

Geochemistry and nano-mineralogy of feed coals, mine overburden, and coal-derived fly ashes from Assam (North-east India): a multi-faceted analytical approach



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ABSTRACT

In order to address the scarcity of information on the nature and mode of occurrence of minerals and elements in coal, coal mine overburden and coal ashes from North-east India, and also the relations between coal mineralogy and ash chemistry, the petrology, mineralogy and nano-mineralogy, and ash chemistry of some industrially important high-sulfur coals, mine overburden materials and fly ash samples from Assam (India) have been evaluated. A combined approach, using petrography, low-temperature ashing plus X-ray diffraction (LTA-XRD), field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscope (HR-TEM), Raman spectroscopy, and inductively coupled plasma mass spectrometry (ICP-MS), has provided new information on the mineralogy and nano-mineralogy of these sub bituminous coals and associated mine overburden. The presence of rare earth elements and yttrium (REY) in Northeast Indian coal, mine overburden and fly ash samples is also reported for the first time. The identification of these components may be significant from an economic point of view. Some Northeast Indian fly ashes, with REE oxides up to 1580 ppm on an ash basis, might possibly represent sources for recovery of rare earth elements.

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1. Introduction

Coal has been and remains one of the major cornerstones of modern industrial society. The development of clean coal technologies is a priority area for research in many countries, with goals such as increased thermal efficiency and decreased pollutant emission. In addition to atmospheric emissions such as CO₂, coal burning produces large amounts of solid waste products annually, including fly ash, bottom ash, and flue-gas desulfurization sludge, some of which may contain Hg, U, Th, As, and other trace elements (Clarke and Sloss, 1992; Dai et al., 2010, 2014; Kukier et al., 2003; Meij, 1994; Ribeiro et al., 2011). Depending in part on the coal characteristics, utilization of coal may be associated with a number of environmental challenges, including soil erosion, dust, noise and water pollution, and impacts on local biodiversity.

The emplacement of overburden rocks and other reject materials generated from opencast coal mines in some areas may represent a major source of ecological and environmental degradation, especially if the materials also contain pyrite (which may form acid leachates)

and high concentrations of potentially toxic trace elements. An area larger than 1000 hectares in the North-eastern coalfields in India has been filled to date with mine overburden waste materials. Due to its high sulphur content (2–12%), part of which is pyritic, the mine overburden from the North-eastern coalfields also tends to produce highly acidic leachates (pH 2.0–3.0) (Baruah et al., 2006; Dowarah et al., 2009).

Fly ash (FA) is the main solid waste product from pulverized coal combustion and is collected by the emission control equipment (usually electrostatic precipitators or fabric filters) in thermo-electric power stations. Depending on the feed coal, the combustion conditions and the ash capture technology, those fly ashes may contain significant concentrations of trace elements which, if mobilised into the environment, could represent a potential pollution source. The coal-based thermal plants in North-east India produce approximately 37,000 t of fly ash per year (Pandey et al., 2011). In order to provide a technical framework from which to address some of these environmental issues, a multi-faceted analytical approach has been carried out, applying advanced level characterization of the feed coals and the associated mine overburden and fly ashes, with special attention to key aspects indicating the geochemical, mineralogical and elemental composition of the different types of material.

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1.1. High sulfur in the northeast Indian coals

The coal samples were taken from the Ledo (ALD) and Tikak (ATK) collieries in the Makum coalfield, Assam, India (Fig. 1). The coal beds mined at these sites are of Oligocene age and occur in the Tikak Parbat Formation, the uppermost member of the Barail Group. The Tikak Parbat Formation, 300–600 m in thickness, is made up of well-bedded and massive, fine-grained sandstones, sandy shales, shales, and claystones, with thick beds of coal in the basal part (Ahmed, 1996). The coals have low ash (<20%) and high volatile matter yields (>35%), and high hydrogen (>5%) and sulfur contents (>2%) in comparison to other Indian coals (Baruah et al., 2006; Saikia et al., 2014). They have lower moisture and oxygen contents than similar low rank coals from the well-known Raniganj coalfield (Chandra et al., 1984). The northeast Indian coals are considered abnormal because their physico-chemical characteristics and behaviour are not commensurate with properties adopted for rank classification (Iyenger et al., 1960), and are mostly classified as sub-bituminous in rank. North-east Indian coals are mostly medium to high sulfur coals and generally produce Acid Mine Drainage (AMD) problems (Baruah et al., 2006). The Ledo and Tikak collieries are among the most AMD-affected mines in the Northeast coalfield, Assam.

1.2. Makum coalfield

The North-Eastern Coalfield (NEC) is located in the States of Assam, Meghalaya, Nagaland, and Arunachal Pradesh, with coal mining activity located in the first three States. The Oligocene coal deposits of Northeast India are spread along a linear belt of over-thrust known as the 'Belt of Schuppen' (Misra, 1992), where Tertiary strata have been folded and dispersed into a number of thrust slices, including the Makum coalfield. The Makum coalfield, largest of all the coalfields of North Eastern region, is located in the Dibrugarh District of Assam, with a small part extending into the Tirap District of Arunachal Pradesh. The adjacent coalfields to the east and west are the Namchik-Namphuk and Dilli-Jaypore coalfields, respectively. The Makum coalfield is located along the outermost northern flank of the Naga-Patkai Range, which is characterized by highly dissected topography caused by numerous rivers, streams, and water channels. The major coal mining activities in the north-eastern region of the country are located in this coalfield.

1.3. Acid mine drainage from high sulfur coals and mine overburden

Acid Mine Drainage (AMD), recognized as one of the most serious environmental problems in the world (Akciil and Koldas, 2006), occurs in the Makum coalfield. Acidic drainage occurs as a result of natural oxidation of sulfide minerals, mostly pyrite (FeS_2), contained in the coal, reject materials, and mine overburden, which are exposed to air and water (Egiebor and Oni, 2007). The problem of AMD has also been widely felt in the coal mining industries of the North Eastern Region of India. The high-sulfur subbituminous coals of this area (2–12% total sulphur) are typically dominated by the organic sulphur fraction (75–90 % of the total sulphur), and thus have only relatively low proportions of pyritic sulphur (Baruah and Khare, 2007; Baruah et al., 2006; Saikia et al., 2014). Even so, the formation of acidic drainage in the coal mines is very much pronounced. In order to understand the origin and extent of AMD formation in these mines, a detailed assessment of the mineralogical composition of the coal and associated mine overburden, including the Fe-mineralogy, needed to be carried out.

The nature and modes of occurrence of various minerals present in coals, mine overburden, and fly ash are important considerations in the design of control strategies for reducing their release and potential impact. The research covered by this investigation therefore included evaluation of the mineralogical and geochemical compositions of typical coals, fly ashes, and mine overburden from the Makum coalfield, and the occurrence of trace elements, including rare earth elements (REEs) as well as potentially hazardous components, in those materials. Such an understanding may also be helpful in assessment and mitigation of similar environmental degradation in other nearby coalfields. The relevant information has been obtained from a multi-faceted analytical approach using a combination of basic and advanced techniques, and is intended to open up an avenue that may assist with environmental management in the region.

2. Methods and materials

2.1. Sampling program

Run-of-mine samples were collected from two most active and industrially important coal mines in the Makum coalfield, the Ledo (ALD) and Tikak (ATK) collieries, using standard methods (ASTM

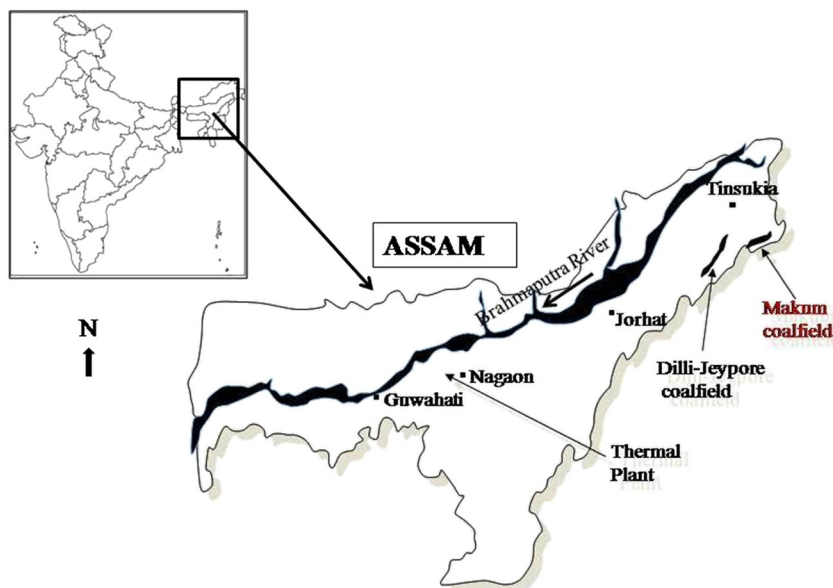


Fig. 1. Location map of the Makum coalfield and the thermal power plant (not to scale).

D2234M, 2010). The coal samples were from the 18-metre seam described by Ahmed (1996).

The rock types included in the overburden at these mines are mainly of fine grained well-bedded massive sandstone, shale, mudstone and carbonaceous claystone. Two grab samples (BROB, TROB) of the mine overburden were collected from the overburden dumps of the Ledo and Tikak mines, respectively. The lithology consists of massive bedded sandstones with intercalations of shales and carbonaceous shales (Nagaon Formation), inter-bedded carbonaceous shales, thin sandstones and thin impersistent coal seams (Boragolai Formation), and the basal part of sequence marked by carbonaceous shales, sandy shales and thin sandstones with 18-m-thick coal seams (Tikak Parbat Formation) (Baruah et al., 2013). Two fly ash samples (SCFA and NCFA) were taken at different times (24 hours) from the fly ash collection system (electrostatic precipitator) of a pulverised coal thermal plant in Nagaon (Fig. 1), in which generally the Makum coals are burned. However, it is understood that blended coals were being used in the thermal plant during sampling, with only a partial contribution from the mines sampled in the present study. The coal fly ashes were air dried, ground to 0.221-mm top size, and kept for further characterization.

2.2. Proximate and ultimate analyses

The coal, mine overburden, and fly ash samples were characterized in the CSIR-NEIST Laboratory (India) to determine their physico-chemical properties. Proximate analysis of the coal samples was carried out using a thermogravimetric analyser (Model: TGA 701; Leco Corporation, USA) according to the ASTM standard method (ASTM, 2011a,b,c). Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 2400 Elemental Analyser, and total sulfur by a 'Sulfur Analyser' (Model: S-144DR; Leco Corporation, USA), following standard methods (ASTM, 2002a, 2009). The forms of sulfur in the coal samples (pyritic and sulfate sulfur) were determined following the ASTM standard method (ASTM, 2002c), and the percentages of organic sulfur calculated by difference. The mine overburden and fly ashes were also subjected to proximate analysis, in order to compare their characteristics to those of the associated coal samples.

2.3. Petrographic characterization

Samples of each coal, overburden, and fly ash were prepared as epoxy-bound particulate pellets, and finished with a final 0.05- μ m-alumina polish. The samples were examined by reflected light microscopy under a Leitz Orthoplan microscope, using a 50 $\times$ oil-immersion objective, to provide petrographic information, especially of the organic matter. Description of the coal and overburden samples followed ICCP (1998, 2001) nomenclature for vitrinite and inertinite and Taylor et al. (1998) for liptinite. Vitrinite reflectance measurement followed the appropriate ASTM standard D2798-11a (2011d). Description of fly ash petrology followed procedures outlined by Hower (2012).

2.4. Low temperature ashing (LTA)-XRD and XRF analysis

A representative portion of each coal sample was ground to fine powder and subjected to low-temperature oxygen-plasma ashing (Gluskoter, 1965; Standards Australia, 2000) using an IPC four-chamber plasma asher, with the percentage of low-temperature ash (LTA) being determined in each case. A representative portion of each LTA, as well as of each other powdered sample (overburden and fly ash), was analysed by X-ray powder diffraction using a Phillips PW1830 diffractometer with Cu K α radiation. The minerals present were identified by reference to the ICDD Powder Diffraction File. Quantitative analyses of mineral phases in each LTA, and also in the untreated overburden and fly ash samples, were conducted using the SiroquantTM, commercial interpretation software, originally developed by Taylor (1991) based on the profile refinement techniques described

by Rietveld (1969). For XRD analysis of the fly ash samples the diffraction pattern of a poorly-crystalline aluminosilicate phase (described in the Siroquant database as "metakaolin") was used to represent the amorphous material, following the procedure described by Ward and French (2006).

A separate representative portion of each coal sample was ashed at 815 °C. The (high-temperature) ashes of the two coals, and also the overburden and fly ash samples (without ashing), were calcined at 1050 °C, fused with lithium metaborate and cast into discs, following the method of Norrish and Hutton (1969). The discs were analysed by X-ray fluorescence (XRF) spectrometry using a Philips PW 2400 spectrometer and SuperQ software, and the results expressed as percentages of the major element oxides in each sample. The loss on ignition at 1050 °C for each overburden and fly ash sample was also determined as part of the analysis process.

2.5. Electron beam and Raman analysis

The morphology, structure, and composition of the coal, overburden and fly ash samples were investigated using a Zeiss Model ULTRA plus field-emission scanning electron microscope (FE-SEM), with charge compensation for conductive as well as non-conductive samples, and a 200 keV JEOL-2010 F high-resolution transmission electron microscope (HR-TEM), equipped with an Oxford energy dispersive X-ray detector, and a scanning (STEM) unit. The FE-SEM was equipped with an energy-dispersive X-ray spectrometer (EDS) and mineral identifications were made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes. EDS spectra were recorded in TEM image mode and then 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 SAED (selected area electron diffraction) or MBD (microbeam diffraction) mode, and the *d* spacings were compared to the International Center for Diffraction Data (ICDD, 2013) 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 a representative portion of each coal, overburden and fly ash sample; this is a commonly used technique for HR-TEM sample preparation (Chen et al., 2004, 2005). 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 (Giere et al., 2006; Silva et al., 2011a,b,c,d). Before FE-SEM and STEM analysis, the TEM specimen holder was cleaned with an Advanced Plasma System (Gatan Model 950) to minimize contamination (Silva et al., 2012a,b,c). A drift correction system was used for the STEM-EDS mapping.

Raman spectroscopy was also carried out for mineral identification, following the procedure reported by several authors (Quispe et al., 2012; Ribeiro et al., 2010; Silva et al., 2011a,b,c). In order to understand composition of any nano-mineral assemblages in the samples, sequential extraction and magnetic separation were conducted following methods reported by Silva et al. (2012c). However, only two-dimensional information was available with those techniques. A dual-beam Focused Ion Beam SEM (FIB-SEM) (FEI Dual BeamTM Helios 600 NanolabTM) was used, equipped with the following primary components: 1: a high-resolution Field Emission Gun (FEG) for SEM; 2: multiple electron detectors for image acquisition, such as through-the-lens detector (TLD), an Everhart-Thornley detector (ETD), and a backscattered electron detector (BSED) for compositional information; and 3: a high-resolution focused Ga⁺ ion beam to precisely select, slice, and image a specific region of the species of interest, with a spatial resolution within the 10-nm range. FIB-SEM is an analytical technique based on the unique combination of an ion gun and an electron gun, where specimens can

Table 1

Physical and chemical characteristics of coal, overburden and fly ash samples (wt. %, as-received basis).

Samples	M	Ash	VM	FC	TS	C	H	N	O	PS	SS	OS
ALD	2.30	8.00	39.60	50.10	2.76	66.60	5.10	0.87	24.67	0.13	0.26	2.37
ATK	12.40	11.40	41.50	44.50	4.84	70.20	6.60	1.00	17.36	0.78	0.61	3.45
BROB	2.70	73.30	14.20	9.80	3.69	12.49	2.05	0.01	5.76	0.60	0.53	2.56
TROB	2.30	78.30	13.10	6.30	1.74	6.10	0.97	0.03	10.56	0.32	0.42	1.00
NCFA	1.98	79.30	8.80	9.80	0.64	15.70	0.29	0.98	1.11	nd	nd	nd
SCFA	2.82	61.10	9.80	26.20	1.19	33.40	0.62	1.10	nd	nd	nd	nd

M: Moisture; VM: Volatile matter; FC: Fixed carbon; TS: Total sulphur; PS: Pyritic sulphur; SS: Sulphate sulphur; OS: Organic sulphur; C: Carbon; H: Hydrogen; N: Nitrogen; nd: Not determined.

be positioned at the intersection point of the electron and ion beam with an accuracy of much less than 1 μm . This permits simultaneous ion milling nano-sectioning and secondary electron imaging of the region of interest at a spatial resolution within the nanometre range (Giannuzzi et al., 1999). The compositions of nano-spheres found in the samples were determined by this technique (Silva et al., 2012c).

2.6. Trace element analysis

Inductively coupled plasma mass spectrometry (ICP-MS) was applied to determine the principal trace element concentrations in the

coal, overburden and fly ash samples. For ICP-MS analysis, the samples were digested using an UltraClave Microwave High Pressure Reactor. The basic load for the digestion tank was composed of 330-ml distilled H_2O , 30-ml 30% H_2O_2 , and 2-ml 98% H_2SO_4 . Initial nitrogen pressure was set at 50 bars and the highest temperature was set at 240 $^\circ\text{C}$ that lasted for 75 min. The reagents for 50-mg fly ash sample digestion were 5 ml 40% HF and 2 ml 65% HNO_3 , but for coal samples 2 ml 40% HF and 5 ml 65% HNO_3 were used. Multi-element standards (Inorganic Ventures: CCS-1, CCS-4, CCS-5, and CCS-6) were used for calibration of trace element concentrations. More details for these coal-related sample digestion and ICP-MS analysis techniques are given by Dai et al. (2011). Arsenic and Se were determined by ICP-MS using collision cell

Table 2a

Macerals and minerals in coal and overburden samples (vol %), plus maximum and random vitrinite reflectances (R_{max} and R_{r} , %) and V-types (% distribution of vitrinite maximum reflectance in 0.1% increments).

Macerals/minerals	ALD		ATK		BROB		TROB	
	Minerals included	Mineral-free basis	Minerals included	Mineral-free basis	Minerals included	Mineral-free basis	Minerals included	Mineral-free basis
Telinite	2.8	2.9	4.2	4.8	0.0	0.0	0.0	0.0
Collotelinite	81.6	83.3	59.2	67.3	12.4	68.1	11.8	62.1
Total telovitrinite	84.4	86.1	63.4	72.0	12.4	68.1	11.8	62.1
Vitrodetrinite	9.2	9.4	15.6	17.7	3.0	16.5	3.0	15.8
Collodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	2.2	11.6
Total detrovitrinite	9.2	9.4	15.6	17.7	3.0	16.5	5.2	27.4
Corpogelinite	0.0	0.0	3.6	4.1	0.0	0.0	0.0	0.0
Gelinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total gelovitrinite	0.0	0.0	3.6	4.1	0.0	0.0	0.0	0.0
Total vitrinite	93.6	95.5	82.6	93.9	15.4	84.6	16.9	89.5
Fusinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Semifusinite	0.0	0.0	0.4	0.5	0.0	0.0	0.0	0.0
Micrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Macrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Secretinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Funginite	1.6	1.6	1.6	1.8	0.0	0.0	0.0	0.0
Inertodetrinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total inertinite	1.6	1.6	2.0	2.3	0.0	0.0	0.0	0.0
Sporinite	1.6	1.6	0.4	0.5	1.2	6.6	0.0	0.0
Cutinite	0.4	0.4	0.4	0.5	0.4	2.2	0.6	3.2
Resinite	0.8	0.8	1.4	1.6	1.0	5.5	1.4	7.4
Alginite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Liptodetrinite	0.0	0.0	0.2	0.2	0.2	1.1	0.0	0.0
Suberinite	0.0	0.0	0.8	0.9	0.0	0.0	0.0	0.0
Exsudatinitite	0.0	0.0	0.2	0.2	0.0	0.0	0.0	0.0
Total liptinite	2.8	2.9	3.4	3.9	2.8	15.4	2.0	10.5
Silicate	1.2		10.0		8.6		13.9	
Sulfide	0.8		1.2		5.0		5.0	
Carbonate	0.0		0.6		0.2		0.0	
Other	0.0		0.2		68.0		62.2	
Total mineral	2.0		12.0		81.8		81.1	
R_{max}	0.59		0.61		0.55		0.48	
st dev	0.04		0.03		0.05		0.05	
R_{random}	0.55		0.58		0.52		0.45	
st dev	0.03		0.03		0.06		0.05	
v3							4	
v4					20		60	
v5	54		30		62		36	
v6	46		70		18			

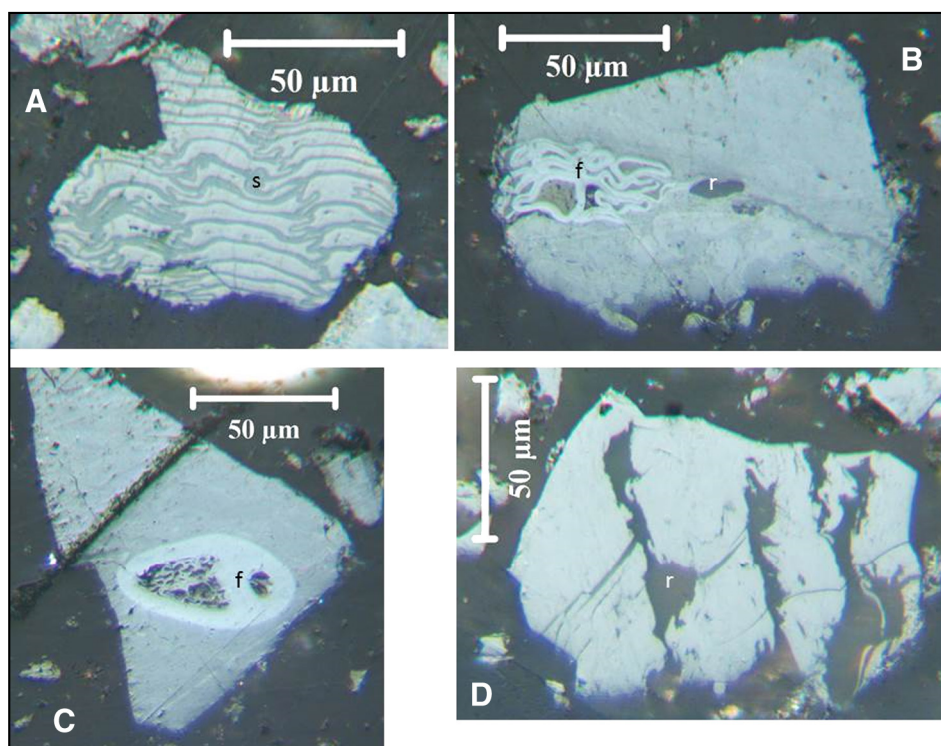


Fig. 2. Macerals in coal samples. A: Suberinite (s) with corpogelinite cell filling (sample ALD); B: Funginite (f) and resinite (r) (sample ALD); C: Funginite (f) (sample ALD); D: Resinite (r) (sample ATK). (All images in reflected-light, oil-immersion optics).

technology (CCT) in order to diminish the disturbance of polyatomic ions (Li et al., 2014).

Mercury was determined using a Milestone DMA-80 Hg analyzer. Fluorine was determined by pyrohydrolysis with an ion-selective electrode, following the methods described in ASTM Standard D 5987 (ASTM, 2002).

3. Results and discussion

3.1. Proximate and ultimate analysis

The physical and chemical characteristics of the coal, overburden, and fly ash samples are summarised in Table 1. The coals are medium to high sulfur in nature, with high organic sulfur contents. The ash yield for sample ATK (11.40%) is higher than for the ALD coal sample (8.0%). The mine overburden samples also have significant total sulfur concentrations (maximum 3.69%) and, as might be expected, high ash yields (maximum 78.30%). Ultimate analysis shows that there is still up to 10% or more carbon present in the overburden samples. Since the XRD data shows that there are no carbonate minerals in the overburden samples (see below), there is therefore some coaly material in the overburden samples that is currently being discarded. The total carbon content (organic plus inorganic) in the SCFA fly ash sample is 33.40%, and the ash has a total sulfur of 1.19%. The carbon, in particular, indicates inefficient burning of the feed coal during combustion.

3.2. Petrology

The organic matter in the coal samples is dominated by vitrinite macerals, which together make up around 95% of the organic components on a mineral-free basis (Table 2a). Telovitrinite is the most abundant vitrinite component, with detrovitrinite, the other main vitrinite component, being more abundant in sample ATK than sample ALD. Examples of some of the macerals are illustrated in Fig. 2. The mean maximum reflectance of the vitrinite in the coal samples is around 0.6%, and

the mean random vitrinite reflectance is 0.55–0.58%. According to the International Standard for Coal Classification (ISO, 2005), the mean random reflectance of the coal samples falls under the range for high volatile C bituminous (medium rank D) coal. The maceral composition of the two coals in the present study is more or less similar. However, the coals are quite different in petrographic characteristics to the coals from other important Indian coalfields (which have high inertinite contents; up to 50%) such as the Ramagundam and Sattupalli coalfields in Southern India (Singh et al., 2011, 2012).

Microscopic study indicates that glassy material is the most abundant component of the fly ash samples (Table 2b), together with a significant proportion of unburned carbon. Quartz and rock fragments are also visible (Fig. 3), especially in sample SCFA. The rock fragments are partially vitrified, with coked carbons bordered by glassy rims (Fig. 3a). The glass matrix also contains spinel (Fig. 3b). The unburned carbon in the ashes is made up mainly of isotropic and anisotropic coke (char) particles; the isotropic char may be generated from burning coal of sub-caking rank. The actual correlation between the feed coal and the associated fly ash must be related to the local conditions of fly ash collection. Therefore, numerous additional samples need to be

Table 2b

Components observed in microscopic study of fly ash samples (vol %).

Composition	NCFA	SCFA
Glass	68.4	75.5
Mullite	0.0	0.0
Spinel	0.0	1.5
Quartz	1.6	4.5
Sulfide	0.0	?
Sulfate	0.8	1.0
Rock fragments	1.2	2.0
Isotropic coke	12.4	7.5
Anisotropic coke	14.4	7.5
Inertinite	1.2	0.5
Pet coke	0.0	?
Unburned coal	0.0	0.0

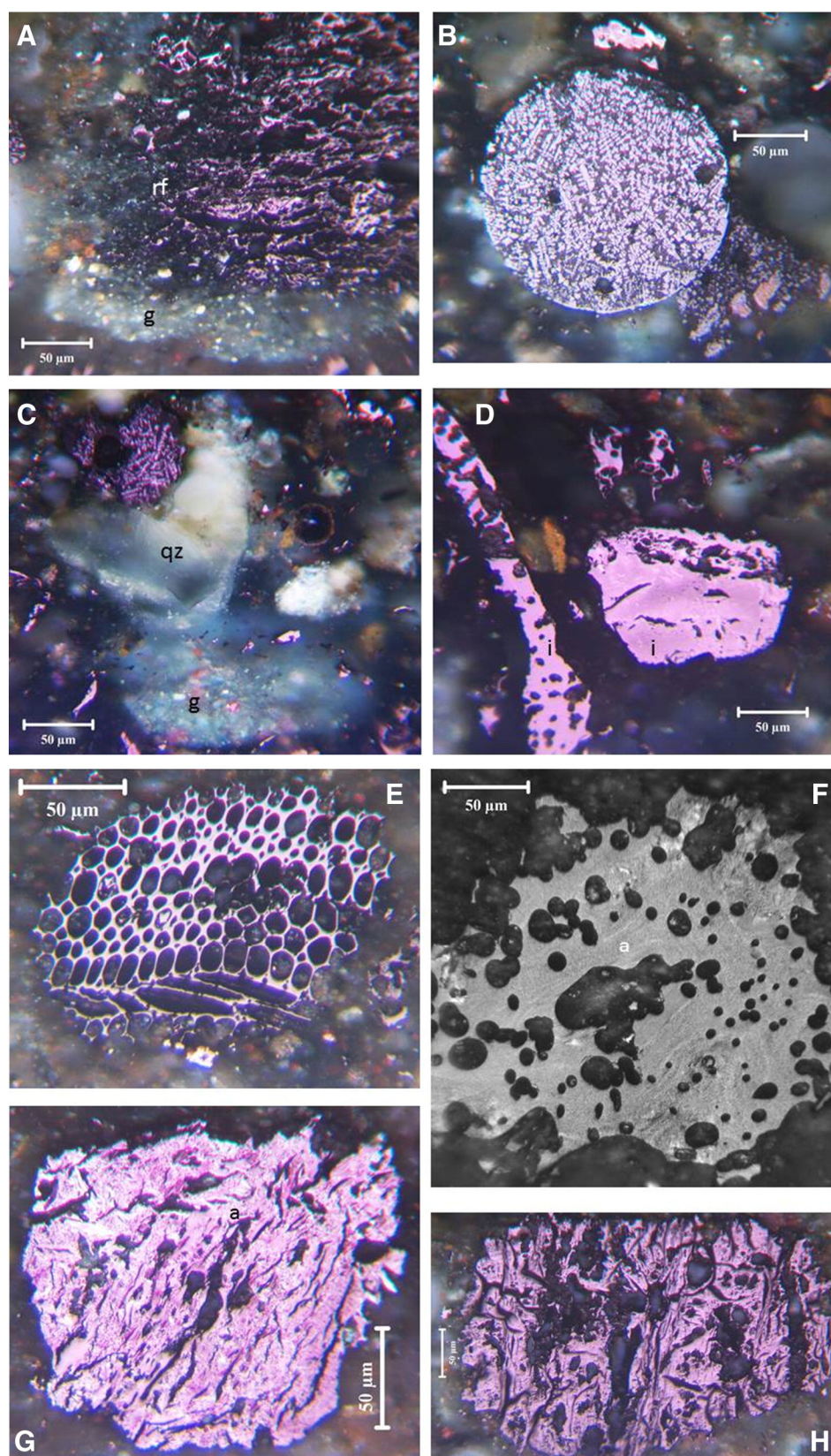


Fig. 3a. Microscopic constituents of fly ash. A: Partially vitrified rock fragment (rk) with coked carbons bordered by glassy rim (g) (sample SCFA); B: Spinel in glass matrix (sample NCFA); C: Glass (g) and quartz (qz) (sample NCFA); D: Isotropic coke (i) (sample NCFA). (All images in polarized reflected-light, oil-immersion optics). b: Microscopic constituents of fly ash. E: Inertinite (sample SCFA); F: Anisotropic coke (a) (sample SCFA); G: Anisotropic coke (a) (sample SCFA); H: Isotropic char from coal of sub-caking-coal rank (sample SCFA). (All images in polarized reflected-light, oil-immersion optics).

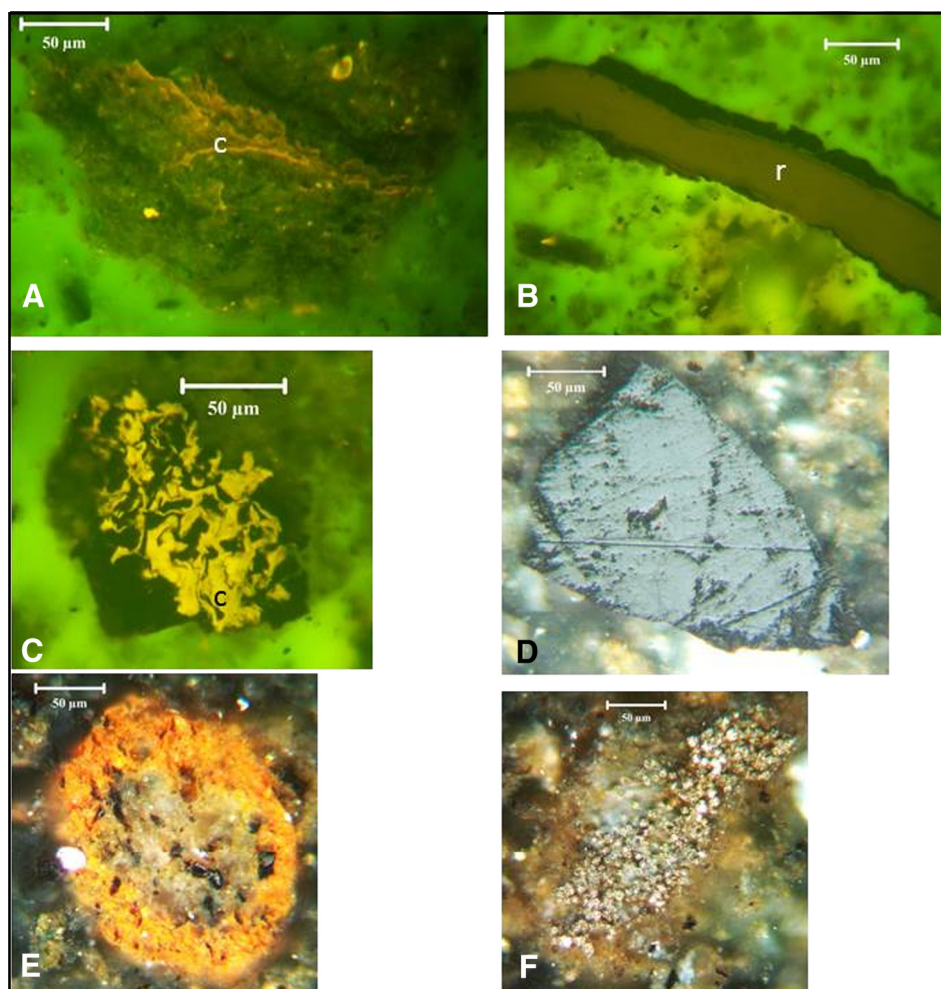


Fig. 4. Macerals and minerals in mine overburden. A: Cutinite (c) (sample BROB); B: Resinite (r) (sample BROB); C: Cutinite (c) (sample BROB); D: Collotelinitite (sample BROB); E: Orange Fe-sulfate or Fe-oxide (sample BROB); F: Framboidal pyrite (sample BROB). (All images in reflected-light, oil-immersion optics. Images A, B, and C were taken with blue-light excitation).

obtained and more thoroughly studied on a hopper-by-hopper level in order to gain an understanding of the properties of representative fly ash samples of the thermal plant.

The organic matter in the mine overburden materials is also vitrinite-rich (Table 2a), with no visible interinite component. Liptinite, mainly sporinite, cutinite and resinite (Fig. 4), is a more abundant component of the organic matter in the overburden rocks than in the coal samples, making up 10–15% of the mineral-free organic matter. Sulphide minerals, including framboidal pyrite, together with Fe-oxides

and/or Fe-sulphates, are also visible under the microscope (Fig. 4), and may be responsible for producing acid mine drainage from the overburden materials.

3.3. Chemistry

3.3.1. Major elements

The percentages of major-element oxides in the samples, based on XRF analysis of ashes prepared at 815 °C for the coal samples and the as-received samples of the other materials, are given in Table 3A. To facilitate comparison, especially between the coal ashes and the other

Table 3A

Chemical analysis data for coal ash, overburden and fly ash samples (wt %).

Oxides	ALD	ATK	BROB	TROB	NCFA	SCFA
SiO ₂	52.71	53.86	48.47	62.29	37.57	41.01
Al ₂ O ₃	21.34	19.93	15.03	14.63	14.72	24.28
TiO ₂	0.90	0.90	0.85	0.92	0.86	1.61
Fe ₂ O ₃	14.31	19.78	6.44	4.02	5.56	6.22
Mn ₃ O ₄	0.195	0.108	0.040	0.029	0.018	0.032
CaO	1.31	0.37	0.15	0.25	0.57	0.50
MgO	1.32	0.85	1.27	1.04	0.47	0.19
K ₂ O	1.64	2.00	1.92	1.59	1.27	0.42
Na ₂ O	1.50	0.89	0.45	0.21	0.36	0.09
P ₂ O ₅	0.071	0.076	0.063	0.056	0.059	0.090
SO ₃	3.11	0.78	1.23	0.79	0.27	0.26
LOI*	nd	nd	23.68	13.87	35.43	24.00
Total	98.41	99.54	99.59	99.70	97.16	98.69

Data for ALD and ATK represent coal ash analyses; others are samples as received. LOI = loss on ignition at 1050 °C; nd = not determined.

Table 3B

Chemical analysis data in Table 3A (wt%), normalised to an LOI-free basis.

Oxides	ALD	ATK	BROB	TROB	NCFA	SCFA
SiO ₂	53.56	54.11	63.85	72.58	60.87	54.90
Al ₂ O ₃	21.68	20.03	19.81	17.05	23.85	32.51
TiO ₂	0.92	0.90	1.11	1.07	1.39	2.16
Fe ₂ O ₃	14.54	19.87	8.48	4.69	9.01	8.32
Mn ₃ O ₄	0.20	0.11	0.05	0.03	0.03	0.04
CaO	1.33	0.37	0.20	0.29	0.93	0.67
MgO	1.34	0.85	1.68	1.21	0.75	0.25
K ₂ O	1.67	2.00	2.53	1.85	2.06	0.57
Na ₂ O	1.53	0.89	0.59	0.25	0.58	0.11
P ₂ O ₅	0.07	0.08	0.08	0.07	0.10	0.12
SO ₃	3.16	0.78	1.61	0.91	0.44	0.35
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table 4

Trace elements concentrations in the samples (ppm, whole-sample basis) (bdl: below detection limit).

Elements	ALD	ATK	BROB	TROB	NCFA	SCFA
Li	5.22	3.58	70.63	65.69	71.66	91.50
Be	0.24	0.20	1.54	1.42	3.61	17.75
Sc	1.69	1.25	14.39	15.15	17.15	21.31
V	11.21	5.94	124.62	120.49	134.12	156.06
Cr	20.15	20.59	167.09	249.00	138.38	111.38
Co	4.78	3.02	21.86	19.95	21.72	23.72
Ni	28.56	42.98	118.46	134.24	118.26	38.64
Cu	5.47	3.20	33.14	33.90	41.47	74.83
Zn	13.41	13.27	101.71	92.45	72.07	128.67
Ga	1.73	1.14	18.72	17.61	20.72	58.29
Ge	0.34	1.64	1.31	1.49	4.79	34.70
Rb	5.39	2.54	101.84	89.31	72.00	20.90
Sr	67.50	56.64	133.86	113.28	259.86	210.81
Y	2.29	2.19	19.57	21.56	35.24	132.97
Zr	11.00	12.49	135.13	177.17	183.36	456.61
Nb	0.75	0.57	11.59	12.09	14.08	48.21
Mo	0.82	0.21	1.67	0.83	4.61	18.98
Cd	0.06	0.03	0.24	0.31	0.35	0.88
In	0.01	0.00	0.08	0.07	0.07	0.18
Sn	0.07	bdl	3.13	3.29	5.40	14.62
Sb	0.10	0.05	0.47	0.37	0.50	0.56
Cs	0.61	0.20	7.52	6.50	6.24	1.82
Ba	119.41	76.19	247.09	221.67	346.28	233.54
La	3.04	1.40	28.34	28.97	40.89	126.77
Ce	5.65	2.99	60.98	61.21	89.83	271.74
Pr	0.72	0.36	6.62	6.98	10.64	31.10
Nd	2.83	1.60	26.26	27.44	42.88	122.20
Sm	0.56	0.34	4.97	5.31	8.64	24.64
Eu	0.15	0.11	1.15	1.18	1.78	4.30
Gd	0.62	0.36	4.91	5.13	8.80	26.18
Tb	0.08	0.06	0.69	0.74	1.23	3.89
Dy	0.45	0.34	3.93	4.39	7.12	23.69
Ho	0.09	0.07	0.78	0.88	1.38	4.80
Er	0.26	0.21	2.28	2.60	3.96	14.43
Tm	0.04	0.03	0.33	0.36	0.55	2.06
Yb	0.25	0.16	2.19	2.56	3.72	13.63
Lu	0.04	0.02	0.33	0.37	0.54	2.09
Hf	0.34	0.37	3.90	5.26	5.50	13.58
Ta	0.05	0.03	0.87	0.94	1.13	3.88
W	0.24	0.28	1.54	1.59	2.23	6.83
Tl	0.15	0.20	0.54	0.46	0.86	2.13
Pb	2.03	0.86	18.37	15.70	21.14	67.79
Bi	0.05	0.07	0.48	0.47	3.20	0.57
Th	1.22	0.35	10.30	10.92	14.51	41.08
U	0.26	0.11	2.18	2.16	4.67	13.35

samples, the XRF data were also recalculated to an LOI-free basis; the recalculated results are given in Table 3B.

The 815 °C ashes of the two coal samples have similar chemical compositions on an LOI-free basis, with around 53–54% SiO₂, 20–21% Al₂O₃, and 15–20% Fe₂O₃, as well as similar proportions of MgO, Na₂O and K₂O.

Table 5

Quantitative X-ray diffraction data for coal LTA, overburden and fly ash samples (wt %).

Sample	ALD (10.0% LTA)	ATK (19.5% LTA)	BROB	TROB	NCFA	SCFA
Quartz	28.1	25.7	31.1	45.1	16.7	8.6
Kaolinite	29.8	26.3	24.3	23.1		
Illite	28.1	31.2	25.8	23.6		
Pyrite	1.7	2.2				
Jarosite	4.3	1.8	6.7	2.8		
Sabieite		8.8				
Melanterite			10.1			
Siderite				0.9		
Anatase			0.8	0.9		
Gypsum	7.0	3.5	1.1	3.6		
Bassanite	1.0	0.5				
Mullite					6.3	5.6
Hematite					2.6	5.8
Anhydrite					0.4	2.6
Amorphous					74.0	77.3

Table 6

Inferred chemical analysis (wt %, LOI-free) for coal ash and overburden samples from XRD analysis data.

Sample	ALD	ATK	BROB	TROB
SiO ₂	60.97	58.06	61.58	71.81
Al ₂ O ₃	23.82	23.44	21.03	18.71
TiO ₂	0.00	0.00	0.89	0.95
Fe ₂ O ₃	3.47	5.39	6.71	2.01
MgO	0.00	0.00	0.00	0.00
CaO	2.90	1.44	0.40	1.24
K ₂ O	3.21	3.25	3.31	2.55
Na ₂ O	0.00	0.00	0.00	0.00
P ₂ O ₅	0.00	0.00	0.00	0.00
SO ₃	5.63	8.42	6.09	2.72
Total	100.00	100.00	100.00	100.00

The ash of sample ALD has slightly a higher percentage of CaO than that of sample ATK; SO₃ is also more abundant in the ash of sample ALD, suggesting that the CaO may be responsible for retention of sulphur in the ash as a CaSO₄ component (Koukousas et al., 2009). The overburden rocks have higher LOI-free proportions of SiO₂ but lower proportions of Fe₂O₃ and (in one case) CaO than the coal ashes. However, the overburden materials have broadly similar proportions of most other elements to the coal ash materials.

Although the fly ashes would be expected to have similar compositions on an LOI-free basis to the laboratory-prepared coal ashes, the two fly ashes in Table 3B have different proportions of a number of key components. For example, sample NCFA has a slightly higher percentage of SiO₂ than sample SCFA, and sample SCFA has a higher percentage of Al₂O₃ than sample NCFA. Perhaps more significantly, the LOI-free proportion of Fe₂O₃ is much lower in both fly ashes than in the laboratory ashes of the two coal samples. The comparisons of properties of coal and fly ash are better if the actual power plant feed and the fly ash produced can be sampled both at the same time, but this was not possible in our study. The dissimilarities between the coal and fly ash compositions are probably due to use of a blend involving several different coals as a feedstock for the thermal plant.

Table 7

Minerals and nanoparticles identified in coals (ALD and ATK), overburden (BROB and TROB) and fly ash samples (NCFA and SCFA). Analytical methods: a = FE-SEM, b = Raman spectroscopy, c = HR-TEM.

Mineral/Phases	ALD	ATK	BROB	TROB	NCFA	SCFA
Anatase	a,b,c	a,b,c	a,b,c	a,b,c		
Anhydrite					a,b,c	a,b,c
Barite			a	a		
Calcite	a,c		a,c	a,c		
Galena		c	c	a,c		
Goethite	b,c		b	a,c	b,c	b,c
Gypsum	a,b	a,b	a,b	a,b		
Hematite	a,b,c	a,b,c	a,b,c	a,b	a,b,c	a,b,c
Illite	a,b,c	a,b,c	a,b,c	a,b,c		
Jarosite	a,b,c	a,b,c	a,b,c	a,b,c		a,c
Kaolinite	a,b,c	a,b,c	a,b,c	a,b,c		
Magnetite				a,b,c	a,b,c	a,b,c
Melanterite		a,b	a,b			
Mullite				a,b	a,c	a,c
Pyrite	a,b,c	a,b,c	a,b,c			
Pyrophyllite				a,b,c		
Pyrrhotite		c	c	c		
Quartz	a,b,c	a,b,c	a,b,c	c	a,b,c	a,b,c
Rutile				a,b,c		a,b,c
Schwertmannite	b,c		c	a,b,c		c
Siderite	a,c	a,b,c	a,c	c		
Sphalerite	b,c		a,b,c	a,c		
Amorphous		a,b,c		b,c	a,b,c	b,c
Micro-walled carbon nanotube (MWCN)					b,c	b,c

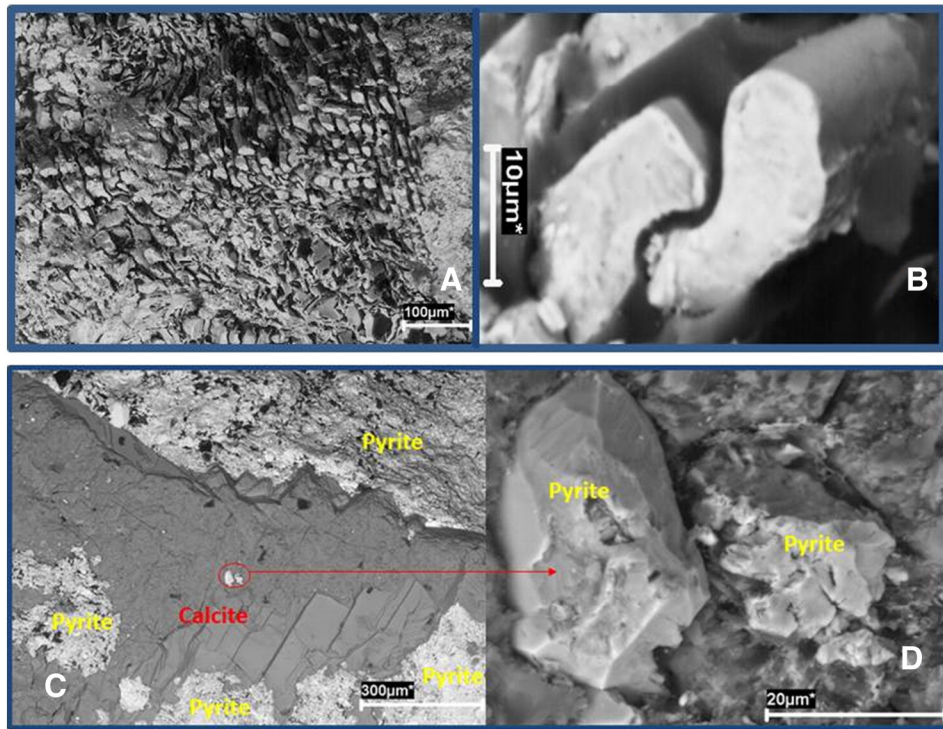


Fig. 5. Syngenetic pyrite in maceral pores: A) sample ALD, B) sample BROB; Pyrite inside and below calcite: C) sample BROB, D) (SE images from SEM).

3.3.2. Trace elements

The determination of trace element contents in coals is becoming increasingly important, and represents a significant challenge for assessment and management of environmental issues associated with coal processing (Dai et al., 2004, 2005, 2012; Finkelman, 1995, 2004; Ribeiro et al., 2011; Riley et al., 2012). It is also important to quantify the elements in coal, mine overburden, fly ash samples to assess the

potential for their economic recovery (Dai et al., 2010; Hower et al., 2013a,b; Seredin and Dai, 2012, 2014; Seredin et al., 2013).

The concentrations of the trace elements in the coal, overburden, and fly ash samples analysed for the present study are listed in Table 4. These show that the concentrations of most of the elements (whole-sample basis) are relatively high in the coal samples in comparison to earlier-reported data for the Northeast coalfield (Saikia et al.,

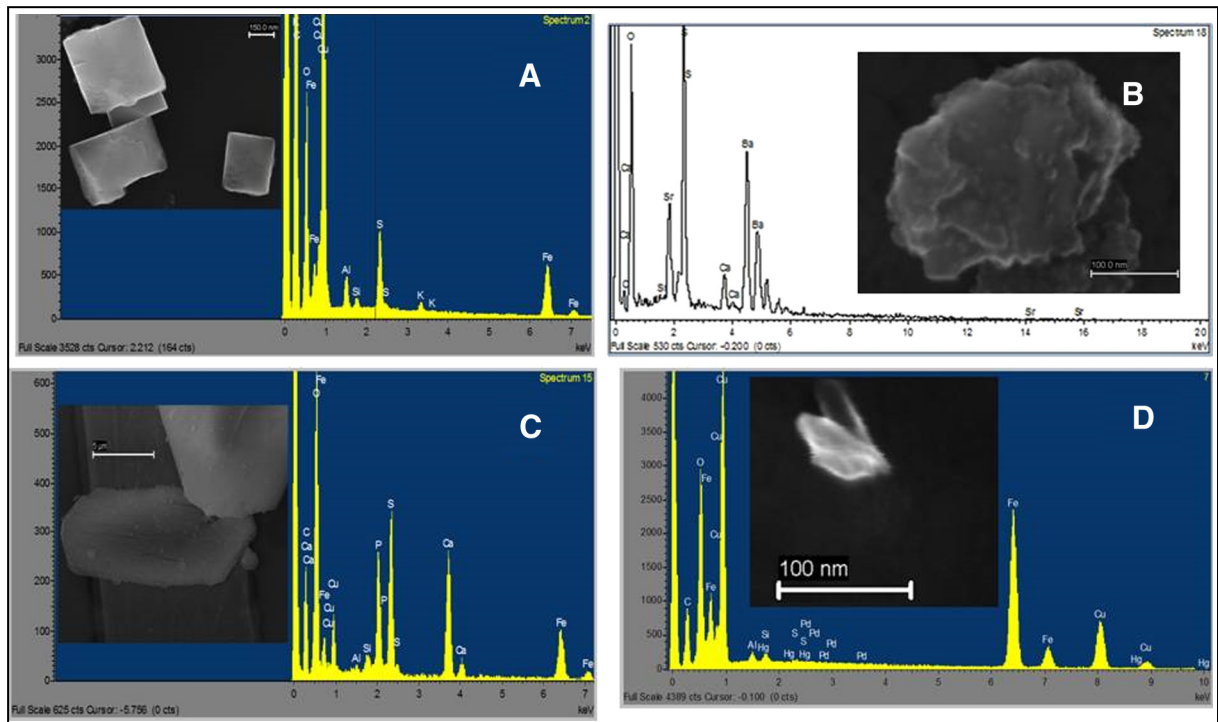


Fig. 6. A) Jarosite crystals and (B) barite agglomerates mixed with Ca-Sr-O-S-amorphous compounds in sample TROB; C) Nanoparticle containing hematite, Fe, S, and various trace elements in sample ALD; D) Gypsum, C-P-Si-Al-O-S-Ca-amorphous compounds, and melanterite containing Cu in sample BROB (SE images).

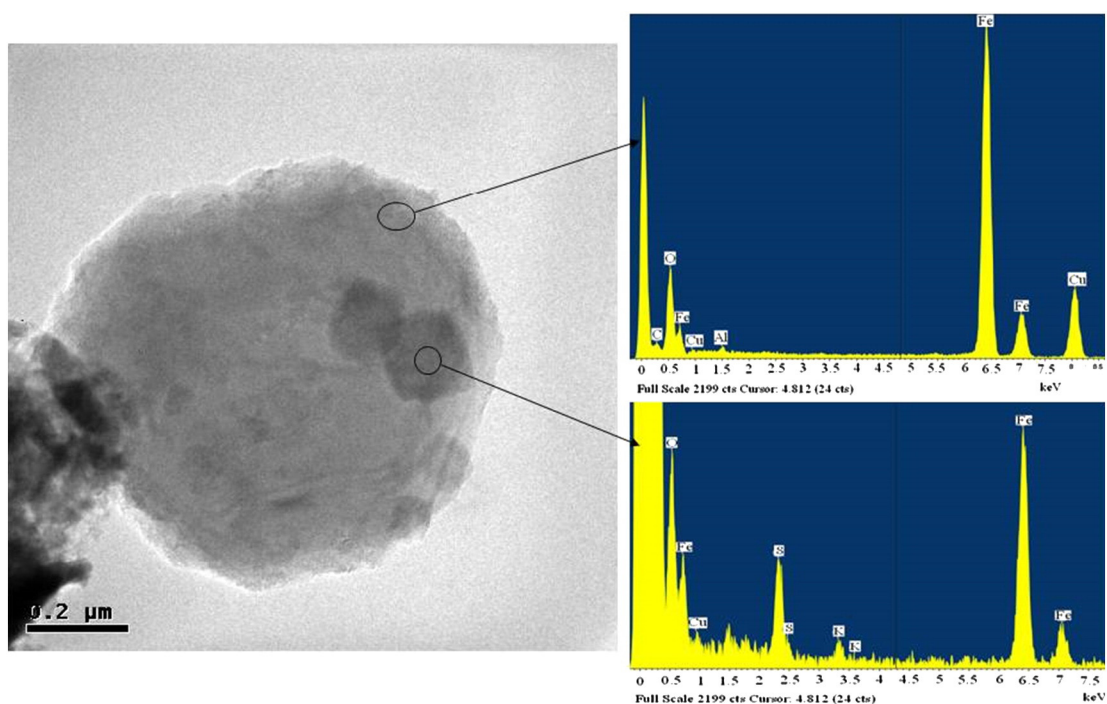


Fig. 7. Spherical ultra-fine hematite particle containing Cu and cubic jarosite in simple ATK (SE image).

2014). The Makum coals are highly enriched in V, Cr, Ni, Zn, Sr, Zr, and Ba in comparison to the world-average concentrations reported by Ketris and Yudovich (2009). On the other hand, concentrations of Li,

Sc, Co, Cu, Ga, Ge, Rb, Pb, Th, and Y are low. There are many factors that may affect the concentration of the trace elements in coal, including the nature of the sediment-source region that supplied terrigenous

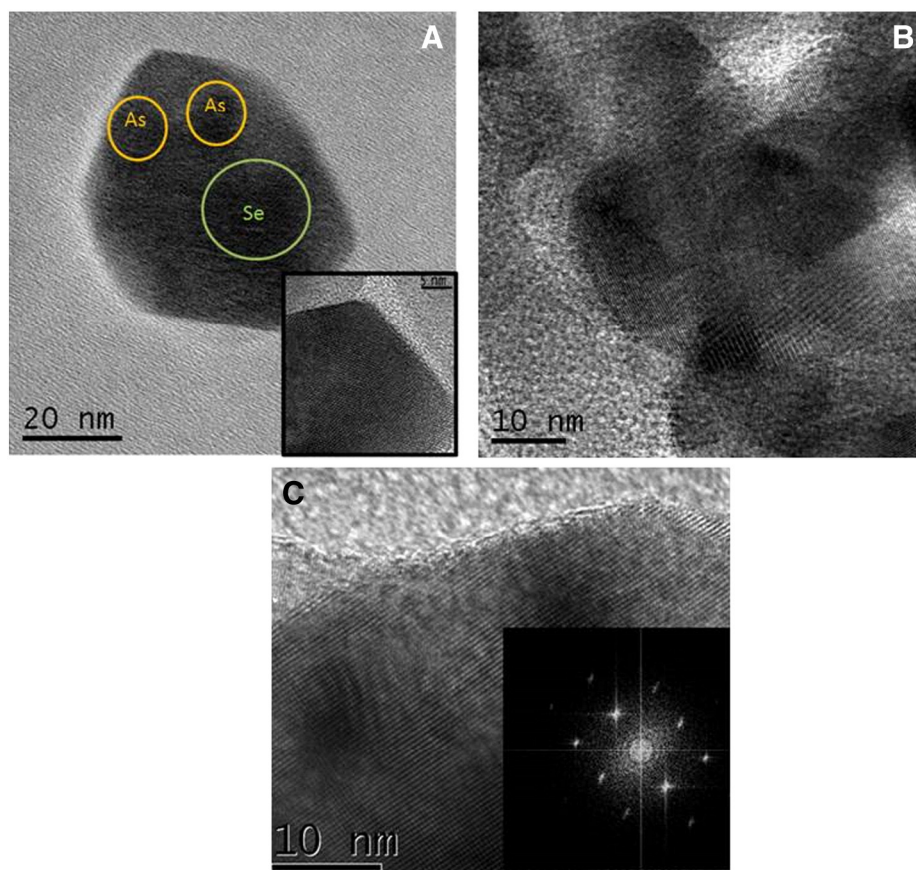


Fig. 8. HR-TEM images: (A) Goethite containing high proportions of As and Se (shown by circled symbols) in sample BROB; (B) Anatase grains agglomerated in sample TROB; (C) massive rutile agglomerate in sample TROB. Crystalline detail from HR-TEM image after Fast Fourier Transform also shown in each case.

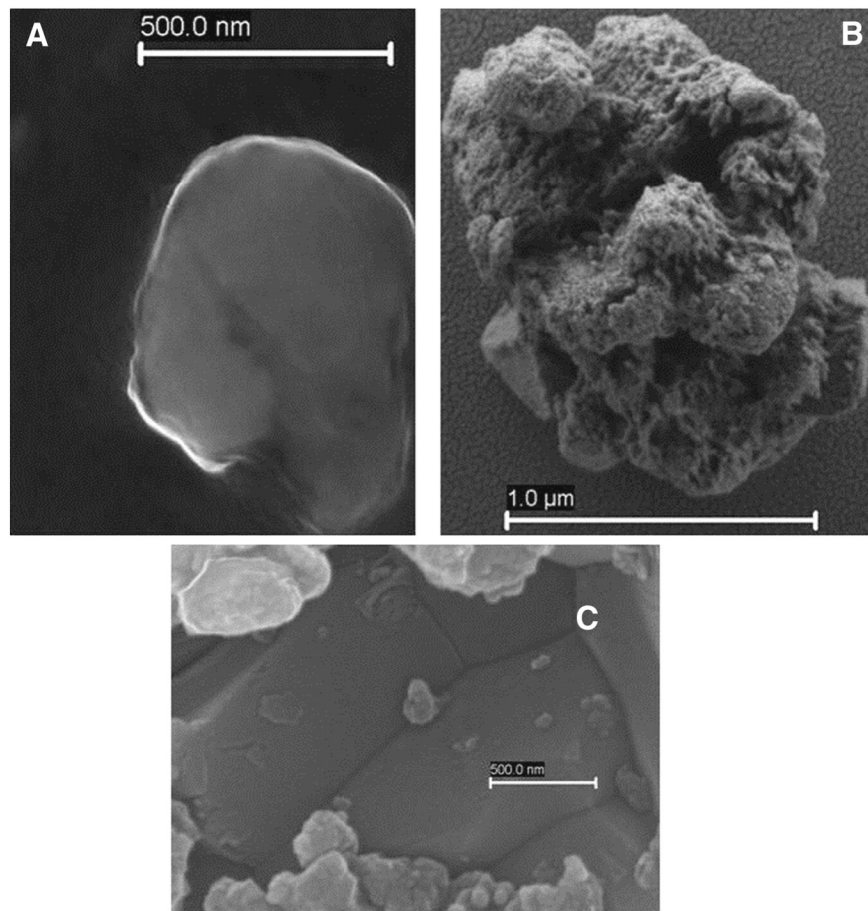


Fig. 9. A) Ultra-fine hematite containing Pb, As, and Mo around agglomerate in sample SCFA; B) Iron oxide (hematite) in sample SCFA; C) Anhydrite in sample NCFA (SE images).

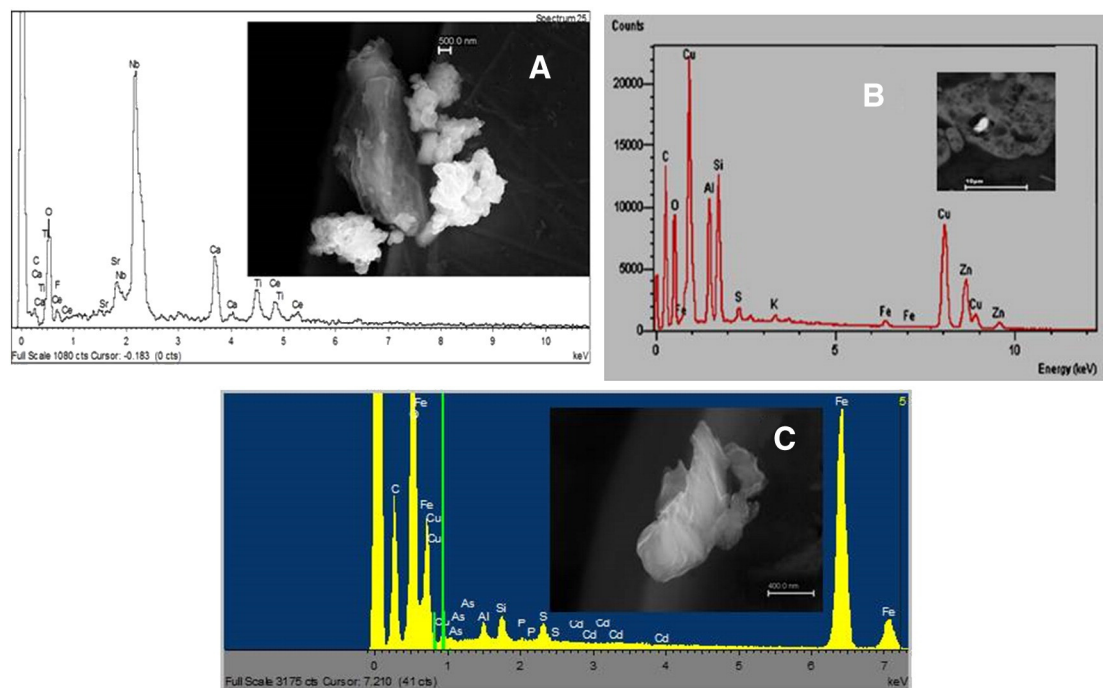


Fig. 10. A) Glasses containing Ca, Ce, C, F, O, Nd, Sr, and Ti in sample SCFA; B) Minor Cu-Zn-Fe-S compound encapsulated by Al-Si-O-K phase in sample NCFA; C) Al-S-C-Fe-amorphous compounds in sample SCFA (SE images).

materials to the coal-forming environment (Dai et al., 2005, 2012), a marine depositional environment (Ren et al., 1999), influx of hydrothermal fluids (Dai et al., 2006c, 2012; Seredin and Finkelman, 2008) and groundwater (Crowley et al., 1989; Hower et al., 1999), and input of volcanic ash (Burger et al., 1990, 2000; Dai et al., 2008; Zhao et al., 2013; Zhou et al., 2000). Strontium and Ba, which are relatively abundant in both coal samples, may be associated with calcite or dolomite and/or phosphate (Saikia et al., 2014; Ward, 1991). Vanadium, Cr, Ni, Mo, and U in coal may be associated with clay minerals and organic matter (Finkelman, 1994; Swaine, 2000). The concentration of Zn in coal may also be related to sphalerite or with clay minerals. Many other elements in coal, including Ni and Mo, are generally considered to be associated with pyrite (Bouska et al., 2000; Saikia et al., 2014). The mine overburden and fly ash samples show the presence of Li, Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Zr, Ba, Ce, Nd, and the other rare earth elements, Hf, Ta, W, Pb, U, and Th, as listed in Table 4. In addition, the NCFA and SCFA samples are enriched in Pb, Th, and U. Mardon and Hower (2004) reported that a few elements, e.g. S, As, Bi, Cd, Ga, Ge, Mo, Pb, Sb, Te, Tl, W, and Zn, show significant concentrations in the cooler fractions of fly ash streams. Many elements, including V, Sc, Cr, Co, Zn, Rb, Sr, La, Ce, Nd, Ba, and other heavy elements, e.g. Hf, Yb, W, Pb, Th, and U, are present in lesser concentrations in the coal samples in comparison to other coals of the world (Ketris and Yudovich, 2009).

The rare earth elements (REEs) are generally considered as useful geochemical indicators for the sediment provenance due to their stability in nature (Henderson, 1984). Some researchers have used REE geochemistry in the assessment of coal-forming processes (Dai et al., 2006a; Hower et al., 1999; Kalaitzidis et al., 2010; Seredin, 1996; Seredin and Dai, 2012). It has been suggested that there are four genetic types of REE plus Y (REY) enrichment in coal: 1) terrigenous type, with REY input by surface waters; 2) tuffaceous type, connected with falling and leaching of acid and alkaline volcanic ash; 3) infiltrational or meteoric ground water driven type, and 4) hydrothermal type, connected

with ascending flows of thermal mineral water and deep fluids (Seredin and Dai, 2012).

The total concentrations of rare earth element oxides are 154 ppm in ATK, 180 ppm in ALD, 267 ppm in BROB, 260 ppm in TROB, 389 ppm in NCFA, and 1580 ppm in SCFA. Seredin and Dai (2012) set the REY cut-off grade as 800–900 ppm and thus fly ash SCFA could be considered as a potential source for REY recovery.

Lead, Th, and U are present in significant amounts in both fly ash samples (NCFA and SCFA). The concentration of elements in coal combustion products depends on different factors, the most important of which is the concentration of elements in the feed coals. There are some differences between the concentrations of a few trace elements in the fly ashes compared to the coals of the present study, indicating the use of other coals (or blends of coals) in the plant just before the sampling time. The combustion and ash collection systems are also important for some of the more volatile elements (e.g. Zn). The fly ash has higher concentrations of Ni, V, and Sn, which has also been reported in other ashes by Hower et al., (2013).

Many trace elements, including Li, Be, Sc, V, Cr, Co, Ni, Cu, Ga, Ge, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, Hf, Ta, W, Re, Th, and U, do not volatilize or volatilize only slightly during coal combustion (Clarke and Sloss, 1992). Gallium is hard to volatilize during coal combustion due to its high boiling point, and is mostly associated with boehmite and organic matter in coal (Dai et al., 2006b, 2008). Some studies indicate that REEs rarely volatilize during coal combustion and are evenly distributed in fly and bottom ashes (Dai et al., 2010). Organically-bound REEs could partly volatilize and condense on the fine particles of fly ash, leading to higher REE contents in fly ash than in bottom ash (Dai et al., 2010). The concentrations of the critical rare earth elements (Nd, Eu, Tb, Dy, Y, and Er) are typically higher in the finer size-fraction fly ash than in the coarser fractions. Lanthanum, Ce, Pr, and Nd could be detected in minerals within some of the glassy phases in other fly ashes (Hower et al., 2013). Volatile trace elements, such as V, Zn, and Pb, have

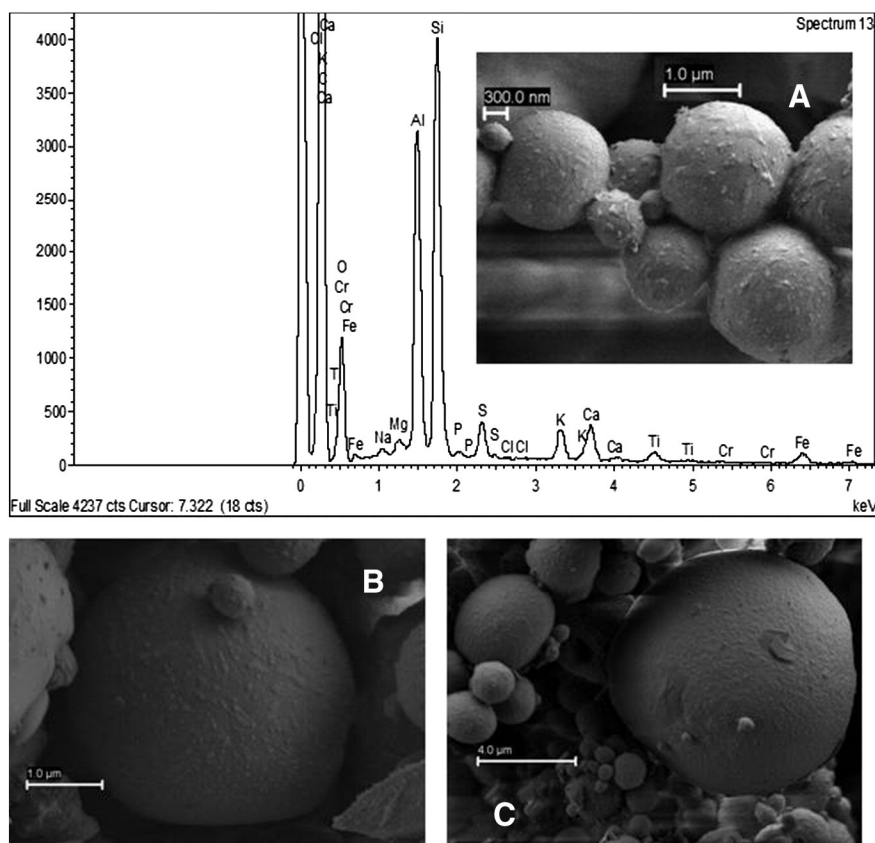


Fig. 11. (A–C) Typical nano-spheres containing Fe, Ca, Cr, Cl, K, Mg, Na, O, P, Ti, and S in SCFA coal fly ash (SE images).

relatively high concentrations in the fine fractions, usually due to the high surface area in those fly ash particles (Dai et al., 2014). However further geological as well as mineralogical studies with more samples are needed to explain the origin of the elements determined in the coals and ashes of the study area.

3.4. Mineralogy

3.4.1. XRD data

Table 5 lists the estimated weight percentages of the crystalline phases recognised in each LTA, overburden and fly ash sample. Notwithstanding the differences in ash (Table 1) and LTA yield, the LTAs of both coal samples have similar proportions of quartz, kaolinite, illite and pyrite, and thus similar overall mineral matter characteristics. Jarosite, probably derived from oxidation of pyrite in the coals before plasma ashing, is also present in both coal samples.

The LTA of both samples also contains gypsum, along with a small proportion of bassanite. These phases are more abundant in the LTA of the ALD sample than in that of the ATK sample, which is consistent with the higher proportion of CaO indicated for the ash of that sample in Table 3A. Although bassanite may be formed by interaction of organically-associated Ca with organic S during the plasma ashing process (Frazer and Belcher, 1973), or by interaction of acids from pyrite oxidation with calcite in the coal (Rao and Gluskoter, 1973), the gypsum in the LTAs of the present study probably occurred as such in the coal itself. It may have been formed, for example, by drying out of pore water containing dissolved Ca and SO₄, either as a groundwater deposit in the coal mine (Ward, 1991) or with drying of the coal after sampling. Some of the bassanite in the LTAs may have then been formed by dehydration of gypsum during the plasma ashing.

In addition to bassanite, a significant proportion of sazeite (NH₄Fe(SO₄)₂) was identified in the LTA of sample ATK. Like bassanite, this may represent an artefact of the plasma ashing process, formed by interaction of Fe, N and S in the organic matter during low-temperature oxidation.

Although sample TROB has slightly higher quartz content, the two overburden materials (samples BROB and TROB) have broadly similar proportions of quartz, kaolinite and illite to the LTAs of the coal samples. This suggests that these minerals in both cases (i.e. the coal and the associated rocks) are mainly of detrital origin. The overburden samples do not contain pyrite, but have significant proportions of jarosite and, in one case (sample BROB), melanterite, that may have been derived from oxidation of pyrite with exposure of the materials to the atmosphere, either at the mine site or during storage after sampling. Gypsum is also present in the overburden materials; since these were not subjected to low-temperature ashing, this further suggests that the gypsum in the coal LTAs was also present in the samples before ashing took place. As with the gypsum in the coals, the gypsum in the overburden may have been formed following evaporation of pore water or ground water containing dissolved Ca and SO₄ components.

Table 6 provides data on the inferred chemical composition of high-temperature ashes derived from the coal mineral matter (LTA) and also of the overburden samples, based on the XRD data in Table 5. To facilitate comparison, the inferred chemical data for the overburden samples have been expressed to an LOI-free basis. Comparison of the inferred percentages for the different oxides to the percentages of the same oxides in the same samples as determined by XRF analysis, normalised to an LOI-free basis (Table 3B), indicates similar values for the overburden materials, but significant differences for the coal LTA samples. The inferred SO₃ percentages for all samples in Table 6, however, are higher than the observed percentages from the XRF analysis in Table 3A; this

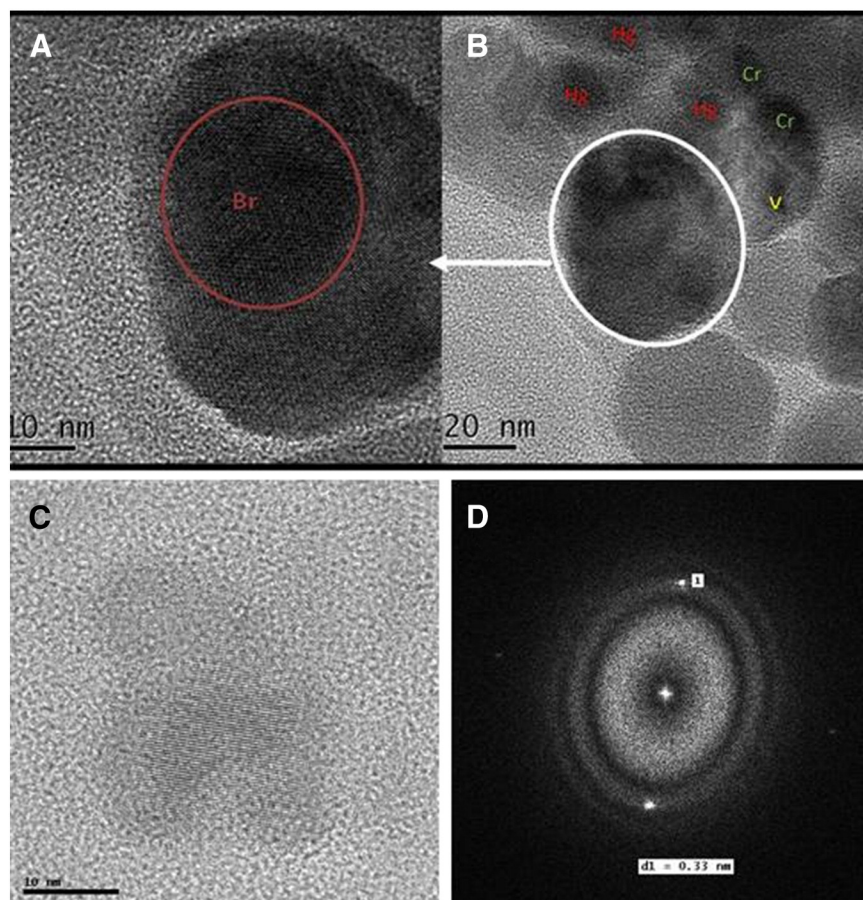


Fig. 12. A and B) Spherical magnetite agglomerate in sample NCFA, showing various trace elements; C and D) Crystalline As-mineral in sample SCFA (SE images).

probably reflects volatilisation of some of the S from the samples at the high temperatures used in the XRF preparation process. If allowance is made for these differences in SO_3 retention, the similarities between the data in Tables 6 and 3A suggest that the XRD analyses for the overburden samples in Table 5 are broadly consistent with the chemical analysis data.

Similar comparisons for the coal samples, however, show that the proportions of Fe_2O_3 inferred from the XRD data on the LTAs are significantly lower than those determined on the ashes of the same coal by XRF analysis. The percentages of the other two main oxides, SiO_2 and Al_2O_3 , as well as CaO and K_2O , are correspondingly higher than those indicated by the XRF data. These differences suggest the occurrence of additional Fe in the coals that was transferred to the LTA in a non-crystalline form, and therefore was not identified by the XRD analysis process.

Similar differences have been noted in other coals from North-east India by Saikia et al. (2014), especially material from the Makum coal-field (sample T2 in Saikia et al., 2014). A similar mode of Fe occurrence was inferred for that coal as well. Although no such analyses have been carried out on the coals of the present study, chemical and electron microprobe analyses of other coals (Benson and Holm, 1985; Kiss and King, 1977; Li et al., 2010; Ward, 1991) have also identified significant proportions of non-crystalline Fe as part of the organic matter, especially in the vitrinite/huminite of lower-rank coals.

As indicated in Table 5, the principal crystalline phases identified by XRD in the fly ashes are quartz, mullite and hematite, together with a small proportion of anhydrite. Although the coals analysed in the study were not necessarily the only coals used to provide the fly ash

(Table 3B indicates quite significant differences in composition), these are consistent in qualitative terms with the nature of the minerals identified in the LTAs of the coal samples. The quartz probably represents quartz grains in the parent coal that passed through the power station furnace with little if any thermal alteration, while the mullite was probably derived from high-temperature overburden thermal alteration of kaolinite or other clay minerals. The hematite was probably produced by alteration of pyrite in the feed coal, but may also in part represent a residue derived from non-mineral Fe in the maceral components. The anhydrite was likewise probably derived from gypsum in the feed coal, as well perhaps as Ca in non-mineral form associated with the organic matter.

The great bulk of the fly ashes, however, consist of amorphous material. In the absence of separate studies of the ashes after calcination, to remove the effects of unburnt organic matter, this appears to embrace both non-crystalline silicate glass and unburnt carbonaceous material. The percentages of the crystalline phases indicated by XRD are higher than those indicated by petrographic analysis (Table 2b), mainly because the XRD data also take into account crystalline phases with particle sizes that are too small to be separately identified by microscopic techniques.

Comparison of the chemical data for the fly ash samples, expressed on an LOI-free basis in Table 3B to eliminate dilution by the unburned carbon component, to the (LOI-free) analyses of the coal ashes (ALD and ATK), indicates that the fly ashes have significantly lower percentages of Fe_2O_3 than the ashes of the coals used in the present study. However, as indicated above, the power station from which the ash samples were obtained burns coals from a wider range of sources, and not all of

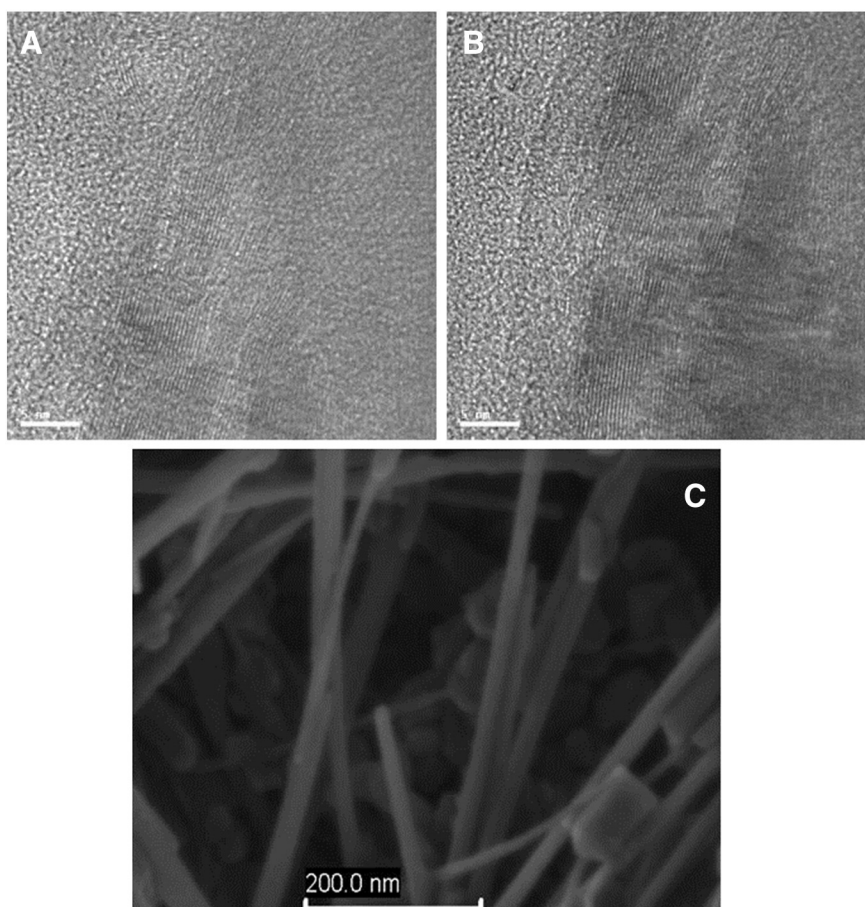


Fig. 13. HRTEM images of carbon nanotubes at different resolutions in fly ash sample SCFA.

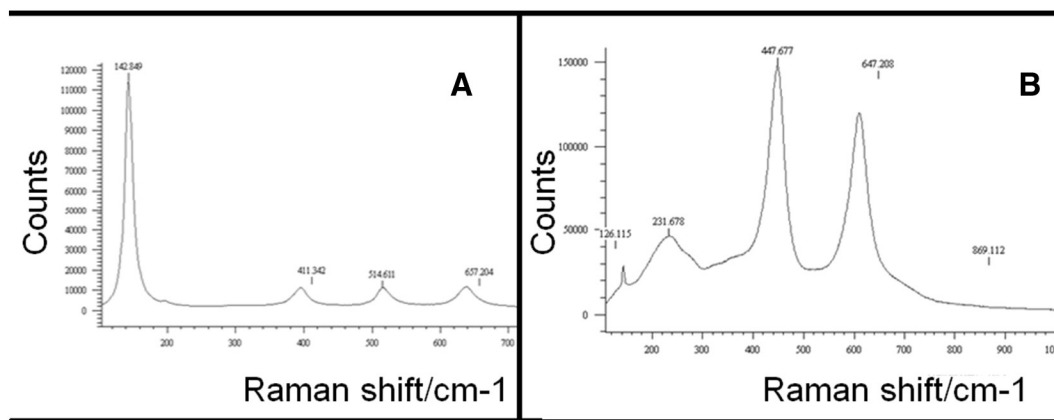


Fig. 14. Distinction between Ti-oxide phases observed using Raman spectrometry. (A) Anatase and (B) Rutile. Both identified using the standard Raman spectrum at 785 nm from a spot on overburden sample BROB.

those being used when the samples were collected may have been from the mines in question, or even from the Makum coalfield area.

3.4.2. Electron beam analysis

In addition to the mineral phases identified by X-ray diffraction, electron beam analysis by FE-SEM/EDS and HR-TEM/SAED/MBD/EDS has identified a number of other components (Table 7). These are typically present in only very minor proportions, and have an overall abundance below the detection limit of the XRD study. The electron beam methods also indicate that the minerals in the coal and mine reject samples occur in many different forms, and may include nano-mineral particles that potentially contain hazardous trace elements.

The dominant sulphide mineral identified by these techniques in samples ALD, ATK and BROB is pyrite, which is generally present as cell- or cavity-infillings or as replacements of the maceral components (Fig. 5A and B). However, pyrite was also observed in different configurations with other minerals, e.g. with calcite in maceral pore spaces; as pyrite framboids; associated with melanterite, schwertmannite, gypsum, jarosite, and hematite; and as cubic pyrite crystals in the BROB material (Fig. 5C and D).

Fig. 6A shows pseudomorphs after pyrite observed in sample TROB, possibly derived from reaction of pyrite-generated sulphuric acid with clays (Silva et al., 2011a). Similar jarosite pseudomorphs after pyrite were also detected in samples ALD, ATK, and BROB. Residual barite agglomerates mixed with amorphous Ca-Sr-O-S compounds were also observed in the TROB sample (Fig. 6B), and a combination of gypsum, amorphous C-P-Si-Al-O-S-Ca compounds, and Cu-bearing melanterite

was also seen in the BROB overburden and ATK coal samples (Fig. 6D). Similar mineral assemblages were also detected in the ATK coal sample. The ALD coal sample contains nano-particles made up of amorphous compounds; hematite, Fe, S, and potentially hazardous elements such as Hg and Cu (Fig. 6C). Hematite is also commonly visible under electron beam analysis, probably reflecting even more complete oxidation of the pyrite. The formation of Fe-oxides and hydroxides in the studied samples is considered to be the trend behind the geochemical cycling of metals and the dissolution of redox-sensitive metal oxide biomineralization products. These oxides are surface-active reservoirs that trap dissolved cations or anions by surface complexation and/or precipitation mechanisms. Spherical ultra-fine hematite containing Cu and cubic jarosite was seen in sample ATK (Fig. 7).

HR-TEM analysis of the coal and mine overburden reveals the presence of nano-minerals containing potentially hazardous elements (PHEs) in agglomerated and crystalline forms. For example, goethite containing high proportions of As and Se occurs in the BROB sample (Fig. 8A). In many cases, the goethite exists in the presence of schwertmannite, such as in samples ALD and TROB. Anatase agglomerates also occur in the TROB sample (Fig. 8B). Similar features were detected in samples ATK, ALD, and BROB. A massive rutile agglomerate, in sample TROB, with the crystal structure as indicated by selected-area electron diffraction, is shown in Fig. 8C.

A number of PHEs were also detected in the coal fly ash samples, which may have been produced by mineral transformations in these and similar coals during combustion. Fig. 9A and B show typical hematite particles, including ultra-fine hematite containing Pb, As, and Mo in one of the fly ash samples, adsorption of which may have occurred as

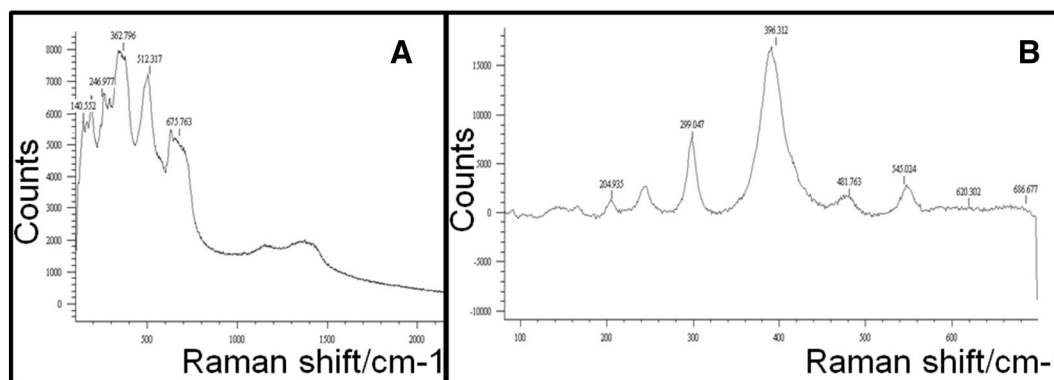


Fig. 15. Distinction between Fe-hydr/oxide phases observed using Raman spectrometry. (A) Magnetite and (B) Goethite. Identified using the standard Raman spectrum at 785 nm, as recorded from a spot on one of the coal fly ash (SCFA).

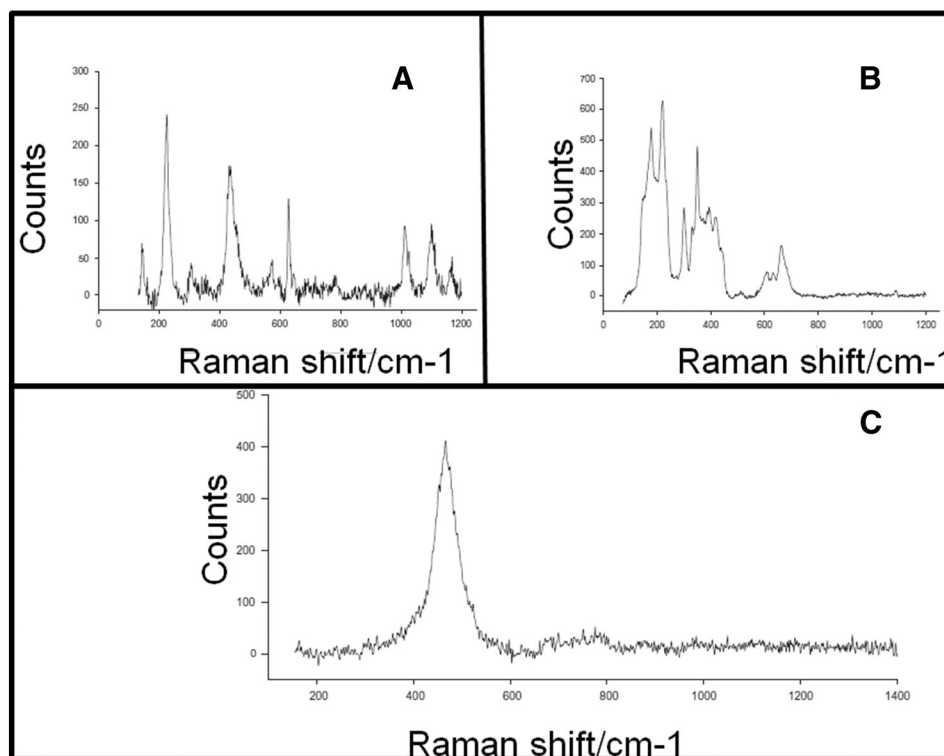


Fig. 16. Raman spectra from (A) jarosite (BROB), (B) sphalerite (BROB) and (C) quartz (ATK), obtained using the standard Raman spectrum at 532 nm. Recorded from a spot on one of the coal and overburden sample.

the ash cooled from the high temperatures of its formation. Ultra-fine anhydrite is also found in the coal fly ash (Fig. 9B).

Glasses containing Ca, Ce, C, F, O, Nd, Sr, and Ti are observed in the fly ash samples (Fig. 10A); these may be residues from clay and phosphate interactions. FE SEM-EDS reveals a minor Cu-Zn-Fe-S compound encapsulated by a major phase composed of Al-Si-O-K in the NCFA sample (Fig. 10B). A similar type of Al-S-C-Fe amorphous phase with a minor proportion of potentially hazardous elements (PHEs), including As, Cd, Cu, and P, was also observed in other fly ash samples (Fig. 10C). Spheres containing Fe, Ca, Cr, Cl, K, Mg, Na, O, P, Ti, and S (Fig. 11A and B) were also detected in both fly ash samples. Spherical magnetite agglomerates

encapsulating PHEs such as Br, Hg, Cr, and V, were identified in both fly ash samples by EDS techniques (Fig. 12A and B). A complex crystalline phase ($d_1 = 0.33$ nm) of a crystalline As mineral was identified by FESEM-EDS (Fig. 12B and C). Carbon nano-tubes (Fig. 13) are a common feature of Indian coal fly ashes (Silva et al., 2009a,b), and were also observed in the present study.

3.4.3. Raman analysis

The use of Raman spectral analysis for identification of minerals in the samples was first applied using the standard Raman spectrum. In general qualitative Raman investigations for the present study have

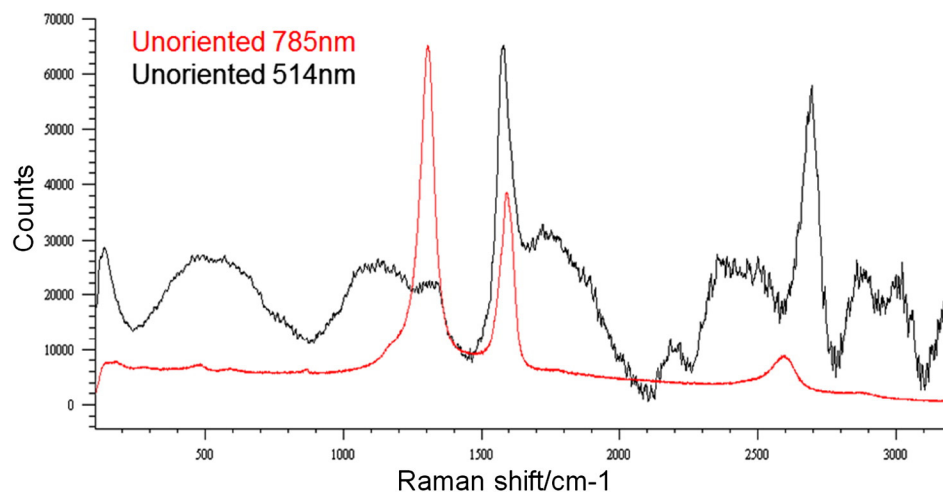


Fig. 17. Micro-walled carbon nanotube (MWCN) with comparative detected using the standard Raman spectrum (in red color) at 514 nm and 785 nm (sample SCFA).

revealed a wide range of other phases with various compositions and structures; for example, Ti-oxides (anatase and rutile), Fe-hydr/oxides (magnetite and goethite), jarosite, sphalerite, and quartz in the coal, overburden, and fly ash samples were all identified using Raman techniques (Figs. 14–16). The Ti-oxides in the overburden samples, as well as Fe-hydr/oxides in the fly ashes, were identified using the standard Raman spectrum at 785 nm, recorded from a spot on the samples. The presence of jarosite, sphalerite, and quartz in the coals and coal mine overburden samples was confirmed using the standard Raman spectrum at 532 nm, recorded from a spot on one of the samples. Micro-walled carbon nanotubes (MWCN) were identified in the fly ash samples using the standard Raman spectrum at 514 nm and 785 nm, as shown in Fig. 17.

4. Conclusions

The Makum coals are vitrinite-rich and of high volatile bituminous rank, with medium to high total sulfur and most of the sulphur being organically bound. The crystalline mineral matter in the coals consists mainly of quartz, kaolinite, and illite, with minor proportions of pyrite and pyrite oxidation products such as jarosite. Similar mineral assemblages occur in the overburden sedimentary rocks, suggesting that the minerals in the coal are mainly detrital in origin. Although only representing a small overall proportion, the organic matter in the overburden rocks is also vitrinite-rich; however, it contains a higher proportion of liptinite macerals, on a mineral-free basis, than the mineral-free organic matter of the coal samples. In addition to these silicate and sulphide minerals, the low-temperature oxygen-plasma ash (LTA) of the coals contains small but significant proportions of gypsum and bassanite. Gypsum is also present in the overburden materials. Although some of the bassanite, and possibly also some of the gypsum, in the coal LTAs may have been derived from interaction of non-mineral Ca in the coal with organic sulfur during ashing, the occurrence of gypsum also in the overburden strata suggests that crystalline gypsum also occurs in the coal themselves, precipitated perhaps from dissolved Ca and SO_4 in the pore water in mine exposures, or during sample air-drying.

Comparison of XRD and chemical analysis data suggests that a significant proportion of the Fe also occurs in the coal in a non-mineral form. This may include Fe in solution in the pore water, amorphous Fe oxides or hydroxides within the mineral matter, or Fe related in some way (e.g. by adsorption) to the organic matter. The presence of saebeite ($\text{NH}_4\text{Fe}(\text{SO}_4)_2$) in the LTA of one of the coal samples may reflect interaction of such Fe with organic nitrogen and sulfur during the plasma-ashing process.

Although pyrite itself was not identified in the mine overburden samples, significant proportions of jarosite and, in one case, melanterite may indicate that any pyrite in those materials has oxidised with exposure to the atmosphere, either at the mine site or during sample storage. These phases suggest that pyrite oxidation has occurred or is occurring in the strata, and may contribute to the formation of acid mine drainage in the region.

Small proportions of many other minerals were identified the coal, overburden and fly ash samples by electron beam methods, including anatase, anhydrite, barite, calcite, galena, goethite, gypsum, hematite, illite, jarosite, kaolinite, magnetite, melanterite, mullite, pyrite, pyrophyllite, pyrrhotite, quartz, rutile, schwertmannite, siderite, and sphalerite. Some minerals, e.g. calcite, goethite, gypsum, hematite, jarosite, kaolinite, magnetite, pyrite, rutile, schwertmannite, and siderite, are present as nanoparticles in many different forms, often with associated trace element components.

The concentrations of most trace elements in the coals are relatively low; however, higher concentrations are present in the overburden and fly ash samples. The coals contain significant amounts of V, Cr, Ni, Zn, Sr, Zr, and Ba, with lesser amounts of Li, Sc, Co, Cu, Ga, Ge, Rb, Pb, Th, and Y. Although the sources and relative abundance of the various elements require further evaluation, some of the coal fly ashes examined in the

present study could possibly be used for recovery of economically-valuable rare earth elements.

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