



Short communication

Occurrence of carbon nanotubes and implication for the siting of elements in selected anthracites

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ABSTRACT

Petrographic, geochemical, and electron microbeam investigations of selected anthracites and anthracite-rank coaly shales were conducted. The Pennsylvania, Rhode Island, and KwaZu-Natal anthracites show an enrichment in the middle to heavy rare earths (REE) while the Virginia semi-anthracite exhibited a decreasing trend through the light REE, a peak in Gd, and a depletion in the heavy REE. Substitution of As, Hg, and Se in pyrite was most apparent in the Virginia coal. The Pennsylvania, Rhode Island, and KwaZu-Natal anthracites contained spherical carbon nanotube (CNT) structures. The CNTs contained several elements, including Hg, Cd, F, Cl, and Br. While CNTs are known to be produced from coals of varying ranks, this seems to be the first report of naturally occurring CNTs.

1. Introduction

Coal currently accounts for nearly half of global electricity, most prominently in countries such as China and India, with declining usage in the US and much of the EU, among others [1]. However, compared to other uses, such as for coke manufacturing, the economic value of coal for energy generation is very low. Given this scenario, we need to seek a better understanding of how economically important constituents, such as critical elements [2–8], raw materials for activated carbon, many common and industrial chemicals [2], and nanometer phases [9–11], can be recovered or produced from coal. C-nanotubes and other C-nanophases are a class of carbon allotropes with various characteristics and unique properties (superconductivity, ferromagnetism, sorption, among others), which makes them of particular interest in different fields of application, such as medicine [12], materials sciences [13], energy [14], and personal care products [15]. Up to now, C-nanotubes have not been detected in coals. The natural and incidental combustion of hydrocarbons can generate C-nanophases, producing an environmental exposure [16]. However, as a result of their incorporation into industrial and consumer products, human and environmental exposure

should increase in the coming years.

The present study aims to identify trace phases such as carbon nanotubes, but also to provide a basis for further studies of carbon nanotubes, graphenes, and other new products from anthracites. To date, the natural occurrence of carbon nanotubes in anthracite samples has not been reported. The aim of this study is to discuss certain features of the geochemistry, petrology and, in particular, the nanometer-scale structure of the coals. In turn, this could establish the basis for further studies of anthracites.

2. Materials and methods

2.1. Sampling and coal areas

Four semi-anthracite, anthracite-, and meta-anthracite-rank samples, as well as a non-coal sample, were collected from Rhode Island, Virginia, Pennsylvania in the USA, KwaZu-Natal in South Africa, and Saxony in Germany (non-coal sample), which were numbered in this paper as 69759, 69761, 69762, 69763, and 69760, respectively. The Rhode Island, Virginia, and German samples were from a collection of

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coals and rocks originally at Vanderbilt University and now archived at the University of Kentucky Center for Applied Energy Research (CAER). The samples came from mines that were active in the late-19th and early-20th centuries. The Pennsylvania sample was collected by Hower at an active mine in Schuylkill County. The South Africa sample was collected by Nicola Wagner (University of Johannesburg) at an active mine. The samples included in this study represent different coal ranks within the broad semi-anthracite/anthracite range and to represent (potentially) different types of metamorphism, including contact metamorphism by an igneous intrusion (KwaZu-Natal).

Previous studies of these coalfields provided the geologic and coal quality framework for this investigation. Lewis and Hower [17] and Hower et al. [18] studied the metamorphism and petrology of the Mississippian Valley Fields Virginia. Quinn and Glass [19] and Skehan et al. [20] investigated the Pennsylvanian-age Narragansett Basin coals, including examples near the Rhode Island coal in this study. The petrology and mineralogy of Pennsylvanian-age anthracites in the Pennsylvania Anthracite Fields have been studied by Levine [21,22], Levine and Davis [23], Juster et al. [24], Daniels and Altaner [25], Daniels et al. [26–28], and Hower et al. [29,30]. These three Appalachian coalfields were also discussed by Hower et al. [31] and Ruppert et al. [32,33]. Hower et al. [29] previously discussed the Permian-age KwaZu-Natal coal.

The Pennsylvanian-age Frankenstein (Saxony, Germany) deposit is less well known than the coals noted above. This is not to be confused with an Upper Silesia, Poland, Ni-rich location of the same name described by Beyschlag et al. [34, p. 453]. As noted above, the Vanderbilt University coal collection, donated to the University of Kentucky CAER in 2006, generally was from mines active in the late-19th/early-20th centuries. This provides a window into deposits not currently being mined, with the caveat that the locations were not necessarily well defined and were not always what would be conventionally considered to be a coal.

2.2. Petrology

Petrographic examination of crushed (840- μ m top size) samples was made on Leitz Orthoplan microscopes at the CAER. The coal particles were mounted in epoxy in 2.54-cm-diameter molds and prepared to a final 0.05- μ m alumina-slurry polish [35]. Maceral identification followed ICCP [36,37] nomenclature for vitrinite and inertinite; at this rank, liptinite is rarely recognized. Natural coke was counted when it was encountered. Vitrinite reflectance determination [38] of 50 particles per sample utilized a 50 $\times$, oil-immersion, reflected-light objective with the incident light was polarized at 45° and the reflected light passing across a 546-nm grating monochromator on the path to the photomultiplier which, in turn, was calibrated using a series of glass standards of known reflectance (based on an extrapolation from D.J. Cole's circa 1980 glass standards; the highest standard is 1.67%R).

2.3. Chemistry

Proximate analyses (moisture, volatile matter, ash yield, and fixed carbon; all in %) followed ASTM International test method D7582-12, using a Leco thermogravimetric analyzer [39]. Total carbon and sulfur analyses (both as %) followed ASTM International test method D4239-12, using a Leco carbon/sulfur analyzer [40].

Concentrations of major oxides (% of ash) and minor elements (ppm of ash) in the coal were determined by quadrupole-based inductively coupled plasma mass spectrometry (Thermo Fisher, X series II ICP-MS) following digestion in a closed-vessel microwave-digestion system (Milestone UltraClave), following the procedures for coal digestion and subsequent ICP-MS analysis [41]. In order to reduce the spectral interferences of the Ar-based polyatomic ions $^{40}\text{Ar}^{35}\text{Cl}$ and $^{40}\text{Ar}^{38}\text{Ar}$ to ^{75}As and ^{78}Se , respectively, the concentrations of As and Se in samples were determined by ICP-MS using collision/reaction cell technology,

following the procedures outlined by Li et al. [42]. Boron concentrations were also determined by ICP-MS after digestion of the solid sample (50 mg) using a mixture of H_3PO_4 , HNO_3 , and HF; a 2% ammonia solution was injected into the spray chamber of the ICP-MS facility to eliminate the memory effect of boron, as described by Dai et al. [43].

2.4. Mineralogy

To determine mineralogy, a representative portion of sample 69760 was ground to < 60 mesh, analyzed by X-ray powder diffraction using a Phillips PW1830 diffractometer with Cu K λ radiation, with mineral identification by reference to the International Center for Diffraction Data (ICDD) Powder Diffraction File [44].

2.5. Microbeam studies

Morphology, structure, and composition of the coal samples were investigated using a Zeiss Model ULTRA plus field-emission scanning electron microscope (FE-SEM), with charge compensation for all applications on conductive as well as non-conductive samples, and a 200-keV JEOL-2010F high-resolution transmission electron microscope (HR-TEM), equipped with an Oxford energy dispersive X-ray detector and a scanning transmission electron microscope (STEM). The FE-SEM was equipped with an energy-dispersive X-ray spectrometer (EDS) and the mineral identifications were based on the morphology and grain composition using secondary electron and back-scattered electron modes and the EDS spectra. EDS spectra recorded in TEM image mode were quantified using ES Vision software that uses the thin foil method to convert X-ray counts of each element into atomic or weight percentages. Electron diffraction patterns of the crystalline phases were recorded in selected area electron diffraction (SAED) or microbeam diffraction (MBD) mode and the d spacings were compared to the ICDD [44] inorganic compound powder diffraction file (PDF) database to identify the crystalline phases.

Sample preparation for electron beam studies involved the use of ultrapure acetone and/or hexane to disperse the representative portion of each coal sample, a commonly used technique for HR-TEM sample preparation [45,46]. The suspension was pipetted on to lacy carbon films supported by Au grids and left to evaporate before inserting the sample into the SEM and TEM. This method may have led to agglomeration, but is a widely used standard procedure for most minerals, including metal sulphates. Before FE-SEM and STEM analysis, the TEM specimen holder was cleaned with an Advanced Plasma System (Gatan Model 950) to minimize contamination. A drift correction system was used for the STEM-EDS mapping.

3. Results and discussion

3.1. Coal petrology

Table 1 presents the coal petrology data for the samples, including the maceral content and vitrinite reflectance. The petrology of some of the coals and coalfields has been discussed elsewhere, either specifically [Valley Fields: 17–18; KwaZu-Natal: 29] or as part of broader studies (Narragansett Basin: 19–20, 31; Pennsylvania Anthracite Fields: 31, 47–48]. The Rhode Island, Germany, and Pennsylvania samples (69759, 69760, and 69762, respectively) are dominated by vitrinite macerals on the mineral-free basis. The Virginia “Sand coal” lithotype (sample 69761) studied by Hower et al. [18], is dominated by inertinite, with secretinite comprising 51% of the mineral-free maceral assemblage. Sample 69763, the KwaZu-Natal anthracite with included natural coke, shows the typical inertinite-rich petrology seen in other Permian Gondwana coals [29].

With only a single sample and no detailed notes on the location, the Frankenstein sample (MA no. 69760) does not have the geological

Table 1

Petrology of the anthracites. The MA number, assigned by the Center for Applied Energy Research (CAER) analytical laboratory, is available for each sample. The Vanderbilt and KCER numbers, listed for cross-referencing purposes, refer to samples in the collections housed at the CAER. Key: $R_{\max}$ – vitrinite maximum reflectance; R_{random} – vitrinite random reflectance, determined as the average of orthogonal reflectance readings (oil immersion, incoming light polarized at 45°) on same areas analyzed for $R_{\max}$; and st. dev. – standard deviation of the $R_{\max}$ or R_{random} measurements. “t” – trace. The second column for each samples represent the mineral-free maceral content as normalized against the sum of the minerals from the first column. **Table 2.** Geochemistry. As-received moisture (%); dry ash, C, H, N, S and O (O by difference) (%); Whole-sample F (ppm); Ash-basis major oxides (%; Na_2O through Fe_2O_3); Whole sample minor and trace elements (ppm) (Li through Nb; Mo through U; Sc, Y, La through Lu); ash-basis minor and trace elements (ppm) (Li through Nb; Mo through U; Sc, Y, La through Lu); REE- La through Lu; REY – REE + Y.

Seam	Rhode Island		Frankenstein		Merrimac		Mammoth		KwaZu-Natal	
State/Region	USA		Sachsen		Virginia		Pennsylvania		South Africa	
Country	USA		Germany		USA		USA		South Africa	
MA no.	69759		69760		69761		69762		69763	
Vanderbilt no.	4059		4082		5047		8658		8659	
KCER no.										
telinite	29.2	30.3	0.0	0.0	7.6	8.4	15.0	15.4	2.6	2.7
collotelinite	51.8	53.7	4.0	100.0	26.0	28.9	66.8	68.7	43.2	44.6
vitrodetrinite	0.8	0.8	0.0	0.0	0.4	0.4	2.2	2.3	0.2	0.2
collodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
corpogelinite	0.8	0.8	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.2
gelinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
fusinite	11.2	11.6	0.0	0.0	10.0	11.1	12.2	12.6	47.2	48.8
semifusinite	1.6	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
micrinite	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2
macrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
secretinite	0.6	0.6	0.0	0.0	46.0	51.1	0.4	0.4	0.8	0.8
funginite	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
inertodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.4	0.0	0.0
sporinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cutinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
resinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
alginite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
liptodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
suberinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
exsudatinit	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
silicate	3.6		0.0		7.2		2.6		2.8	
sulfide	t		0.0		0.4		0.0		0.4	
carbonate	0.0		0.0		2.0		0.2		0.0	
quartz	0.0		53.0		0.4		0.0		0.0	
metal oxide			43.0							
natural coke									2.4	2.5
$R_{\max}$	4.35		2.91		2.44		4.72		3.35	
st. dev.	0.22		0.24		0.16		0.14		0.17	
R_{random}	3.74		2.63		2.23		4.33		2.91	
st. dev.	0.23		0.24		0.18		0.19		0.22	

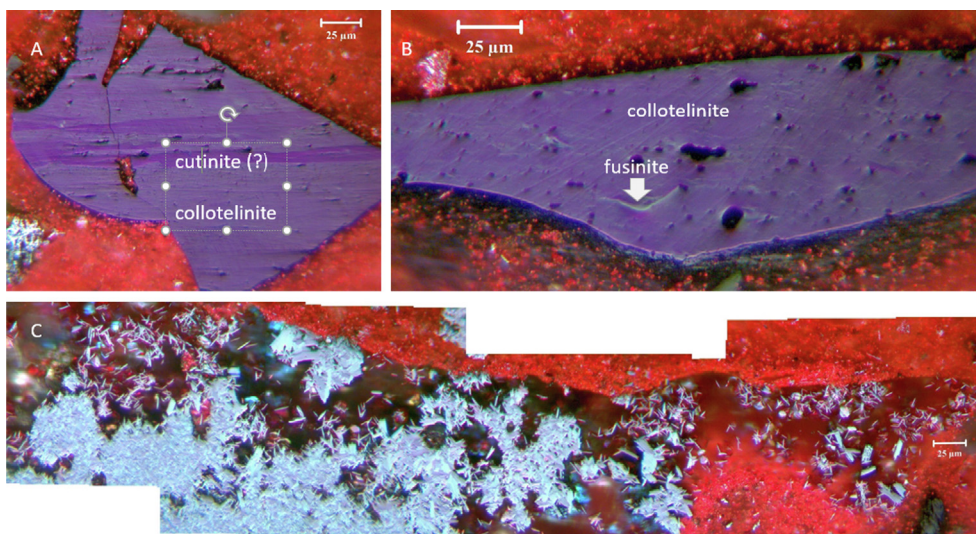


Fig. 1. Frankfurt (Saxony, Germany) “coal”. A/Collotelinite with possible cutinite. B/Collotelinite with fusinite. C/Fe- (and other) oxides in silicate matrix. All images taken with reflected-light, crossed polars with wavelength plate, oil-immersion 50x objective and crossed polars with wavelength plate. Scale bars on images.

Table 2
 Geochemistry. As-received moisture (%); dry ash, C, H, N, S and O (O by difference) (%); Whole-sample F (ppm); Ash-basis major oxides (%; Na₂O through Fe₂O₃); Whole sample minor and trace elements (ppm) (Li through Nb; Mo through U; Sc, Y, La through Lu); ash-basis minor and trace elements (ppm) (Li through Nb; Mo through U; Sc, Y, La through Lu); REE- La through Lu; REY – REE + Y.

	MA no.	Vandy no.	KCER no.	Mois	Ash	C	H	N	S	O	F								
Rhode Island	69759	4059		3.01	7.50	83.39	2.95	0.97	0.58	4.61	24								
Frankenstein	69760	4082		0.11	96.03	2.15	0.45	< 0.01	0.01	1.36	57								
Virginia	69761	5047		1.79	20.67	67.43	3.03	0.62	3.32	4.93	66								
Pennsylvania	69762		8658	3.87	7.66	83.19	2.94	0.91	0.54	4.76	109								
South Africa	69763		8659	2.09	9.70	79.34	2.95	1.77	0.88	5.36	64								
<i>ash basis</i>	MA no.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃							
Rhode Island	69759	0.06	0.33	41.60	52.53	0.10	0.27	0.68	0.81	0.85	0.00	2.44							
Frankenstein	69760	0.00	0.08	0.61	49.10	0.15	0.19	0.01	2.49	0.02	0.11	47.46							
Virginia	69761	0.18	3.90	18.72	35.95	0.25	4.16	0.86	7.45	0.58	0.09	18.82							
Pennsylvania	69762	0.36	0.45	37.86	52.22	1.70	0.41	1.14	2.39	2.60	0.00	2.49							
South Africa	69763	0.64	0.76	31.65	48.97	0.41	0.59	2.76	2.12	1.46	0.84	9.01							
<i>Whole sample</i>	MA no.	Li	Be	V	Cr	Co	Ni	Cu	Zn	Ga	As	Se	Ge	Rb	Sr	Zr	Nb		
Rhode Island	69759	36.7	0.4	20.2	14.1	5.2	18.9	12.5	12.1	5.8	1.3	1.0	0.5	2.4	14.0	14.6	1.6		
Frankenstein	69760	17.1	0.7	51.6	102.6	12.9	98.8	8.1	9.9	2.7	17.2	0.5	3.1	0.3	14.0	3.5	0.5		
Virginia	69761	22.6	0.7	42.7	21.2	7.5	15.9	11.5	96.5	5.1	39.5	1.4	0.6	9.6	63.0	22.3	2.1		
Pennsylvania	69762	16.8	1.6	20.7	19.5	6.7	13.7	17.1	8.3	6.2	3.1	1.9	0.9	4.1	98.4	31.1	3.4		
South Africa	69763	9.5	3.7	18.5	22.7	5.8	10.3	17.4	10.0	6.2	4.1	0.9	4.4	7.7	82.5	45.8	3.1		
<i>Whole sample</i>	MA no.	Mo	Ag	Cd	In	Sb	Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U			
Rhode Island	69759	1.7	0.10	0.09	4.17	0.35	0.13	97.7	0.39	1.44	0.6	0.06	32.1	0.12	1.5	0.45			
Frankenstein	69760	96.1	0.07	0.52	0.02	2.13	0.28	12.1	0.06	0.03	6.8	0.03	8.3	0.55	0.0	0.81			
Virginia	69761	0.5	0.32	0.18	0.18	0.45	1.37	40.3	0.58	0.15	0.8	0.38	55.1	0.06	1.6	0.64			
Pennsylvania	69762	2.1	0.28	0.15	3.56	0.40	0.36	149.9	0.80	0.27	1.2	0.05	8.0	0.18	2.1	0.69			
South Africa	69763	0.5	0.32	0.16	0.04	0.15	0.79	59.0	1.12	0.27	1.1	0.67	11.8	0.39	3.0	0.97			
<i>Whole sample</i>	MA no.	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Rhode Island	69759	1.5	3.3	3.6	9.4	1.1	4.0	0.8	0.17	0.8	0.12	0.7	0.12	0.33	0.05	0.29	0.04		
Frankenstein	69760	BDL	5.1	2.5	3.6	0.5	2.2	0.6	0.17	0.7	0.11	0.6	0.12	0.33	0.05	0.28	0.04		
Virginia	69761	2.2	7.2	17.4	34.1	3.3	11.2	1.9	0.35	2.1	0.25	1.2	0.24	0.65	0.09	0.59	0.09		
Pennsylvania	69762	2.8	7.4	7.0	15.9	1.7	6.3	1.2	0.27	1.4	0.20	1.2	0.24	0.71	0.11	0.70	0.11		
South Africa	69763	1.1	9.4	8.6	17.9	2.0	7.3	1.5	0.27	1.6	0.24	1.4	0.29	0.83	0.12	0.80	0.12		
<i>Ash basis</i>	MA no.	Li	Be	V	Cr	Co	Ni	Cu	Zn	Ga	As	Se	Ge	Rb	Sr	Zr	Nb		
Rhode Island	69759	489	5	269	188	69	252	167	162	78	17	14	6	32	187	195	21		
Frankenstein	69760	18	0.7	54	107	13	103	8	10	3	18	0.5	3	0.3	15	4	0.5		
Virginia	69761	109	3	207	103	36	77	55	467	24	191	7	3	46	305	108	10		
Pennsylvania	69762	220	21	270	254	88	179	223	108	82	40	25	11	54	1285	406	45		
South Africa	69763	105	42	205	252	64	115	194	111	69	46	10	49	85	917	509	35		
<i>Ash basis</i>	MA no.	Mo	Ag	Cd	In	Sb	Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U			
Rhode Island	69759	23	1.4	1.1	56	5	2	1303	5	19	8	0.8	428	1.6	19	6			
Frankenstein	69760	100	0.1	0.5	0.0	2	0.3	13	0.1	0.0	7	0.0	9	0.6	0.0	0.8			
Virginia	69761	2	2	0.9	0.9	2	7	195	3	0.7	4	2	267	0.3	8	3			
Pennsylvania	69762	27	4	2	46	5	5	1957	10	3	15	1	105	2.3	28	9			
South Africa	69763	5	4	2	0.4	2	9	656	12	3	12	7	131	4.4	33	11			
<i>Ash basis</i>	MA no.	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	REY
Rhode Island	69759	20	44	48	125	14	53	11	2	11	2	9	2	4	0.6	4	0.6	286	330
Frankenstein	69760	BDL	5	3	4	0.6	2	0.6	0.2	0.7	0.1	0.6	0.1	0.3	0.0	0.3	0.0	12	18
Virginia	69761	11	35	84	165	16	54	9	2	10	1	6	1	3	0.4	3	0.4	356	390
Pennsylvania	69762	37	96	92	208	22	82	16	4	18	3	15	3	9	1.4	9	1.4	483	579
South Africa	69763	12	105	96	199	22	81	16	3	18	3	15	3	9	1.4	9	1.3	476	581
<i>UCC correction</i>	MA no.	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Rhode Island	69759			1.61	1.95	2.00	2.04	2.46	2.54	2.78	2.53	2.56	2.07	1.91	1.88	1.78	1.77		
Frankenstein	69760			0.09	0.06	0.08	0.09	0.13	0.20	0.18	0.18	0.18	0.16	0.15	0.14	0.13	0.13		

(continued on next page)

Table 2 (continued)

	69761	2.81	2.58	2.26	2.08	2.00	1.95	2.69	1.90	1.73	1.44	1.37	1.34	1.30	1.29	La/Sm type
Virginia	69762	3.06	3.25	3.07	3.16	3.52	4.07	4.67	4.08	4.30	3.98	4.04	4.27	4.14	4.48	
Pennsylvania	69763	3.19	3.10	3.06	3.13	3.61	3.37	4.71	4.15	4.36	4.00	4.02	4.19	4.04	4.18	
South Africa																
UCC correction	MA no.	CeN/CeN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	GdN/GdN*	La/Lu type
Rhode Island	69759	1.08	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	H
Frankenstein	69760	0.72	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	H
Virginia	69761	1.02	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	L
Pennsylvania	69762	1.06	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	H
South Africa	69763	0.99	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	1.19	H

context of the other samples examined here. Indeed, the Frankenstein sample, dominated by minerals, is not a coal according to conventional definition. Nevertheless, since it was described as a coal by the original collector, it is retained in this study. The Frankenstein “coal”, not previously described, consists of collotelinite (Fig. 1A) with traces of inertinite (Fig. 1B) in a quartz/clay/metal oxide matrix (Fig. 1C).

3.2. Geochemistry

As noted, the Frankenstein “coal”, with 96% ash, is not really a coal (Table 2). Despite the high content of Fe (47.46% Fe₂O₃), the sample is not enriched in other metals; note that it contains only 0.02% TiO₂, 107 ppm Cr, and 103 ppm Ni (all on ash basis). Overall, only Mo, with 100 ppm on the ash basis, stands out as having a relatively high concentration.

Among the other coals, the high Sr and Ba in the Pennsylvania anthracite (MA no. 69762) corresponds with the 1.7% P₂O₅ content, the highest among the studied coals, and likely also the REY of 579 ppm (ash basis). Both Hower and Dai [48] and Hower et al. [47] examined the REE content of Pennsylvania anthracites; in those cases, with a few exceptions, the REY was in the 600–700-ppm range for the coal (both studies) and the 700–800-ppm range for stoker combustion ash [47]. Hower and Dai [48] also summarized the USGS data [49], concluding that, while there was a much wider range of REY values (up to 1722 ppm for a Northern Anthracite Field sample), the Schuylkill County (the source county for our Pennsylvania sample) coal average was similar to the Hower and Dai [48] analyses. The REE spider plot for samples from Rhode Island, Virginia, Pennsylvania, and South Africa (the German sample was not plotted because of its very low REE concentrations) shows at least two distinct patterns (Fig. 2; Table 2). The patterns for the Pennsylvania and KwaZulu-Natal anthracites, 69762 and 69763, respectively, are similar to each other while the Rhode Island anthracite (69759) follows a similar path with lower concentrations, through Dy. In general, these patterns were characterized by middle-heavy REY enrichment types [50], resemble the trends found by Hower and Dai [48]. The Virginia semi-anthracite, characterized by a light REY enrichment type (after Seredin and Dai [50]), shows a decrease in concentration with increasing atomic weight though the light REE, a peak in Gd, and a depletion in the heavy REE. Sample 69761 has positive La_N/Lu_N and La_N/Sm_N values [after 51,52] in contrast to the negative values for the other three anthracites. Most of the Pennsylvania anthracites in the USGS database [after 48] and the collection of sized anthracites studied by those same authors have negative La_N/Lu_N values. Their Trevorton site, a semi-anthracite, is the exception, having

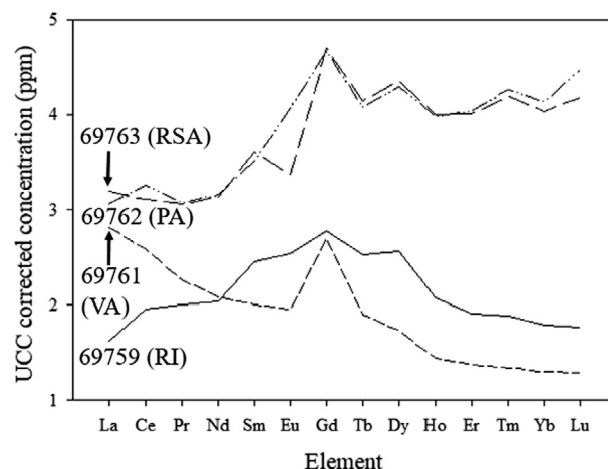


Fig. 2. Rare earth “spider plot” for Upper Continental Crust (UCC)-corrected rare earth concentrations for four of the samples. Sample 69760 (Germany) was excluded from the plot because of the extreme low-REE (ppm) concentrations. RAS – South Africa); PA – Pennsylvania; VA – Virginia; RI – Rhode Island.

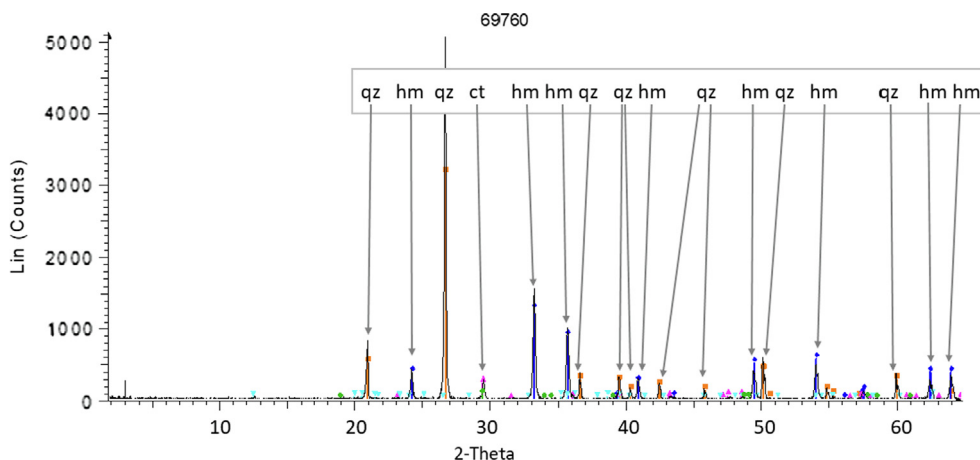


Fig. 3. X-ray diffraction scan of the German sample showing peaks identified as quartz (qz), hematite (hm), and calcite (ct).

the largest (most positive) La_N/Lu_N and La_N/Sm_N . The Virginia semi-anthracite La_N/Sm_N value exceeds any of the sized anthracites studied by Hower and Dai [48] and is surpassed by only one sample in the USGS collection from Pennsylvania. Overall, while intriguing, the sample base is too small to draw inferences about the influences responsible for the REE anomalies. Further studies of fresh samples, although on a limited basis, would be feasible with respect to the Pennsylvania anthracites.

The Pb content of the Rhode Island (MA no. 69759) and Virginia (MA no. 69761) coals (and the As content of the latter coal) is notably higher than in other coals. Both regions were subjected to hydrothermal metamorphism [31], a possible factor in Pb and As enrichment. Alabama and Central Appalachian coals with known hydrothermal influences have similar As and Pb enrichments [53–54]. While the coal metamorphism in the Pennsylvania Anthracite Fields has been ascribed to hydrothermal influences [24–29,31–33], the alteration described in those studies seems to have been largely confined to the metamorphism of clay minerals and not to sulfide and other mineralization.

3.3. Mineralogy and nano-scale geochemistry

The Frankenstein “coal” sample’s X-ray diffraction mineralogy indicates that it has abundant quartz and hematite (Fig. 3) with trace quantities of chalcopryrite, calcite, and kaolinite. TEM examination shows that samples 69760 and 69761 (Fig. 4A) contain jarosite in association with Fe-nanospheres. Generally, hematite mixed with magnetite and ferrihydrite with some amorphous phases occurs in the samples. EDS analysis in the spherical areas indicates the presence of hazardous elements; for example, the As signals in Fig. 4B from the Virginia sample with noted As enrichment. Iron nanospheres from the

Frankenstein sample show the presence of As and Pb (Fig. 5).

Among all of the samples, both Fe-disulfides (i.e. marcasite and pyrite) contain minor substituted metals. Metalloids with As, Co, Cu, Cd, Ga, Hg, Ni, Pb, and Se were ubiquitous minor constituents of the anthracites. EDS measurements coupled to HR-TEM/SAED and FE-SEM results indicate that pyrite grains in MA no. 69761 (Virginia) are the most As-, Hg-, and Se- rich. However, the Virginia coal has low Co, Cu, Cd, Ga, Ni, and Pb proportions ($< 0.01\%$) in the pyrite. Previous authors working with As substitution for S in pyrite [4,55] demonstrated expanded lattice parameters and electrochemical differences between As-rich and As-poor domains, both of which should de-stabilize arsenian pyrite relative to pure FeS_2 .

The Frankenstein and Virginia samples contain complex amorphous Al-Fe-O-Si-agglomerates containing hazardous elements (V, Sb, and Ti) (Fig. 6). Their formation was probably the result of chemical reactions of the decomposition of the Fe-sulfides that become sulfates (like jarosite) and iron oxides (e.g. hematite and magnetite). The resulting sulfuric acid attacked the aluminum-silicate minerals present in the latter samples, generating the amorphous phases.

3.4. Carbon nanotube structures

Among the five samples, the Rhode Island, Pennsylvania anthracites, and KwaZu-Natal natural coke/anthracite contained mostly spherical carbon nanotube (CNT) structures (Fig. 7). Certainly, graphitic structures are well documented in anthracite [56] and other rocks at that metamorphic level [57]. Bratek et al. [58] expanded Franklin’s [59–60] studies of graphite and Ergun et al.’s [61] investigation of a graphite and a Rhode Island meta-anthracite. Bratek et al. [58] noted the differences between the properties of low volatile

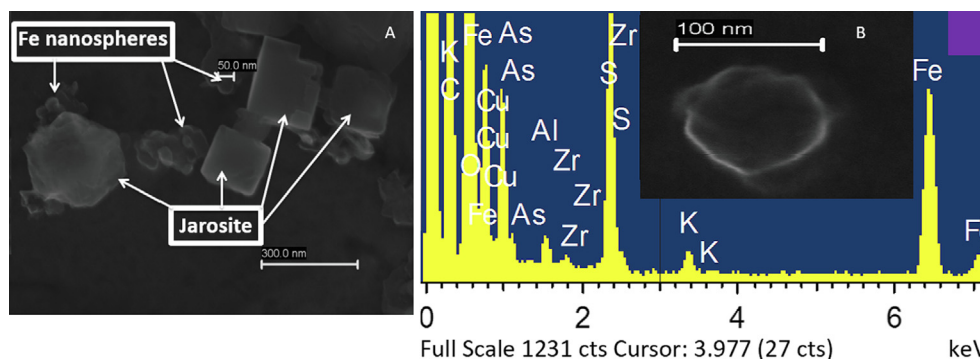


Fig. 4. A/ TEM image of jarosite and Fe-nanospheres (primarily hematite) in the German sample. Scale bars equal 50 (top) and 300 nm. B/ Inset of TEM image of jarosite from the Virginia sample. Accompanying EDS scan shows the presence of As ($L\alpha$ and $L\beta$ peaks at 1.282 and 1.317 keV, respectively).

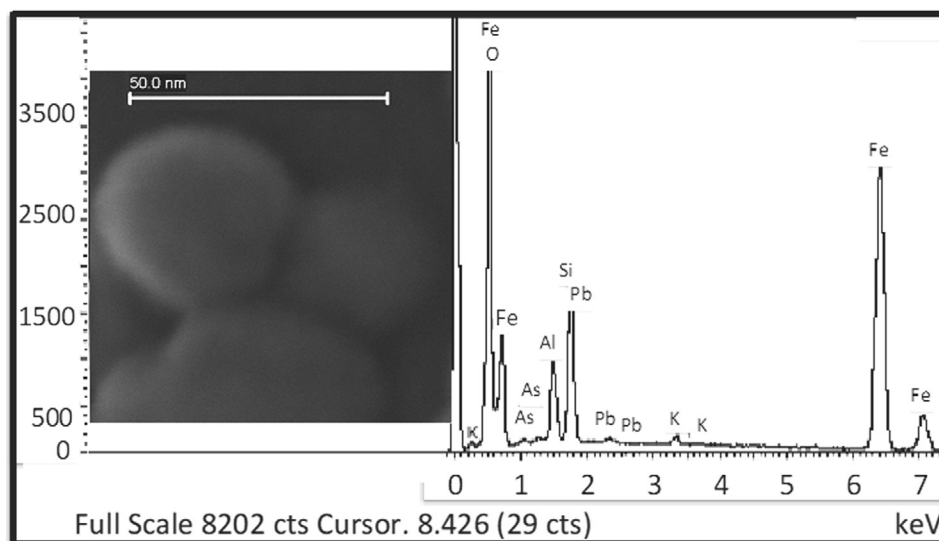


Fig. 5. Arsenic- and Pb-bearing Fe-nanosphere from the German sample. Scale bar equals 50 nm.

bituminous coal (1.60–1.81%R (maximum vs. random not specified by authors); note, the reflectances refer to the samples in their study, not to the reflectances for the entire rank range), semi-anthracite and anthracite (2.35–5.15%R), and meta-anthracite (5.41 and 5.69%R). The 002 peak (at 26.53° for pure graphite) for the coals becomes sharper ($< 3.5 \text{ \AA}$ for the meta-anthracites vs. nearly $3.6 \text{ \AA}$ for the low volatile bituminous coals) and the L_a , a measure of the crystallite diameter, increases with an increase in rank. To date, though, no significant natural occurrences of CNTs have been recorded in anthracite. Thus, while this study is the first time such CNT has been reported in the literature, it is expected to motivate future studies that utilize or take advantage of naturally occurring CNTs from coal from different geological formations, in order to achieve greater economic value for the coals.

The occurrence of CNTs in anthracite might have implications in their thermal and other properties. Expanding upon the work of Herrin and Deming [62] and Kosowska-Golachowska et al. [63], Weisenberger et al. [64] demonstrated that thermal conductivity ($\text{W/m}^\circ\text{K}$) and thermal diffusivity (mm^2/sec) was higher in coals of, at least, 5.30% R_{max} than in lower-rank anthracites (the highest R_{max} of the lower

group was 5.13%) and semi-anthracites. The connection between the CNTs and thermal properties calls for further exploration.

The CNT particles almost always contained associated inorganic elements, including toxic elements such as Hg and Cd, or more benign elements such as Si, Al, and K, among others. The multiple crystallinities varied from particle to particle and from coal sample to coal sample, however many times the same particle presented different crystal ordering, as shown in Fig. 7C. Aside from the ubiquitous occurrence of trace element associations with organic matter, including Mo and Ni with Fe-rich particles with $\text{K} > \text{S} > \text{Ti} > \text{Ca} \approx \text{Ni}$, are found to be associated with the CNTs (Fig. 8). Among the halogens, F, Cl, and Br were the most easily detected in CNTs (Fig. 9). While F and Cl were detected by EDS in the same areas, in most occurrences, the organic matter contained only one of these three halogens. Of the coal samples studied, the Pennsylvania anthracite was the sample with the most abundant halogen-bearing CNTs; this is further supported by the abundance of F in the whole coal sample (109-ppm F vs. 66 ppm and 64 ppm for the Virginia and South Africa anthracites; Table 2). Fluorine was also detected in amorphous Al-Si-K-Na-K-Mg nanoparticles in the Pennsylvania, Virginia, and South Africa anthracites (Fig. 10).

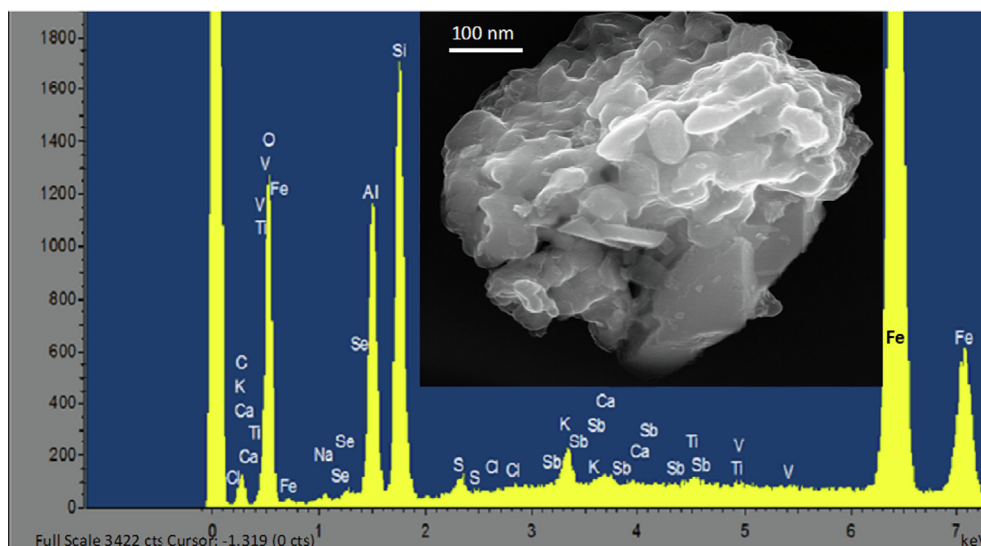


Fig. 6. Inset of TEM image of Al-Si-Fe agglomerate the Virginia sample. The EDS scan shows the presence of Ti ($K\alpha$ and $K\beta$ peaks at 4.512 and 4.933 keV, respectively) along with more tenuous peaks for V, Sb, and Se.

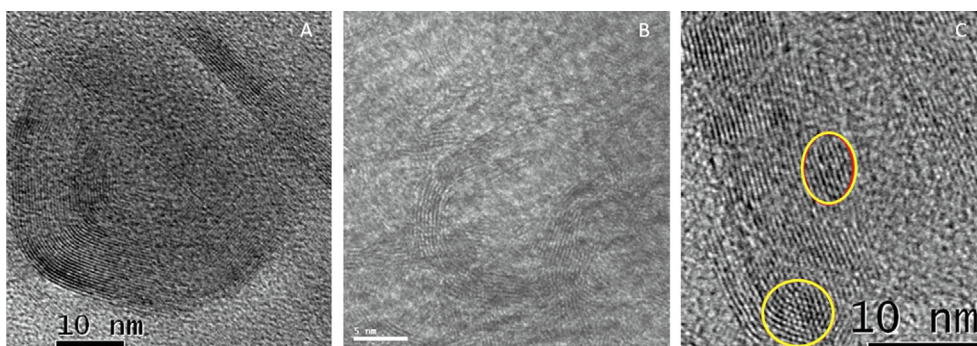


Fig. 7. Carbon nanotubes (CNT) in (A) the Rhode Island sample (scale = 10 nm), (B) the Pennsylvania sample (scale = 5 nm), and (C) the South Africa sample (scale = 10 nm). The ovals in (C) mark areas with different crystal ordering.

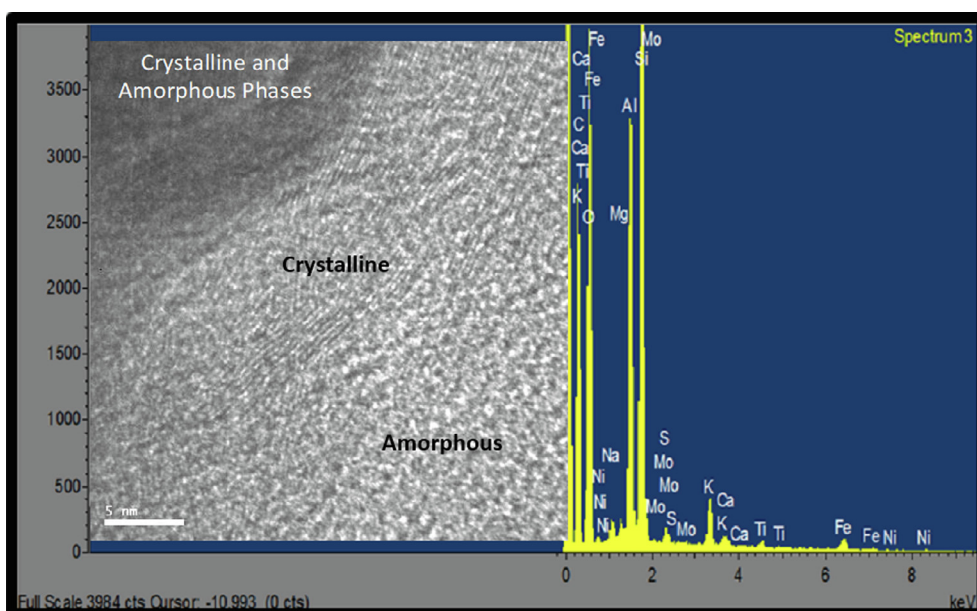


Fig. 8. Left: Crystalline and amorphous phases in carbon nanotubes (CNT) from the Pennsylvania sample. Right: EDS scan of CNT-rich area showing relative elemental composition.

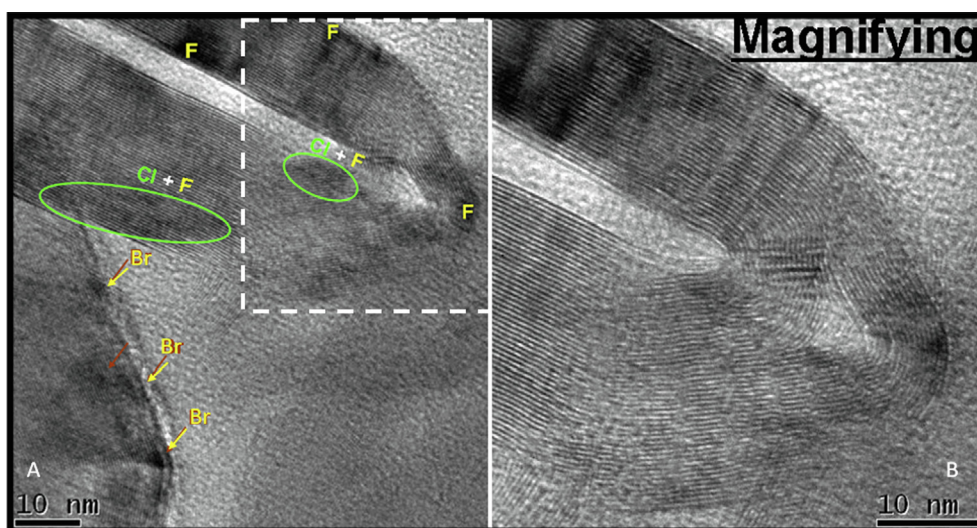


Fig. 9. Carbon nanotubes (CNT) in the Pennsylvania sample. A/ CNT with Br, Cl, and F. B/ Magnification of dotted-box area on (A) showing the details of the fine structure of the CNT. In both cases the scale = 10 nm.

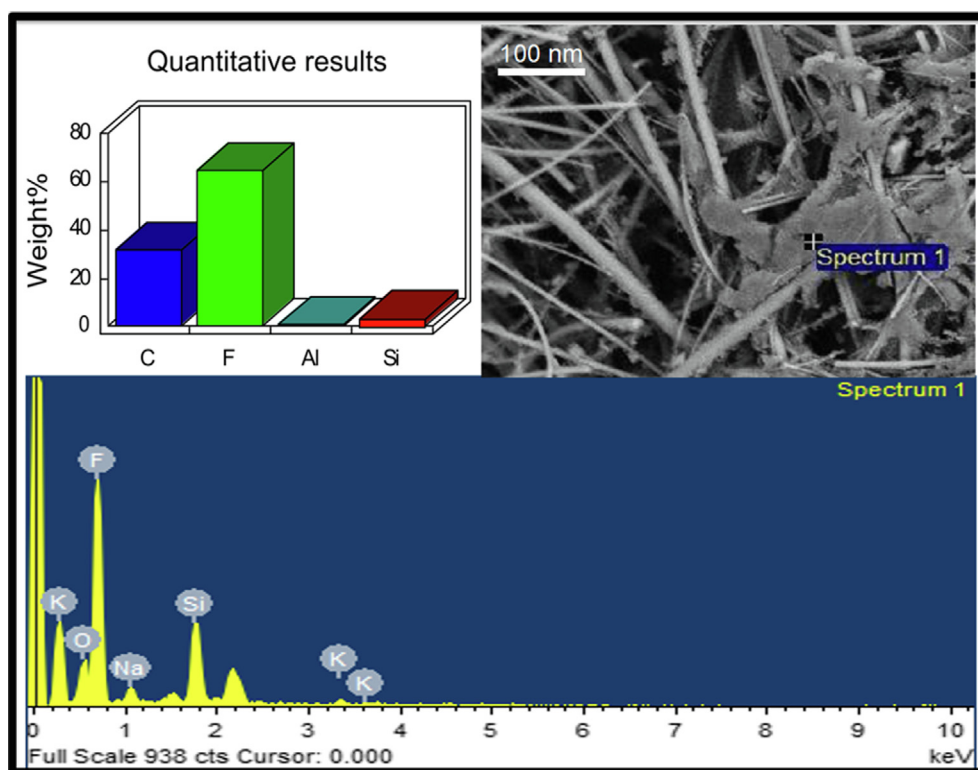


Fig. 10. Fluorine-, C-, and (minor) Si-bearing particle in the Pennsylvania sample.

4. Summary

As noted in the introduction, this study is a survey of a few Paleozoic-age anthracites; it is not a comprehensive overview of all anthracites. However, it does provide a basis for the identification of naturally occurring C-nanoparticles in anthracites and for studies of their impact on the properties of the coals.

Among the chemical properties of the anthracites, the enrichment of Pb and As in the Rhode Island and Virginia anthracites corresponds to expectations with respect to metamorphism by hydrothermal fluids. The Rhode Island anthracite is in a region with notable metamorphic facies gradients, from low-grade metamorphic rocks in the north to staurolite zone metamorphism in the south [19–20]. The Valley Fields, Virginia, semi-anthracites were influenced by hydrothermal fluid flow [17]. The Pennsylvania anthracite, while in a region subject to intense thrust faulting and known fluid flow, does not have as high of a concentration of chalcophile elements as the Rhode Island and Virginia coals. Instead, the metamorphism of the Pennsylvania anthracites is reflected in the mineralogy of clays and other phyllosilicates in the coal, cleat, and surrounding rocks [24–28,31].

Some of the variability in the concentration of chalcophile elements lies in their varied concentrations in forms of pyrite and marcasite and in the occurrence of metalloid forms with As, Co, Cu, Cd, Ga, Hg, Ni, Pb, and Se.

The Pennsylvania anthracite had the highest P_2O_5 , Sr, Ba, and REE content of the coals analyzed. The ash-basis REE exceeds 1700 ppm in a Pennsylvania Northern Anthracite Field coal [49]. In general, the Bragg et al. [49] analyses fall into the mid-100's-1000-ppm-REE range, similar to Pennsylvania anthracites analyzed by Hower and Dai [48] and Hower et al. [47].

The Rhode Island, Pennsylvania anthracites, and KwaZu-Natal samples, the three highest-reflectance coals in the sample set contained carbon nanotube (CNT) structures. Several inorganic elements, including Hg and the halogens, are associated with the CNTs. To the best of our knowledge, this is the first report of naturally occurring CNTs in

anthracites.

CRediT authorship contribution statement

Luis F.O. Silva: Formal analysis, Writing - original draft, Writing - review & editing. **Tito J. Crissien:** Formal analysis, Writing - original draft. **Carlos H. Sampaio:** Formal analysis, Writing - original draft. **James C. Hower:** Conceptualization, Data curation, Writing - original draft, Writing - review & editing. **Shifeng Dai:** Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] BP, 2019. Coal. <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/coal.html#coal-consumption>. (Accessed 26 August 2019).
- [2] Dai S, Finkelman RB. Coal as a promising source of critical elements: progress and future prospects. *Int J Coal Geol* 2018;186:155–64.
- [3] Fiket Ž, Medunić G, Furdek Turk M, Kniewald G. Rare earth elements in superhigh-organic-sulfur Raša coal ash (Croatia). *Int J Coal Geol* 2018;194:1–10.
- [4] Kolker A, Scott C, Hower JC, Vazquez JA, Lopano CL, Dai S. Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe. *Int J Coal Geol* 2017;184:1–10.
- [5] Laudal DA, Benson SA, Addleman RS, Palo D. Leaching behavior of rare earth elements in Fort Union lignite coals of North America. *Int J Coal Geol* 2018;191:112–24.
- [6] Lin R, Soong Y, Granite EJ. Evaluation of trace elements in U.S. coals using the USGS COALQUAL database version 3.0. Part I: Rare earth elements and yttrium

- (REY). *Int J Coal Geol* 2018;192:1–13.
- [7] Stuckman MY, Lopano CL, Granite EJ. Distribution and speciation of rare earth elements in coal combustion by-products via synchrotron microscopy and spectroscopy. *Int J Coal Geol* 2018;195:125–38.
- [8] Zhang W, Honaker RQ. Rare earth elements recovery using staged precipitation from a leachate generated from coarse coal refuse. *Int J Coal Geol* 2018;195:189–99.
- [9] Gogotsi Y, Libera JA, Yoshimura M. Hydrothermal synthesis of multiwall carbon nanotubes. *J Mater Res* 2000;15:2591–4.
- [10] Qiu J, Li Y, Wang Y, Wang T, Zhao Z, Zhou Y, et al. High-purity single-wall carbon nanotubes synthesized from coal by arc discharge. *Carbon* 2003;41:2170–3.
- [11] Varma AK, Sahoo A, Saikia BK, Das T. Petrographic controls of coal from Ib valley Basin for carbon nano-products formation. *Int J Coal Geol* 2019;211:103211.
- [12] Montellano A, Da Ros T, Bianco A, Prato M. Fullerene C60 as a multifunctional system for drug and gene delivery. *Nanoscale* 2011;3:4035–41.
- [13] Goyal RN, Gupta VK, Sangal A, Bachheti N. Voltammetric determination of uric acid at a fullerene C60 modified glassy carbon electrode. *Electroanalysis* 2005;17:2217–23.
- [14] Brabec CJ, Gowrisanker S, Halls JJM, Laird D, Jia S, Williams SP. Polymer–fullerene bulk heterojunction solar cells. *Adv Mater* 2010;22:3839–56.
- [15] Benn TM, Westerhoff P, Herckes P. Detection of fullerenes (C60 and C70) in commercial cosmetics. *Environ Pollut* 2011;159:1334–42.
- [16] Farré M, Pérez S, Gajda-Schranz K, Osorio V, Kantiani L, Ginebreda A, et al. First determination of C60 and C70 fullerenes and N-methylfulleropyrrolidine C60 on the suspended material of wastewater effluents by liquid chromatography hybrid quadrupole linear ion trap tandem mass spectrometry. *J Hydrol* 2010;383:44–51.
- [17] Lewis SE, Hower JC. Thermal events and thrust emplacement sequence in the Appalachian fold and thrust belt: some new vitrinite reflectance data. *J Geol* 1990;98:927–42.
- [18] Hower JC, O'Keefe JMK, Eble CF. Tales from a Distant Swamp: Petrological and Paleobotanical Clues for the Origin of the Sand Coal Lithotype (Mississippian, Valley Fields, Virginia). *Int J Coal Geol* 2008;75:119–26.
- [19] Quinn AW, Glass HD. Rank of coal and metamorphic grade of rocks of the Narragansett Basin of Rhode Island. *Econ Geol* 1958;53:563–75.
- [20] Skehan JW, Murray DP, Raben JD, Chace Jr. HB. Exploration and exploitation of the Narragansett coal basin. In: Farquhar OC, editor. *Geotechnology in Massachusetts*. Geotechnology in Massachusetts Conference, Amherst, MA, March 1980. 1982. p. 381–97.
- [21] Levine JR. Tectonic history of coal-bearing sediments in eastern Pennsylvania using coal reflectance anisotropy (PhD thesis) University ParkPA: Pennsylvania State University; 1983. p. 314.
- [22] Levine JR. Deep burial of coal-bearing strata: Anthracite region, Pennsylvania: sedimentation or tectonics? *Geology* 1986;14:577–80.
- [23] Levine JR, Davis A. Reflectance anisotropy of Upper Carboniferous coals in the Appalachian foreland basin, Pennsylvania, U.S.A. *Int J Coal Geol* 1989;13:341–73.
- [24] Juster TC, Brown PE, Bailey SW. NH₄-bearing illite in very low-grade metamorphic rocks associated with coal, northeastern Pennsylvania. *Am Mineral* 1987;72:555–65.
- [25] Daniels EJ, Altaner SP. Clay mineral authigenesis in coal and shale from the Anthracite region, Pennsylvania. *Am Mineral* 1990;75:825–39.
- [26] Daniels EJ, Altaner SP, Marshak S. Hydrothermal alteration in anthracite from eastern Pennsylvania: implications for mechanisms of anthracite formation. *Geology* 1990;18:247–50.
- [27] Daniels EJ, Aronson JL, Altaner SP. Late Permian age of NH₄-bearing illite in anthracite from eastern Pennsylvania: temporal limits on coalification in the Central Appalachians. *Geol Soc Am Bull* 1994;106:760–6.
- [28] Daniels EJ, Marshak S, Altaner SP. Use of clay-mineral alteration patterns to define syntectonic permeability of joints (cleat) in Pennsylvania anthracite coal. *Tectonophysics* 1996;263:123–36.
- [29] Hower JC, Rimmer SM, Mastalerz M, Wagner NJ. Notes on the mechanisms of coal metamorphism in the Pennsylvania Anthracite Fields. *Int J Coal Geol* 2019;202:161–70. <https://doi.org/10.1016/j.coal.2018.12.009>.
- [30] Hower JC, Rimmer SM, Mastalerz M, Wagner NJ. Migmatite-like structures in anthracite. *Int J Coal Geol* 2020. in review.
- [31] Hower JC, Levine JR, Skehan JW, Daniels EJ, Lewis SE, Davis A, Gray RJ, Altaner SP. Appalachian anthracites. *Org Geochem* 1993;20:619–42.
- [32] Ruppert LF, Hower JH, Levine JR, Ryder RT, Trippi MH, Grady WC. Geologic controls on thermal maturity patterns in Pennsylvanian coal-bearing rocks in the Appalachian basin. *Int J Coal Geol* 2010;81:169–81.
- [33] Ruppert LF, Trippi MH, Hower JH, Grady WC, Levine JR. Thermal maturity patterns in Pennsylvanian coal-bearing rocks in Alabama, Tennessee, Kentucky, Virginia, West Virginia, Ohio, Maryland, and Pennsylvania. Chap. F.2. In: Ruppert LF, Ryder RT, editors. *Coal and petroleum resources in the Appalachian basin; Distribution, geologic framework, and geochemical character*. U.S. Geological Survey Professional Paper 1708. 2014. p. 13. oversized material, doi: 10.3133/pp1708F.2.
- [34] Beyschlag F, Kruwisch P, Vogt JHL. Die Lagerstätten der Nutzbaren Mineralien und Gesteine nach Form, Inhalt und Entstehung. Stuttgart: Ferdinand Enke; 1913. p. 727.
- [35] ASTM. D2797/D2797M-11a, Standard practice for preparing coal samples for microscopical analysis by reflected light. Philadelphia, USA: American Society for Testing and Materials; 2019. p. 4.
- [36] International Committee for Coal Petrology (ICCP). The new vitrinite classification (ICCP System 1994). *Fuel* 1998;77:349–58.
- [37] International Committee for Coal Petrology (ICCP). The new inertinite classification (ICCP System 1994). *Fuel* 2001;80:459–71.
- [38] ASTM D2798-11a. Standard test method for microscopical determination of the vitrinite reflectance of coal. Philadelphia, USA: American Society for Testing and Materials; 2019. p. 4.
- [39] ASTM International. ASTM Standard D7582 – 15; Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis. Annual Book of ASTM Standards, Section 5, Volume 05.06, Gaseous Fuels; Coal and Coke. West Conshohocken, PA, USA: ASTM International; 2015. p. 837–45.
- [40] ASTM International. ASTM Standard D4239 – 18e1; Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke using High-Temperature Tube Furnace Combustion. Annual Book of ASTM Standards, Section 5, Volume 05.06, Gaseous Fuels; Coal and Coke. West Conshohocken, PA, USA: ASTM International; 2018. p. 556–61.
- [41] Dai S, Wang X, Zhou Y, Hower JC, Li D, Chen W, et al. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. *Chem Geol* 2011;282:29–44.
- [42] Li X, Dai S, Zhang W, Li T, Zheng X, Chen W. Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS). *Int J Coal Geol* 2014;124:1–4.
- [43] Dai S, Song W, Zhao L, Li X, Hower JC, Ward CR, et al. Determination of Boron in Coal Using Closed-Vessel Microwave Digestion and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). *Energy Fuels* 2014;28(7):4517–22.
- [44] International Center for Diffraction Data (ICDD), 2013. <http://www.icdd.com>. [Access: 20 November 2013].
- [45] Chen Y, Shah N, Huggins FE, Huffman GP. Investigation of the microcharacteristics of PM2.5 in residual oil fly ash by analytical transmission electron microscopy. *Environ Sci Technol* 2004;38:6553–60.
- [46] Chen Y, Shah N, Huggins FE, Huffman GP, Dozier A. Characterization of ultrafine coal fly ash particles by energy-filtered TEM. *J Microsc* 2005;217:225–34.
- [47] Hower JC, Hood MM, Taggart RK, Hsu-Kim H. Chemistry and petrology of paired feed coal and combustion ash from anthracite-burning stoker boilers. *Fuel* 2017;199:438–46. <https://doi.org/10.1016/j.fuel.2017.03.007>.
- [48] Hower JC, Dai S. Petrology and Chemistry of sized Pennsylvania anthracite, with emphasis on the distribution of Rare Earth Elements. *Fuel* 2016;185:305–15.
- [49] Bragg LJ, Oman JK, Tewalt SJ, Oman CL, Rega NH, Washington PM, et al., 1998. U. S. Geological Survey coal quality (COALQUAL) database: version 2.0. U.S. Geological Survey, open-file report; p. 97–134.
- [50] Seredin VV, Dai S. Coal deposits as a potential alternative source for lanthanides and yttrium. *Int J Coal Geol* 2012;94:67–93.
- [51] Dai S, Graham IT, Ward CR. A review of anomalous rare earth elements and yttrium in coal. *Int J Coal Geol* 2016;159:82–95.
- [52] Hower JC, Granite EJ, Mayfield D, Lewis A, Finkelman RB. Notes on contributions to the science of rare earth element enrichment. *Minerals* 2016;6. <https://doi.org/10.3390/min6020032>.
- [53] Diehl SF, Goldhaber MB, Hatch JR. Modes of occurrence of mercury and other trace elements in coals from the Warrior field, Black Warrior Basin, Northwestern Alabama. *Int J Coal Geol* 2004;59:193–208.
- [54] Diehl SF, Goldhaber MB, Koenig AE, Lowers HA, Ruppert LF. Distribution of arsenic, selenium, and other trace elements in high pyrite Appalachian coals: Evidence for multiple episodes of pyrite formation. *Int J Coal Geol* 2012;94:238–49.
- [55] Kolker A, Huggins FE. Progressive oxidation of pyrite in five bituminous coal samples: an As XANES and ⁵⁷Fe Mossbauer spectroscopic study. *Appl Geochem* 2007;22:778–87.
- [56] Kwiecińska B, Petersen HI. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. *Int J Coal Geol* 2004;57:99–116.
- [57] Dill HG, Kus J, Goldman S, Suárez-Ruiz I, Neumann T, Kaufhold A. The physical-chemical regime of a sulfide-bearing semi-graphite mineral assemblage in meta-basic rocks (SE Germany) – a multidisciplinary study of the missing link between impsonite and graphite. *Int J Coal Geol* 2019. <https://doi.org/10.1016/j.coal.2019.103262>.
- [58] Bratek K, Bratek W, Gerus-Piasecka I, Jasieński S, Wilk P. Properties and structure of different rank anthracites. *Fuel* 2002;81:97–108.
- [59] Franklin RE. The interpretation of diffuse X-ray diagrams of Carbon. *Acta Crystallogr A* 1950;3:107–21.
- [60] Franklin RE. The structure of graphitic carbons. *Acta Crystallogr A* 1951;4:253–61.
- [61] Ergun S, Mentser M, O'Donnell HJ. Three-dimensional X-ray reflections from anthracite and meta-anthracite. *Science* 1960;132:1314–6.
- [62] Herrin JM, Deming D. Thermal conductivity of US coals. *J Geophys Res* 1996;101:25381–6.
- [63] Kosowska-Golachowska M, Gajewski G, Musiał T. Determination of the effective thermal conductivity of solid fuels by the laser flash method. *Arch Thermodyn* 2014;35:3–16.
- [64] Weisenberger MC, Burgess J, Schober HH, Hower JC. 2020. Thermal properties of Pennsylvania anthracite. In review.