern to the Clearfield mine site data, with Ca and K being the most concentrated cations. Major cation data from the Homer City site (Fig. 5c) show enrichment of Mn in the overburden, but the remaining four analytes are essentially equal in the overburden and the underclay.

At the Ogle mine site, the overburden and underclay have roughly the same concentrations of the elements plotted (Fig. 5d). Coal ash data show the same high concentrations of Ca and K in the coal ash compared to the other analytes in the plot. At the West Freedom mine site, the overburden is slightly enriched in all plotted elements relative to the underclay, except Ca (Fig. 5e); as with all of the sites, Ca and K concentrations in the coal are the highest of all elements plotted (Fig. 5e). For the analyzed Northern Appalachian Basin samples, the overburden is enriched in the majority of alkali, alkaline earth, and Mn cations of interest at all sites except Homer City. Consequently, the data generally replicate the same geochemical trends observed in the Central Appalachian Basin for the coal overburden and the underlying rock (Schatzel, 2009).

4.3. Rare earth element data

Rare earth element concentrations for Northern Appalachian Basin samples are presented and discussed by Schatzel and Stewart (2003).

Table 2
Cation concentration determinations for Northern Appalachian Basin samples.

Analyte symbol	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
Sample number	%									
ocfd08401040	57.1	18.2	8.2	0.1	1.5	0.4	0.2	3.5	0.9	0.2
ocfd00720795	48.2	17.0	15.0	0.3	1.0	0.8	0.3	2.6	0.9	0.1
ocfd00000165	49.6	20.9	7.8	0.1	1.4	0.2	0.2	3.8	0.8	0.2
ccfd00000070	36.1	16.1	29.3	0.0	0.4	0.7	0.1	1.0	1.5	0.7
ccfd00210290	10.9	10.9	65.2	0.0	0.1	1.5	0.1	0.1	0.1	0.1
ucfd00530640	60.4	21.8	2.8	0.0	0.9	0.1	0.2	3.3	1.10	0.1
oevy00200450	52.9	21.0	9.0	0.1	1.7	0.5	0.2	3.6	0.96	0.2
oevy00000200	44.9	20.5	5.8	0.0	1.4	0.3	0.2	3.3	0.80	0.1
cevy00000140	39.1	21.9	24.7	0.01	0.6	0.5	0.2	1.9	0.76	0.15
cevy00253351	54.2	21.4	8.8	0.01	0.3	1.3	0.2	1.1	2.02	2.06
uevy00730870	54.0	25.7	1.6	0.01	0.4	0.3	0.1	1.5	1.63	0.09
uevy02670000	54.3	27.3	1.7	0.00	0.4	0.3	0.1	1.3	1.64	0.07
ohcy00000185	24.1	8.8	18.8	0.08	0.4	0.2	0.1	1.5	0.41	0.1
chcy00000110	54.2	24.6	8.4	0.03	1.0	0.2	0.2	3.1	1.39	0.07
chcy00110162	52.0	28.8	6.4	0.00	0.6	0.6	0.1	1.7	1.18	0.5
chcy00690840	16.3	13.4	53.5	0.02	0.3	1.5	0.2	0.4	0.34	0.03
uhcy16451855	64.5	16.5	4.4	0.03	0.5	0.1	0.1	2.4	0.97	0.03
uhcy21552355	56.3	16.0	13.1	0.06	0.7	0.2	0.2	2.6	0.96	0.03
uhcy9000190	51.2	25.0	2.9	0.01	0.5	0.1	0.2	2.0	1.39	0.08
oogl00000150	65.7	15.0	1.4	0.01	0.6	0.1	0.2	2.7	0.88	0.05
cogl000951050	39.7	30.1	12.6	0.07	0.3	1.5	0.6	0.3	1.36	0.23
cogl00630900	47.1	35.4	3.0	0.01	0.6	2.0	0.2	2.2	1.59	0.19
uogl00110124	47.8	23.8	3.8	0.02	0.3	0.1	0.1	1.2	1.66	0.11
uogl00124130	63.2	17.6	3.1	0.02	0.5	0.1	0.2	1.9	1.58	0.06
owfm00000195	46.5	22.8	4.5	0.02	1.2	0.3	0.2	3.4	0.93	0.13
cwfm00730142	47.7	25.0	15.0	0.01	1.1	0.8	0.2	3.1	0.92	0.14
cwfm00427560	40.6	32.3	11.9	0.01	0.4	1.8	0.2	0.9	0.74	1.17
uwfm00780820	51.4	26.5	1.8	0.00	0.7	0.8	0.2	2.6	1.24	0.54

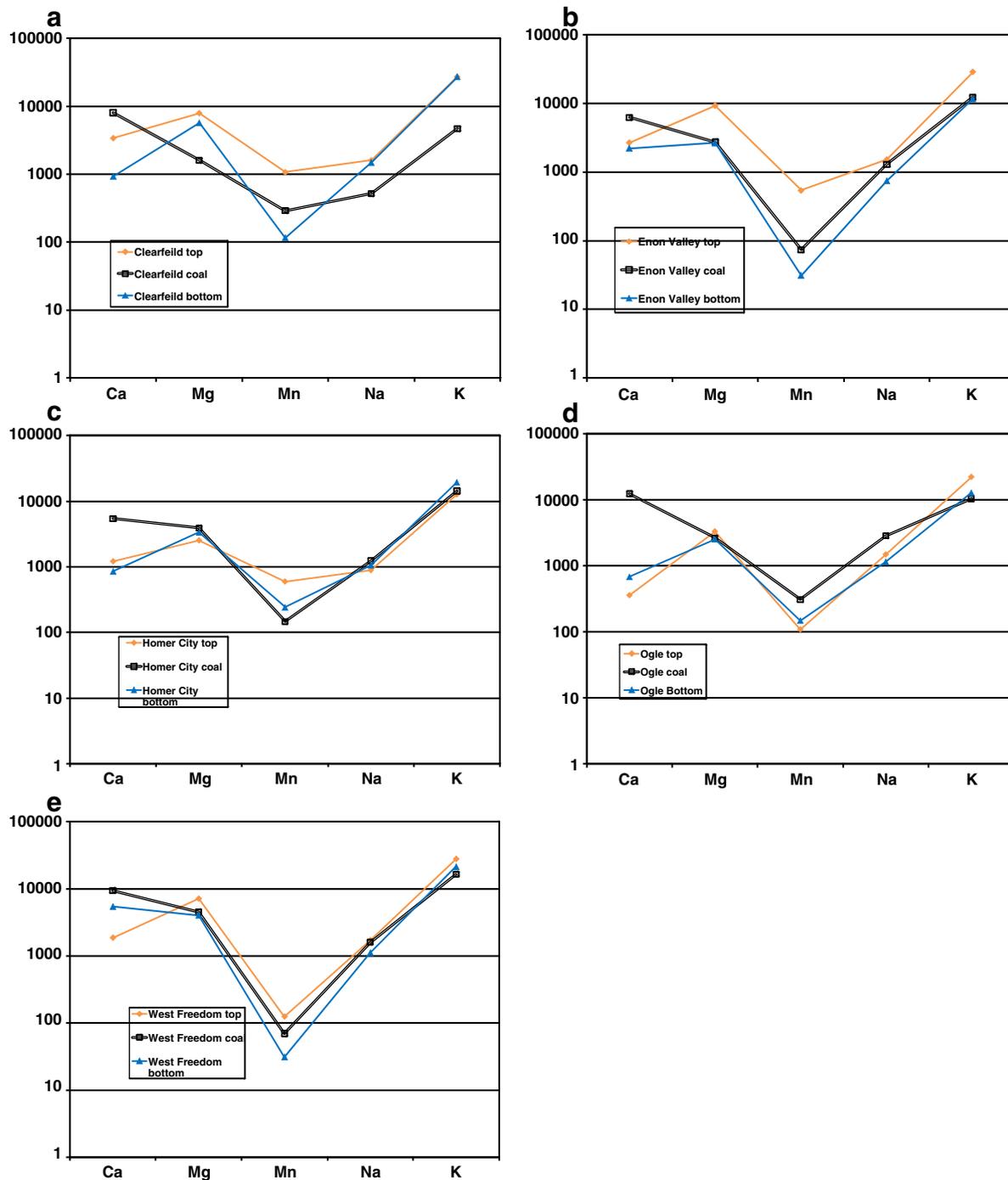


Fig. 5. Northern Appalachian Basin rock and coal sample ICP analyses showing average alkali, alkali earth, and Mn concentrations.

Sample concentrations were compared to the North American Shale Composite (NASC) sedimentary rock standard (Gromet et al., 1984; McLennan, 1989). All of the data from the Northern Appalachian Basin were produced by INAA analysis and therefore show only La, Ce, Nd, Sm, Eu, Tb, Y, and Lu concentrations, making it somewhat more difficult to discern Ce and Eu anomalies.

Fig. 6a shows REE data from the Northern Appalachian Basin. A different plot of this data was given in Schatzel and Stewart (2003). This graph is shown for comparison to a similar plot of REE data from the Central Appalachian Basin. In general, the Northern Appalachian Basin samples show light REE (LREE) enrichment compared to chondrites, and a relatively flat pattern of heavy REE (HREE, Er to Lu). The plot shows that the samples from the underlying rock unit

generally contain higher REE concentrations than the overlying sample REE suites. The exception to this trend is the Clearfield site, where the overlying rock samples are more enriched in REE than the underlying rock unit.

The REE concentrations determined for Central Appalachian Basin samples are presented in Table 3, and plotted in Fig. 6b, which shows the immediate coal bed overburden, the underlying strata, and NASC for comparison. All samples exhibit enrichment in LREE compared to chondrites, as well as negative Eu anomalies. The ICP-MS data from the Central Appalachian Basin produced Eu anomalies ranging from 0.58 to 0.68 for the overburden and 0.36 to 0.64 from the underlying strata. These patterns would appear to be reflective of a common or very similar sediment source and mineral matter composition.

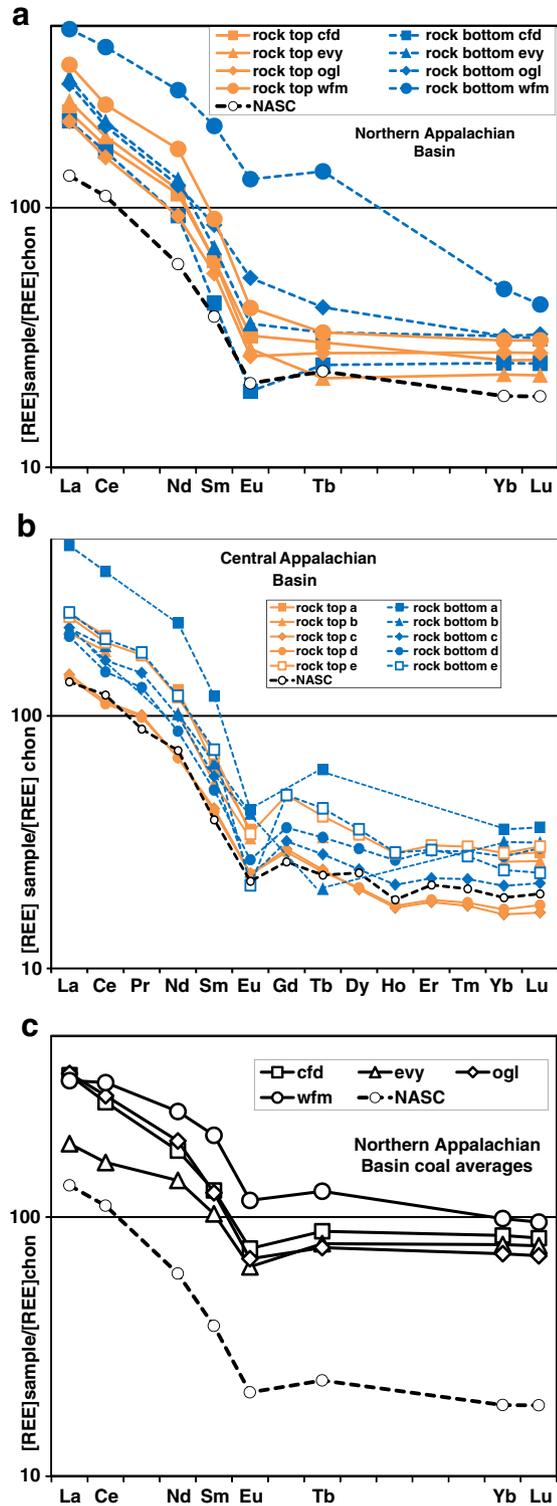


Fig. 6. Rare earth element concentration patterns for the Northern and Central Appalachian sites. (a) Rare earth element concentrations of overburden and underclay for the Northern Appalachian Basin sample sites. (b) Rare earth element concentrations of overlying and underlying formation at the Central Appalachian Basin sample sites.

These data are also very similar to the pattern produced by the NASC, which should be typical for North American sedimentary rock, with an Eu anomaly of 0.69. At the Central Appalachian Basin sites, all samples show elevated concentrations of REE in the underlying rock strata compared to the overlying strata, except for Mine e, in which the overlying and underlying strata have roughly equal REE concentrations.

Most of the overlying and underlying strata from both sites have small negative Ce anomalies, indicating some loss of Ce as Ce^{4+} from oxidative conditions during weathering and/or transport. Cerium anomalies have been used as indicators of marine depositional environments by some researchers although wide variations exist in the application of this concept and in the interpretation of findings (McLennan, 1989; Wilde et al. 1996).

Fig. 7c shows averaged data produced from three coal samples taken from the Lower Kittanning Coal bed, Northern Appalachian Basin. Some differences between the REE patterns produced from the sites are visible. The coal samples (ash) produced REE chondrite normalized with patterns that are quite similar to the rock patterns in the LREE range. However, in the HREE range, the coal patterns show higher concentrations than the rock samples analyzed from either basin. A possible exception is the West Freedom site of the Northern Appalachian Basin, where the bottom rock REE concentrations were elevated. However, the West Freedom site shows relatively high REE concentrations throughout the elemental suite, not just in the HREE range. The coal Eu and Ce anomalies are similar to those determined for the rock samples (Fig. 7c). Comparing the coal REE patterns to the NASC in the figure also shows relative enrichment of HREE concentrations for the coal samples.

4.4. Samarium–neodymium isotope systematics, Northern Appalachian Basin

Samarium–neodymium concentration and Nd isotopic data from the Northern Appalachian Basin samples are presented in Table 4. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are also shown in ϵ notation, where the ϵ_{Nd} value at time T is given by:

$$\epsilon_{\text{Nd}}(T) = 10^4 \frac{^{143}\text{Nd}/^{144}\text{Nd}(T)_{\text{SAMPLE}}}{^{143}\text{Nd}/^{144}\text{Nd}(T)_{\text{CHUR}}} - 1$$

Here the $^{143}\text{Nd}/^{144}\text{Nd}(T)_{\text{CHUR}}$ is the chondritic uniform ratio (assumed to be approximately the same as the bulk earth value) at time T, where T is some time in the past (in years before present), typically the age of formation of the rock unit, when known. $\epsilon_{\text{Nd}}(0)$ is the present-day (measured) value for the sample.

All measured $\epsilon_{\text{Nd}}(0)$ values from the Lower Kittanning Coal and adjacent units are negative (Table 4), with an average of -11.4 , typical of time-averaged growth of $^{143}\text{Nd}/^{144}\text{Nd}$ from a LREE-enriched crustal source. There does not appear to be a consistent trend in $\epsilon_{\text{Nd}}(0)$ between coal ash and the underlying or overlying strata. However, as noted previously (Schatzel and Stewart, 2003), the coal ash is somewhat enriched in REE, including Nd and Sm, relative to the bounding units. In a plot of $\epsilon_{\text{Nd}}(0)$ vs. Nd/Si ratio (Fig. 7), the coal ash defines a field that is enriched in [Nd] but with a greater range of ϵ_{Nd} values than in the combined overlying and underlying strata. This enrichment of [Nd] in coal is also seen Nd/Al, Sm/Si, and Sm/Al ratios (not shown). As both Si and Al are associated with clastic mineral matter and are thought to be relatively immobile during diagenesis, this suggests possible addition of Nd to the coal in excess of the clastic components. Although the dominant mode of most REE in coal is reported to be associated with mineral matter, a portion of the REE content has been found to be combined with coal organic matter (Eskenszy, 1987; Finkelman, 1982; Palmer et al., 1990; Willett et al., 2000). This could account for some differences between the REE concentrations of coal and rock samples. Differences between the Lower Kittanning Coal overburden and the coal and underclay patterns may also be the product of epigenetic mineralization. One possibility is that Nd is captured by vegetation in the coal mire, and later incorporated with the organic matter or pyrite.

To determine the origin of Nd in the coal bed, it is necessary to correct for decay of ^{147}Sm since the time of deposition of the mineral

Table 3
Rare earth element concentrations determined in samples from the Central Appalachian Basin.

Sample number	Elemental concentration, ppm													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
arock4top	57.4	122	nd	60.0	9.0	2.00	nd	1.7	nd	nd	nd	nd	4.5	0.69
arock7top	60.7	131	nd	53.0	9.8	2.10	nd	1.5	nd	nd	nd	nd	4.8	0.72
arock9top	63.2	127	nd	63.0	9.2	2.00	nd	1.4	nd	nd	nd	nd	4.6	0.70
arock11top	55.3	120	nd	50.0	9.1	1.60	nd	1.2	nd	nd	nd	nd	4.3	0.65
arock11Atop	57.1	124	nd	57.0	9.1	2.10	nd	1.2	nd	nd	nd	nd	4.7	0.73
arock3bot	84.6	178	nd	81.0	13.4	1.90	nd	1.7	nd	nd	nd	nd	4.9	0.75
arock6bot	89.9	182	nd	83.0	11.9	2.10	nd	1.7	nd	nd	nd	nd	5.9	0.90
arock10bot	122.0	250	nd	122.0	21.3	3.00	nd	2.4	nd	nd	nd	nd	5.2	0.79
arock12bot	147.0	290	nd	136.0	23.8	2.50	nd	3.1	nd	nd	nd	nd	7.1	1.08
brock3top	44.9	102	nd	40.0	7.8	1.70	nd	1.3	nd	nd	nd	nd	4.3	0.65
brock4top	53.0	112	nd	49.0	8.0	1.80	nd	1.1	nd	nd	nd	nd	4.1	0.61
brock7top	51.8	113	nd	50.0	8.1	2.00	nd	1.2	nd	nd	nd	nd	4.5	0.68
brock1bot	55.0	108	nd	45.0	6.9	1.40	nd	-0.5	nd	nd	nd	nd	4.1	0.60
brock6bot	49.1	120	nd	47.0	12.2	3.20	nd	2.0	nd	nd	nd	nd	6.2	0.93
crock3top	47.6	94.6	12.23	41.6	8.2	1.64	7.2	1.1	6.1	1.2	3.5	0.52	3.2	0.48
crock8top	20.8	42.9	5.71	20.2	4.4	1.02	4.5	0.7	3.8	0.8	2.3	0.34	2.2	0.33
crock1bot	60.2	111.9	14.86	49.4	8.3	1.12	5.5	0.9	5.3	1.1	3.4	0.53	3.5	0.53
crock7bot	44.5	88.2	11.51	40.9	8.7	1.46	7.0	1.1	6.6	1.3	3.9	0.56	3.4	0.52
drock2top	44.6	88.6	11.5	40.8	8.2	1.70	7.4	1.1	6.6	1.2	3.7	0.54	3.4	0.52
drock5top	21.9	46.0	6.06	21.0	4.1	0.95	4.0	0.6	3.6	0.7	2.3	0.34	2.2	0.34
drock1bot	58.7	110	14.0	46.9	8.7	1.69	8.0	1.4	8.0	1.6	4.7	0.70	4.4	0.70
drock1bot	57.2	108	14.1	48.1	9.1	1.69	7.7	1.3	7.5	1.6	4.7	0.71	4.6	0.75
drock3bot	39.1	75.1	9.86	34.8	7.0	1.51	7.4	1.3	7.8	1.6	5.2	0.80	5.1	0.84
drock6bot	48.1	86.3	10.7	35.6	6.5	1.32	6.0	1.0	6.2	1.3	4.0	0.60	3.9	0.61
erock4top	69.4	143	18.7	64.3	12.3	2.09	11.2	1.7	9.6	1.8	5.8	0.88	5.7	0.90
erock6top	46.4	92.9	12.3	43.0	8.6	1.73	7.9	1.2	6.9	1.3	4.0	0.59	3.6	0.57
erock3bot	51.6	94.9	12.1	41.1	7.7	1.58	7.4	1.3	7.4	1.5	4.7	0.71	4.4	0.69
erock5bot	69.0	149	19.7	67.7	13.9	0.81	11.7	1.9	9.9	1.7	4.6	0.64	3.6	0.47

nd—not determined.

matter. In Fig. 8, the data are plotted in a standard isochron diagram. The combined coal ash and adjacent strata from the four sites define a linear trend with a slope that is consistent with the Westphalian D depositional age (~308 Ma; Fig. 8) of the Kittanning Coal unit (Cecil et al., 1985). The actual linear correlation of the data ($R^2 = 0.83$) corresponds to a calculated Sm–Nd “age” of deposition of 318 ± 81 Ma, with an initial $\epsilon_{Nd}(T)$ of -8.9 , consistent with previous work on Paleozoic clastic sediments in eastern North America (Bock et al., 1994, 1998; Cullers et al., 1997; Patchett et al., 1999). While the scatter is significant (as is typical for sedimentary rocks), and well outside of the limits required for accurate age determination, the correlation suggests a partial resetting of the Sm–Nd system at or near the time of deposition. Similar effects were observed by Bock et al. (1994, 1998) in the Middle Ordovician Austin Glen Member of the Normanskill Formation in New York State. Samarium and Nd could have been redistributed along with the rest of the REE during epigenetic

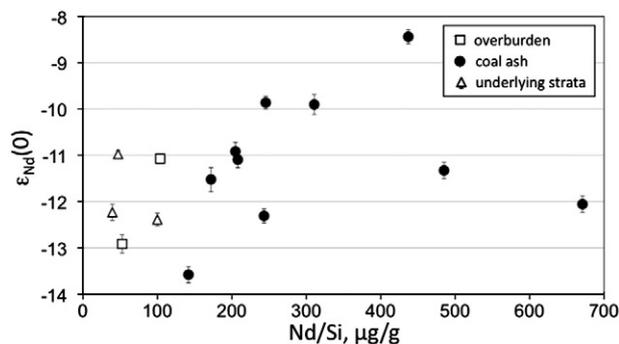


Fig. 7. Nd/Si ratios plotted against $\epsilon_{Nd}(0)$ values for the northern Appalachian sample suite. The $\epsilon_{Nd}(0)$ values represent the present-day chondrite normalized $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. The highest Nd/Si ratios and the greatest range of $\epsilon_{Nd}(0)$ were found in the coal samples compared to the rock samples retrieved from overlying and underlying strata.

formation of pyrite or during early coalification processes, as suggested by Schatzel and Stewart (2003). Most of the higher Sm/Nd samples defining the linear trend in Fig. 8 are coal, consistent with the higher HREE observed in coal relative to the underclay and overburden (Schatzel and Stewart, 2003).

Despite the partial resetting, it can still be possible to obtain useful data about the provenance of the source material for the clastic sediments and coal mineral matter. In Table 4 we show the calculated depleted mantle model age (T_{DM}) for each sample, which can be interpreted as the time that the continental crust material constituting the clastic source was derived from the Earth's mantle (Bock et al., 1994, 1998; DePaolo et al., 1991). For these calculations we use the depleted mantle evolution curve of DePaolo (1981). As indicated, the samples yield a wide range of model ages, from 1.35 to 4.18 Ga. There is a clear disturbance of the T_{DM} systematics, as exemplified by Clearfield coal sample ccfd00360500, which never converges with the mantle value. The theoretical isotopic evolution of these samples and their intersection with the depleted mantle are shown in Fig. 9. While a number of the samples give model ages around 1.5 Ga, several are significantly offset to higher values; most of these are coal samples (solid lines). The convergence of these evolution curves at around the deposition age of ~308 Ma also indicates that Sm/Nd ratios were significantly altered at this time, with many of the coal samples becoming enriched in Sm relative to Nd near the time of deposition. Those samples that appear to be least affected by the Sm/Nd redistribution yield model ages in the range of 1.35 to 1.62 Ga. This is consistent with a sedimentary source consisting of Grenville age rock mixed with an older crustal component, as observed by Bock et al. (1998) for the Normanskill Formation. Most of the variation observed in present-day ϵ_{Nd} values appears to have resulted from the partial resetting and disturbance of Sm/Nd ratios at the time of deposition, rather than from large isotopic differences in source material among the underclay, coal mineral matter, and overburden. The key compositional differences between the three units are expected to be in the syngenetic and authigenic fractions

Table 4

Sm–Nd isotope data for Lower Kittanning Coal, overburden, and underlying strata.

Mine/sample	[Nd] ^a	[Sm] ^a	¹⁴⁷ Sm/ ¹⁴⁴ Nd ^b	¹⁴³ Nd/ ¹⁴⁴ Nd ^c	$\epsilon_{Nd}(0)^{c,d}$	$\epsilon_{Nd}(T)$ (308 Ma)	T _{DM} ^e
	ppm						
Clearfield							
ocfd00000165	24.9	8	0.1205	0.511280 ± 0.000005	− 11.08 ± 0.10	− 8.08	1.59
ccfd00000070	87.3	17.5	0.1214	0.511267 ± 0.000009	− 11.33 ± 0.18	− 8.37	1.62
ccfd000007015	60.8	13.5	0.1345	0.511217 ± 0.000008	− 12.31 ± 0.16	− 9.87	1.99
ccfd00360500	46.8	15.4	0.1986	0.511415 ± 0.000008	− 8.44 ± 0.16	− 8.52	n/a
ucfd00530640	30	4.8	0.0965	0.511213 ± 0.000007	− 12.39 ± 0.14	− 8.45	1.35
Enon Valley							
oevy00000200	12.1	2.2	0.1083	0.511186 ± 0.000010	− 12.91 ± 0.20	− 9.44	1.54
cevy00000140	41.6	10.3	0.1497	0.511279 ± 0.000009	− 11.10 ± 0.18	− 9.25	2.33
cevy00351451	43.5	12.6	0.175	0.511340 ± 0.000011	− 9.91 ± 0.21	− 9.06	3.82
cevy00549730	46.6	13.7	0.1776	0.511342 ± 0.000007	− 9.87 ± 0.14	− 9.12	4.18
uevy00026700	10.3	2	0.117	0.511221 ± 0.000009	− 12.23 ± 0.18	− 9.1	1.62
Homer							
chcy00000110	34	6.1	0.1087	0.511152 ± 0.000009	− 13.58 ± 0.18	− 10.12	1.59
uhcy11151305	11.8	2.8	0.1431	0.511285 ± 0.000004	− 10.98 ± 0.08	− 8.87	2.09
Ogle							
cog00000100	47.1	11.9	0.1523	0.511288 ± 0.000010	− 10.92 ± 0.20	− 9.18	2.41
cog00574840	107.4	20.6	0.1158	0.511230 ± 0.000009	− 12.05 ± 0.18	− 8.87	1.59
cog01020110	32.7	7	0.1288	0.511257 ± 0.000013	− 11.53 ± 0.25	− 8.86	1.78

^a Determined by isotope dilution.^b Uncertainty ≤ 0.3% of measured value.^c In-run uncertainty shown.^d Normalized to ¹⁴³Nd/¹⁴⁴Nd_{CHUR} = 0.511847.^e Calculated relative to the depleted mantle model of DePaolo (1981).

in each unit and the addition of large volumes of preserved organic matter in the coal unit.

The Sm–Nd isotope data from this study suggest that the Lower Kittanning coal and adjacent units are derived from a source region with relatively uniform isotope signatures. Thus the mineralogy of dust-producing materials in lower Kittanning coal mines should not show significant stratigraphic variability. For application of ¹⁴³Nd/¹⁴⁴Nd as a tool to discriminate dust sources, a dust source signature would thus be most effective when there are extraneous sources of Nd in the coal mine system. One example of this would be tonsteins of volcanic origin. The clastic portion of coal mineral matter has an isotope signature reflective of its weathering source, while volcanic ash could have sources that are quite variable, from suboceanic mantle (positive ϵ_{Nd} values) to Precambrian lower crust (highly negative ϵ_{Nd} values). In this case, ϵ_{Nd} would be very effective at differentiating between tonstein-derived dust and other sources.

4.5. Implications on respirable dust composition from this study

Results from this research were produced from rock samples taken from two different coal basins with very different tendencies in producing silicosis or CWP. The Lower Kittanning Coal bed shows one set of compositional characteristics, and the Central Appalachian units display similar compositions to each other and very different mineralogy compared to the Central Appalachian Basin. Samples retrieved from the Central Appalachian Basin represent a region with the most severe incidence rates for CWP in the US (Huang et al., 2005). The Northern Appalachian Basin, including the Lower Kittanning stratigraphy, has not produced unusually high incidence rates of silicosis or CWP. It is also well established that, although there can be variations in overburden and underlying rock units associated with coal seams due to facies changes, the Central Appalachian Basin is dominated by sandstones and siliciclastic rocks above and

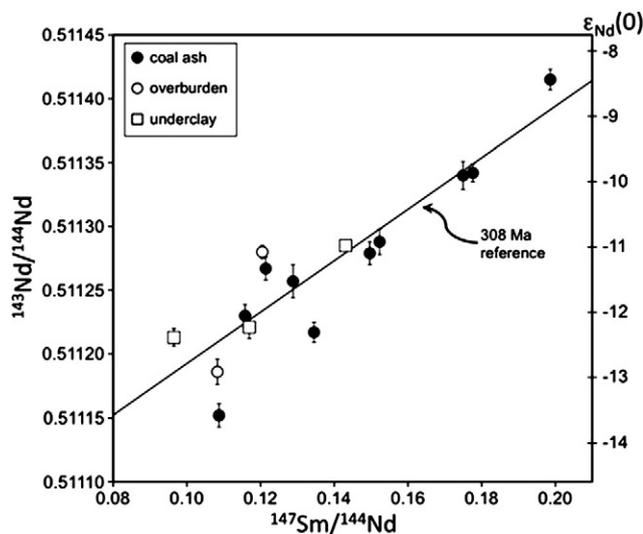


Fig. 8. Pseudo-isochron plot for the Lower Kittanning Coal bed, the overlying Columbian Shale, and the underlying paleosol, Northern Appalachian Basin. The calculated “age” from this plot is broadly consistent with the depositional age of the sediments, suggesting partial resetting of the Sm–Nd system at the time of deposition.

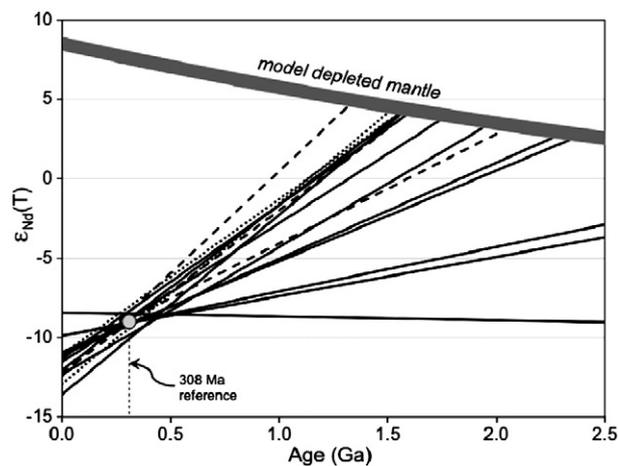


Fig. 9. Depleted mantle model age evolution diagram for Northern Appalachian Basin samples. Solid lines are coal mineral matter, dashed lines are underclay samples, and dotted lines are overburden samples. The convergence of the lines around the 308 Ma deposition age suggests partial resetting of the Sm–Nd system at that time with an ϵ_{Nd} value of about 9.0 (gray circle). Model ages older than ~1.6 Ga are probably spurious, caused by redistribution of Sm/Nd during resetting. Note that most of these data are from coal mineral matter.

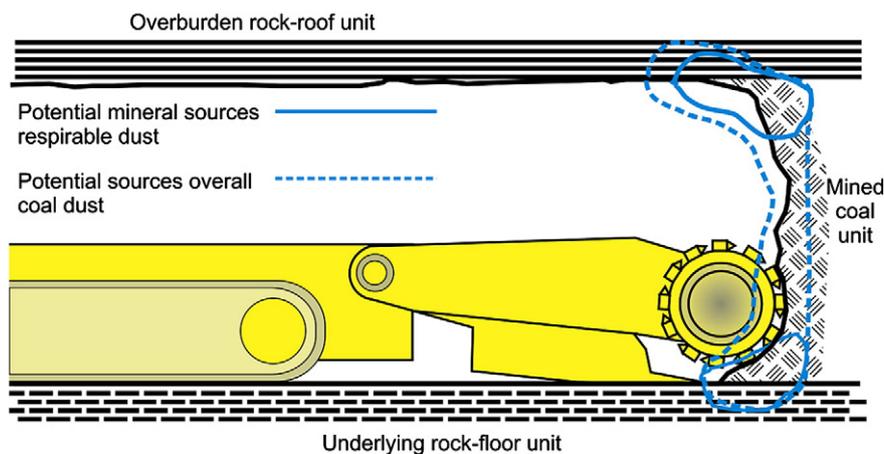


Fig. 10. Continuous mining machine producing mine dust.

sometimes below the coal beds (Cecil, 1990). The Northern Appalachian Basin sites typically included shale or sandy shale overburden and an underlying paleosol.

The mineralogy and geochemistry data from this study offer some additional explanation for the differing silicosis and CWP incidence rates for the basins. The Northern Appalachian Basin contains significant pyrite and therefore relatively high quantities of bio-available iron (Huang et al., 2005). Both overburden and coal samples from this study, associated with the Lower Kittanning Coal bed contained visibly abundant quantities of pyrite and carbonate, as observed in the samples and shown by ICP-AES analyses (Schatzel and Stewart, 2003). Although research shows the high pyrite content would exacerbate CWP and silicosis tendencies, the carbonate content tends to have a buffering effect and neutralizes, to a degree, the health hazard posed by the high iron content (Huang et al., 1998). A Chinese study found nano-quartz particles in a bituminous coal seam and in the lungs of rural residents who were burning this coal in their homes (Dai et al., 2008). Although the studies focused on the particles as a carcinogen, the authors documented a mechanism for respirable silica produced from coal becoming embedded in victim's lungs. In a petrographic characterization of organic matter, no nano-quartz particles were observed in coal samples from either Appalachian basin. However, the submicron particle size observed in the Chinese samples was near the limit of resolution for optical mineralogy. Any nano-quartz that was present would have been included in the digestion and bulk analysis techniques used in this study.

In the Central Appalachian Basin samples, both iron and carbonates contents were very low. Both hand sample examination and XRD analysis failed to find significant quantities of iron sulfides or carbonates (Table 1). However, the high Si and quartz content produces dust particles that are silica rich during the mining process, which present a respiratory hazard to the miners (Schatzel, 2009). The Central Appalachian Basin portion of this study generally includes small, near surface mines, which typically require only the minimum ventilation air quantities to remove noxious gases. The airflow quantities measured at the mines' last open crosscut were about 14 m³/s; the minimum quantity allowed by federal statutes to remove noxious gases produced by the mining process. The limited airflow typical of this mining region restricts the amount of air available to dilute respirable dust.

Data from the Nd isotope analyses show that the primary mineral matter in the Lower Kittanning Coal bed, Northern Appalachian Basin, is produced from the same source as the clastic mineral matter in the rock units above and below the coal bed. A wealth of research has produced compositional data on coal samples, but far less information is available on the geochemistry and mineralogy of rock units adjacent to coal beds. For Northern Appalachian Basin coal beds, it is

anticipated that primary mineralogy will have a common source throughout the Pennsylvanian period of coal deposition, due to unchanging source terrains and distribution patterns (Patchett et al., 1999). Although Nd analysis was not done in the Central Appalachian Basin, the apparent constancy of erosional patterns distributing material from source terrains to basins in this region during the Pennsylvanian suggests the primary mineral source was the same between the mined coal bed, overburden, and underlying unit.

Data from the Central Appalachian Basin samples show that respirable dust samples were most likely produced from the rock overlying the mined coal beds (Schatzel, 2009). A similar geochemical trend is present in the rock samples from the Northern Appalachian Basin. Although no dust samples were collected in this basin, it is proposed that respirable dust samples can be linked to their source on the basis of sample geochemistry. Due to the relative commonality of continuous miner practices, it is expected that the roof source of respirable dust will not change, although this will require validation (Fig. 10). It is suggested that continuous miner water sprays can be modified to more directly address roof dust sources if the parent rock for respirable dust is shown to be consistently overlying rock at all sites. This knowledge could be very valuable for the configuration of water sprays for dust control on continuous miners. A water spray block directed at the mine roof is undergoing trials at an Illinois Basin mine, based in part on the findings from the published study by Schatzel (2009) (Chugh et al., 2011).

5. Summary and conclusions

This research combines analyses from multiple prior studies and new analysis to investigate mineral matter provenance utilizing REE and Nd isotopes. To complete this study, 11 mine sites in the Northern and Central Appalachian Basins of the United States were visited and sampled. The methods in the earlier studies were not identical, but the geochemical data presented here offer a range compositional analyses and insights for the sample suite. Of the geochemical methods utilized in this study, some techniques are conventional practices routinely used by commercial laboratories. Other geochemical techniques employed were novel for coal research, and were only possible in a laboratory research environment.

The mineralogy of rock samples retrieved from the Central Appalachian Basin was characterized by XRD. Quartz and clays (illite and kaolinite) were the most abundant minerals detected in the sample suite. These three minerals accounted for the great majority of the sample mineralogies, with albite (plagioclase feldspar) and chlorite being the next most abundant minerals. The abundance of these minerals in the samples is quite typical of bituminous rank, Pennsylvanian age coal. Carbonate and the iron-bearing minerals pyrite and

siderite are rare in the Central Appalachian Basin, and were rarely found in hand samples and in the XRD results. The ICP-AES data reflected these mineral matter compositions.

Samples from the Northern Appalachian Basin showed significant carbonate and iron sulfide mineral content. Carbonates were present in the form of siderite and calcite. Abundant pyrite was noted in the coal and overburden samples. The ICP-AES data showed a tendency toward enriched Ca, Mg, Mn, Na, and K in the overburden above the mined coal seams in both basins when compared to the underlying rock. It has been hypothesized that this geochemical tendency may have been produced by late stage epigenesis associated with marine incursions. This geochemical trend was observed in both basins, despite the significant differences between the basins in the mineralogy of the coal beds and adjacent rock units.

Rare earth element data were reviewed for rock samples from the Northern and Central Appalachian Basins. Predominantly negative anomalies for Eu and Ce were present in the samples when compared to chondrite data. The negative Ce anomalies may be indicative of oxidative loss of Ce^{4+} during weathering and/or transport. The TREE totals for the samples are inferred from the graphs and do show a tendency towards enrichment in the underlying rock when compared to the overburden. For the Northern Appalachian samples, the coal mineral matter is generally enriched in REE, especially HREE, compared to underlying and overlying units.

Neodymium isotopic studies have been performed on sedimentary rocks for provenance studies, but are extremely rare in coal science. Determinations of Nd isotopic ratios were made for Northern Appalachian Basin samples. For the Lower Kittanning Coal bed, the overlying rock unit and underlying rock strata, measured $\epsilon_{Nd}(0)$ values range from -13.6 to -8.4 , with no clear trends between the coals and the under/overlying rock units. The $\epsilon_{Nd}(T)$ (time T, the time of deposition, estimated at ~ 308 Ma) fell within a much narrower range, averaging -8.9 . We interpret these results as indicating partial re-equilibration of the samples at the time of deposition, with a greater spread in Sm/Nd produced during deposition or diagenesis. While calculated depleted mantle model ages are variable due to this resetting, we suggest that the source region was a relatively restricted mixture of Grenville and older continental crust. The findings of this study are consistent with those of Patchett et al. (1999), which showed an Appalachian sedimentary source terrain throughout the Pennsylvanian of eastern North America.

There are implications related to respiratory health for underground coal mine workers based on the study findings. The compositional data from coal measure rocks associated with both basins are in agreement with CWP and silicosis incidence rates for underground coal mine workers. Findings from recent studies have shown that respirable dust composition plays an important role in determining its toxicity. If a parent rock source can be demonstrated to be in the overlying rock (roof) in all continuous miner operations, dust controls on miner can be reconfigured to preferably address overhead dust sources. The data presented here can be used in part to validate parent source rocks for respirable dust in mines.

Disclaimer

The findings and conclusions in this report are those of the author and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

References

- Bennett, P.C., Melcer, M.E., Seigel, D.I., Hassett, J.P., 1988. The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C. *Geochimica et Cosmochimica Acta* 52, 1521–1530.
- Bock, B., McLennan, S.M., Hanson, G.N., 1994. Rare earth element redistribution and its effects on the neodymium isotope system in the Austin Glen Member of the Normanskill Formation, New York, USA. *Geochimica et Cosmochimica Acta* 58, 5245–5253.
- Bock, B., McLennan, S.M., Hanson, G.N., 1998. Geochemistry and provenance of the Middle Ordovician Austin Glen Member (Normanskill Formation) and the Taconian Orogeny in New England. *Sedimentology* 45, 635–655.
- Bohor, B.F., Triplehorn, D.M., 1993. Tonsteins: altered volcanic ash layers in coal-bearing sequences. *Geological Society of America Special Paper* 285, pp. 44.
- Cecala, A.B., O'Brien, A.D., Schall, J., Colinet, J.F., Fox, W.R., Franta, R.J., Joy, J., Reed, W.R., Reeser, P.W., Rounds, J.R., Schultz, M.J., 2012. *Dust Control Handbook for Industrial Minerals Mining and Processing*. NIOSH RI 2012–112.
- Cecil, C.B., 1990. Paleoclimate controls on stratigraphic repetition of chemical and silicate rocks. *Geology* 18, 533–536.
- Cecil, C.B., Stanton, R.W., Allshouse, S.D., Finkelman, R.B., 1978. Geologic controls on mineral matter in the Upper Freeport coal bed. *Proceedings: Symposium on coal cleaning to energy and environmental coals*, U.S. Environmental Protection Agency, 600017-79-098a, 1, pp. 110–125.
- Cecil, C.B., Stanton, R.W., Neuzil, S.G., Dulong, F.T., Ruppert, L.F., Pierce, B.S., 1985. Paleoclimate controls on late Paleozoic sedimentation and peat formation in the Central Appalachian Basin, USA. *International Journal of Coal Geology* 5, 195–230.
- Chen, W., Hnizdo, E., Chen, J.-Q., Attfield, M.D., Gao, P., Hearl, F., Lu, J., Wallace, W.E., 2005. Risk of silicosis on cohorts of Chinese tin and tungsten miners and pottery workers (I): an epidemiological study. *American Journal of Industrial Medicine* 48, 1–9.
- Chugh, Y.P., Mondal, K., Kollipara, V.K., Gurley, H., Yerram, R., Relangi, D.D., 2011. Characterization of coal and quartz and dust in Interior Basin coal mines. *SME Annual Meeting Preprint* 11-132, pp. 7.
- Colinet, J.F., Rider, J.P., Listak, J.M., Organiscak, J.A., Wolfe, A.L., 2010. Best practices for dust control in coal mining Pittsburgh, PA: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2010-110, Information Circular 9517, pp. 1–76.
- Condie, K.C., 1991. Another look at rare earth elements in shales. *Geochimica et Cosmochimica Acta* 55, 2527–2531.
- Crowley, S.S., Ruppert, L.F., Belkin, H.E., Stanton, R.W., Moore, T.A., 1993. Factors affecting the geochemistry of a thick, sub-bituminous coal bed in the Powder River Basin: volcanic, detrital, and peat forming processes. *Organic Geochemistry* 20, 843–853.
- Cullers, R.L., Bock, B., Guidotti, C., 1997. Elemental distributions and neodymium isotopic compositions of Silurian metasediments, Western Maine, USA. *Redistribution of the rare earth elements. Geochimica et Cosmochimica Acta* 61 (9), 1847–1861.
- Dai, S., Tian, L., Chou, C.L., Zhou, Y., Zhang, M., Zhao, L., Wang, J., Yang, Z., Cao, H., Ren, D., 2008. Mineralogical and compositional characteristics of Late Permian coals from an area of high lung cancer rate in Xuan Wei, Yunnan, China: Occurrence and origin of quartz and chamosite. *International Journal of Coal Geology* 76, 318–327.
- DePaolo, D.J., 1981. Neodymium isotopes in the Colorado Front Range and crust-mantle evolution in the Proterozoic. *Nature* 291, 193–196.
- DePaolo, D.J., Linn, A.M., Schubert, G., 1991. The continental crustal age distribution: Methods of determining mantle separation ages from Sm–Nd isotopic data and application to the southwestern United States. *Journal of Geophysical Research* 96, 2071–2088.
- Dodgson, J.G., Hadden, G.G., Jones, C.O., Walton, W.H., 1971. Characteristics of the airborne dust in British coal mines. In: Walton, W.H. (Ed.), *Inhaled Particles III*. Unwin Brothers Ltd., Surrey, England, pp. 757–781.
- Eskenazy, G.M., 1987. Rare earth elements and yttrium in lithotypes of Bulgarian coals. *Organic Geochemistry* 11 (2), 83–89.
- Eskenazy, G.M., 1999. Aspects of the geochemistry of rare earth elements in coal: an experimental approach. *International Journal of Coal Geology* 38, 285–295.
- Finkelman, R.B., 1982. The origin occurrence, and distribution of the inorganic constituents in low rank coals, DOE sponsored workshop on Basic Coal Science, pp. 69–90. Houston, TX, December 8–9, 1981.
- Finkelman, R.B., 1993. Trace and minor elements in coal. In: Engles, M.H., Macko, S.A. (Eds.), *Organic geochemistry: Principles and Applications*. Plenum, New York, pp. 593–607.
- Finkelman, R.B., Stanton, R.W., 1978. Identification and significance of accessory minerals from a bituminous coal. *Fuel* 57, 763–768.
- Gluskoter, H.J., 1967. Clay minerals in Illinois coals. *Fuel* 44, 285–291.
- Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B., Kuhn, J.K., 1977. Trace elements in coal: occurrence and distribution. *Illinois State Geological Survey Circular*, 499, pp. 154.
- Gromet, P.L., Dymek, R.F., Haskin, L.A., Korteve, R.L., 1984. The North American shale composite: its compilation, major and minor trace element characteristics. *Geochimica et Cosmochimica Acta* 48, 2469–2482.
- Hanson, G.N., 1980. Rare earth elements in petrogenetic studies of igneous systems. *Annual Review of Earth and Planetary Sciences* 8, 371–406.
- Harrison, J.C., Chen, J.-Q., Miller, W., Chen, W., Hnizdo, L.J., Chisolm, W., Keane, M., Gao, P., Wallace, W., 2005. Risk of silicosis on cohorts of Chinese tin and tungsten miners and pottery workers (II): workplace-specific silica particle surface composition. *American Journal of Industrial Medicine* 48, 10–15.
- Harvey, R.D., Ruch, R.R., 1986. Mineral matter in Illinois and other US coals. In: Vorres, K.S. (Ed.), *Mineral Matter in Ash and Coal: American Chemical Society Symposium Series*, 301, pp. 10–40.
- Hicks, D., Nagelschmidt, G., 1943. Special Report of the Service Medical Research Council, 244, pp. 153–186.
- Hill, P.A., 1988. Tonsteins of Hat Creek, British Columbia: a preliminary study. *International Journal of Coal Geology* 10, 155–175.

- Hower, J.C., Williams, D.F., Eble, C.F., Sakulpitakafon, T., Moecher, D.P., 2001. Brecciated and mineralized coals in Union County, western Kentucky. *International Journal of Coal Geology* 47, 223–234.
- Huang, X., Fournier, J., Koenig, K., Chen, L.C., 1998. Buffering capacity of coal and its acid soluble Fe²⁺ content, possible role in coal workers' pneumoconiosis. *Chemical Research in Toxicology* 11, 722–729.
- Huang, X., Li, W., Attfield, M.D., Nadas, A., Frenkel, K., Finkelman, R.B., 2005. Mapping and prediction of coal worker's pneumoconiosis with bioavailable iron content in the bituminous coals. *Environmental Health Perspectives* 113, 964–968.
- IARC, 1997. IARC monographs on the evaluation of carcinogenic risks to humans: silica, some silicates, coal dust and para-aramid fibrils, Vol. 68. World Health Organization, International Agency for Research on Cancer, Lyon, France.
- Laney, A.S., Petsonk, E.L., Attfield, M.D., 2010. Pneumoconiosis among underground bituminous coal miners in the United States: is silicosis becoming more frequent? *Occupational and Environmental Medicine* 67, 652–656.
- Linn, A.M., DePaolo, D.J., Ingersoll, R.V., 1991. Nd–Sr isotopic provenance analysis of Upper Cretaceous Great Valley fore-arc sandstones. *Geology* 19, 803–806.
- Mackowsky, M.Th., 1968. Mineral matter in coal. In: Murchison, D.G., Westoll, D.S. (Eds.), *Coal and Coal Bearing Strata*. Oliver and Boyd, London, pp. 309–321.
- Mariano, A.N., 1989. Economic geology of rare earth minerals. In: Lipin, B.R., McKay, G.A. (Eds.), *Geochemistry and mineralogy of rare earth elements: Mineralogical Society of America Reviews in Mineralogy*, 21, pp. 309–334.
- McCabe, P.J., 1993. Sequence stratigraphy of coal bearing strata. AAPG short course, AAPG New Orleans, LA, April 25–28, 1993, pp. 81.
- McLennan, S.M., 1989. Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. In: Lipin, B.R., McKay, G.A. (Eds.), *Geochemistry and mineralogy of rare earth elements: Mineralogical Society of America Reviews in Mineralogy*, 21, pp. 169–200.
- Miller, R.G., O'Nions, R.K., Hamilton, P.J., Welin, E., 1986. Crustal residence ages of clastic sediments, orogeny and crustal evolution. *Chemical Geology* 57, 87–99.
- Nelson, B.K., DePaolo, D.J., 1988. Comparison of isotopic and petrographic provenance indicators in sediments from Tertiary continental basins of New Mexico. *Journal of Sedimentary Petrology* 58, 348–357.
- Palmer, C.A., Lyons, P.C., 1996. Selected elements and major minerals from bituminous coals as determined by INAA: implications for removing environmentally sensitive elements from coal. *International Journal of Coal Geology* 32, 151–166.
- Palmer, C.A., Lyons, P.C., Brown, Z.A., Mee, J.S., 1990. The use of trace element concentrations in vitrinite concentrates and companion whole coals (hvA bituminous) to determine organic and inorganic associations. *Geological Society of America Special Paper* 248, 55–62.
- Patchett, P.J., Ross, G.M., Gleason, J.D., 1999. Continental drainage in North America during the Phanerozoic from Nd isotopes. *Science* 283, 671–673.
- Ramani, R.V., Mutmanský, J.M., Bhaskar, R., Qin, J., 1987. Experiments, Results and Analysis. Contract Report H058031. : *Fundamental Studies on the Relationship Between Quartz Levels in the Host Material and the Respirable Dust Generated During Mining*, Volume 1. U.S. Bureau of Mines.
- Rao, P.D., Gluskoter, H.J., 1973. Occurrence and distribution of minerals in Illinois coal. Illinois State Geological Survey, Circular, 476. pp. 56.
- Rao, P.D., Walsh, D.E., 1997. Nature and distribution of phosphorous minerals in Cook Inlet coals, Alaska. *International Journal of Coal Geology* 33, 19–42.
- Rao, P.D., Walsh, D.E., 1999. Influence of environments of coal deposition on phosphorus accumulation in a high latitude, northern Alaska coal seam. *International Journal of Coal Geology* 38, 261–284.
- Rimmer, S.M., Davis, A., 1986. Geologic controls on the inorganic composition of the Lower Kittanning Coal Seam. In: Vorres, K.S. (Ed.), *Mineral Matter in Coal*, American Chemical Society Symposium Series No. 301, pp. 41–51.
- Robock, K., Bauer, H.D., 1990. Investigations into the specific fibrogenicity of mine dusts in hardcoal mines of counties of the European Community. *Proc. VIlth International Pneumoconiosis Conference, Part 1: Pittsburgh, 1988: DHHS (NIOSH) publication No. 90-108, Part 1, pp. 280–283.*
- Ruppert, L.F., Neuzil, S.G., Cecil, C.B., Kane, J.S., 1993. Inorganic constituents from samples of a domed and lacustrine peat, Sumatra, Indonesia. In: Cobb, J.C., Cecil, C.B. (Eds.), *Modern and ancient coal forming environments: Geological Society of America Special Paper*, 286, pp. 83–96.
- Schatzel, S.J., 2009. Identifying sources of respirable quartz and silica dust in underground coal mines in southern West Virginia, western Virginia, and eastern Kentucky. *International Journal of Coal Geology* 78, 110–118.
- Schatzel, S.J., Stewart, B.W., 2003. Rare earth element sources and modification in the Lower Kittanning coal bed, Pennsylvania: implications for the origin of coal mineral matter and rare earth element exposure in underground coal mines. *International Journal of Coal Geology* 54, 223–251.
- Sholkovitz, E.R., Shen, G.T., 1995. The incorporation of rare earth elements in modern coral. *Geochimica et Cosmochimica Acta* 59, 2749–2756.
- Stach, E., Mackowsky, M.-T.h., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., 1982. *Stach's Textbook of Coal Petrology*. Gebrüder Borntraeger, Berlin. 535 pp.
- Taylor, C.D., Chilton, J.E., Goodman, G.V., 2010. Guidelines for the control and monitoring of methane gas on continuous mining operations. DHHS (NIOSH) Publication No. 2010-141, Report of Investigations 9523, pp. 1–75.
- Vance, D., Burton, K., 1999. Neodymium isotopes in planktonic foraminifera: a record of the response of continental weathering and ocean circulation rates to climate change. *Earth and Planetary Science Letters* 173, 365–379.
- Vassilev, S.V., Vassileva, C.G., 1996. Occurrence, abundance and origin of minerals in coals and coal ashes. *Fuel Processing Technology*, 48, pp. 85–106.
- Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, 134–168.
- Ward, C.R., Corcoran, J.F., Saxby, J.D., Read, H.W., 1996. Occurrence of phosphorus minerals in Australian coal seams. *International Journal of Coal Geology* 30, 185–210.
- Wilde, P., Quinby-Hunt, M.S., Erdtmann, B.D., 1996. The whole-rock cerium anomaly: a potential indicator of eustatic sea-level changes in shales of the anoxic facies. *Sedimentary Geology* 101, 43–53.
- Willett, J.C., Finkelman, R.B., Mroczkowski, S., Palmer, C.A., Kolker, A., 2000. Semi-quantitative determination of the modes of occurrence of elements in coal: results from an international round robin project. In: Davidson, R.M. (Ed.), *Modes of occurrence of trace elements in coal. : Reports from an International Collaborative Programme*. IEA Coal Research, London, UK. CD-ROM.
- Williams, E.G., 1957. *Stratigraphy of the Allegheny series in the Clearfield Basin*. PhD. Thesis, The Pennsylvania State University, Vol. 1 and 2, pp. 582.
- Williams, E.G., Bragonier, W.A., 1974. Controls of early Pennsylvanian sedimentation in western Pennsylvania. In: Briggs, G. (Ed.), *Carboniferous of Southeastern United States: Geological Society of America Special Paper*, 148, pp. 135–152.
- Worrall, F., Pearson, D.G., 2001. Water-rock interaction in an acidic mine discharge as indicated by rare earth element patterns. *Geochimica et Cosmochimica Acta* 65, 3027–3040.
- Yang, J.-H., Zhou, X.-H., 2001. Rb–Sr, Sm–Nd, and Pb isotope systematics of pyrite: Implications for the age and genesis of lode gold deposits. *Geology* 29, 711–714.
- Yokoyama, T., Makishima, A., Nakamura, E., 1999. Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. *Chemical Geology* 157, 175–187.
- Zhang, S., Shan, X.Q., Li, F., 2000. Low molecular weight organic weight acids as extractant to predict plant bioavailability of rare earth elements. *International Journal of Environmental Analytical Chemistry* 76 (4), 283–294.
- Zhong, S., Mucci, A., 1995. Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25 °C and 1 atm, and high dissolved REE concentrations. *Geochimica et Cosmochimica Acta* 59, 443–453.