

Potassium-metasomatism in Anthracite: A Cluster of Geochemical Evidences

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Research

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Abstract

The present study focuses on the inorganic geochemical features of the bituminous coal samples from the Raniganj and the Jharia Basin, as well as the anthracite samples from the Himalayan fold-thrust belts of Sikkim, India. The SiO_2 content (48.05 to 65.09 wt% in the ash yield of the bituminous coal samples and 35.92 to 50.11 wt% in the ash yield of the anthracite samples) and the ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2$ (6.97 to 17.03 in the bituminous coal samples and 10.34 to 20.07 in the anthracite samples) reveal the intermediate igneous source rock composition of the minerals. The ratio of the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ in the ash yield of the bituminous coal samples (0.03 to 0.09) may suggest the presence of kaolinite mixed with montmorillonite, while its range in the ash yield of the anthracite samples (0.16 to 0.27) may imply the presence of illite mixed with kaolinite. The chemical index of alteration values may suggest the moderate to strong chemical weathering of the source rock under sub-humid to humid climatic conditions. The plot of the bituminous coal samples in the A-CN-K diagram depicts the traditional weathering trend of parent rocks, but the anthracite samples plot near the illite field and are a bit offset from the weathering trend. This may imply the plausible influences of the potassium-metasomatism at post coalification stages. The Fourier transform infrared spectra further reveal the hydroxyl stretching intensity of the illite in the anthracite samples substantiating the effect of the epigenetic potassium-metasomatism. The decrease in total kaolinite intensity/compound intensity of quartz and feldspar may provide additional evidence towards this epigenetic event.

1 Introduction

The nature and the abundances of the minerals in coals may influence their utilization in industries (Dai et al. 2018; Zhao et al. 2013). Accurate knowledge of the mineral matter in the coal is necessary to avoid ash deposition in boilers, emission of volatiles during coal combustion (Dai et al. 2018) as well as to reduce abrasion, corrosion, stickiness associated with coal processing (Finkelman et al. 1994; Ward 2002, 2016). In complementary, the mineral matter in the coal can act as graphitization catalyst for coal char, turbostratic carbon, coal tar pitch matrix, etc. (González et al. 2005; Oya and Marsh 1982; Rodrigues et al. 2012; Wang et al. 2001). Kaolinite and illite are observed as the potential catalysts for carbonaceous materials (Bonijoly et al. 1982; Marsh and Warburton 1970; Oberlin and Terriere 1975; Oya and Marsh 1982; Rodrigues et al. 2012; Wang et al. 2001), and in the presence of iron (González et al. 2005; Oya and Marsh 1982), they can improve the degree of structural ordering of the carbonaceous materials during high-temperature treatment.

The X-ray fluorescence (XRF), and Fourier transform infrared (FTIR) spectroscopy, among many other methods, document the inorganic geochemical characteristics of organic-rich source rocks efficiently. The major elemental oxides obtained from the XRF data reveal the parent rock composition and intensity of chemical weathering of those parent rocks (Bai et al. 2015; Fedo et al. 1995; Hazra et al. 2016; Moradi et al. 2016; Nesbitt and Young 1982; Tao et al. 2017; Varma et al. 2018; Zhang et al. 2018) as well as the palaeotectonic setting (Roser and Korsch 1986). The XRF data also discriminates the input of feldspar and clays through the ratio of potassium oxide to alumina ($\text{K}_2\text{O}/\text{Al}_2\text{O}_3$) as well as from the index of compositional variation (ICV) (Cox et al. 1995) in the organic-rich rocks. The FTIR data reveals the absorbance intensities of mineral matter like kaolinite, quartz, feldspar, siderite, etc. (Hazra et al. 2016; Varma et al. 2018) present in the organic-rich source rocks.

In this study, the inorganic geochemical characteristics of the bituminous coal samples from the Raniganj and the Jharia Basin as well as that of the anthracite samples from the Sikkim Himalayan fold-thrust belts of India have been studied employing XRF, and FTIR techniques. The authors have proposed the epigenetic potassium-metasomatism (K-metasomatism) in the anthracite samples in this study for the first time and discussed the influences of this metasomatic event on the clay mineralogical framework of these samples, which define the novelty of this investigation. To point out the influences of K-metasomatism on the clay mineralogy in a more precise way, they have also compared these samples with the ash yield of some selected bituminous coal samples, which are found not to experience this event. Additionally, the total intensities of kaolinite (TI_K) and quartz along with feldspar (TI_{Q-F}) are introduced to support the influences of the K-metasomatism on the clay mineralogy of the anthracite samples. Further, the authors have introduced a new index, namely the palaeohumidity factor (PHF), to determine the paleoclimatic condition during the source rock weathering episodes through modifying the 'C-value' proposed by Zhao et al. (2007). Hence, the objectives of the present study are to manifest the clay mineralogy from the ash yield of the bituminous and the anthracite coal samples, as well as to document plausible secondary alteration of the clay mineral framework of these samples. The knowledge of the clay mineralogy of the studied bituminous coal samples can be employed for their better utilization in the industries. On the other hand, the information on the clay mineral framework of the anthracite samples may help in understanding the catalytic effects of these minerals for synthetic graphite production.

2 Geological Setting

2.1. Raniganj Basin

The Raniganj Basin (Fig. 1; following Gee 1932), a significant part of the Damodar Valley Basin, is situated between $23^{\circ}22' \text{ N} - 23^{\circ}52' \text{ N}$; $86^{\circ}36' \text{ E} - 87^{\circ}30' \text{ E}$ and encompasses an aerial extent of 1900 km^2 . This basin was initially a sag basin that later formed a homoclinal geometry with the deposition of the Talchir and the Barakar sediments (Gee 1932). The meandering rivers on the north side of this basin supplied the organic matter, whereas, in the eastern part, the peat mires were developed with fanglomeratic cones (Ghosh 2002). The west-bound rivers in this basin contributed the organic detritus along with clastic sediments to deposit peats in the western part of this basin (Ghosh 2002). Table 1 presents the general stratigraphy of the Raniganj Basin (following GSI 2003; Mukhopadhyay et al. 2010). As two of the studied bituminous coal samples were collected from the Barakar and the Raniganj Formation of the Raniganj Basin, brief discussions of those two formations are mentioned below:

Table 1
Stratigraphic successions of the Raniganj Basin (following GSI 2003 and Mukhopadhyay et al. 2010)

Age	Formation	Lithology	Thickness (m)
Recent and Quaternary		Alluvial and residual soils; lateritic capping	90
—————Unconformity—————			
Tertiary		Light grey mudstone and siltstone with bands of marlstone; white, soft fine grained clayey sandstone, mottled clay and loose sand with pebbles of vein quartz; occasionally lignite at the basal part	300
—————Unconformity—————			
Cretaceous	Igneous intrusives	Basic (dolerite) dykes; Ultrabasic (mica-peridotite, mica-lamprophyre, lamprophyre) sills and dykes	—
Cretaceous	Rajmahal Formation	Greenish grey to black, fine to medium grained vesicular porphyritic basalt and volcanic breccia; weathered aphanitic basalt at places; one to five inter-trappeans consisting of grey shale, fine grained sandstone and carbonaceous shales	120
—————Unconformity—————			
Upper Triassic	Supra-Panchet	Massive, very coarse to coarse quartzose sandstone, conglomeratic at places; bands of dark red silty shale	300
Lower Triassic	Panchet	Coarse grained greenish yellow and greenish grey soft, micaceous, cross-bedded sandstone with slump structures; khaki green fissile silty shale; alternate bands of yellow coarse grained immature sandstone and bright reddish-brown claystone with calcareous concretions; conglomeratic at the base	600
Upper Permian	Raniganj	Grey to light grey fine and medium grained micaceous feldspathic sandstone with calcareous clayey matrix in the upper part; siltstones and shales, often interlaminated with fine grained sandstone; carbonaceous shales and coal beds	1150
	Barren Measures	Dark grey to black micaceous or carbonaceous, fissile shales with ferruginous laminae and thin bands of dense, hard, cryptocrystalline clay ironstones; rarely interbanded with fine-grained sandstone	600
Lower Permian	Barakar Formation with Kaharbari Formation (?) at base	Very coarse to medium grained arkosic sandstones, often cross-bedded; grey and carbonaceous shales, at times interbanded with fine grained sandstone; fire clay lenses and coal beds; pebbly and carbonaceous in lower part	750
	Talchir	Tillite or diamictite with sandy or clayey matrix at the base; medium to fine grained khaki or yellowish green feldspathic sandstone; siltstone, silty shale, needle shale and rhythmite with dropstones.	500
Precambrian	Chotanagpur Gneissic Complex	Granite gneiss with migmatitic gneiss, hornblende schist, hornblende gneiss, metabasic rocks, pegmatite and quartz veins etc.	—

Barakar Formation

The Barakar Formation comprises white to fawn-colored sandstone carbonaceous shale, fire-clays, and coal beds reflecting a braided to fluvio-lacustrine alluvial deposit. The lower and the middle units of this formation comprise a thicker coal seam than the upper unit. The Barakar Formation is the principal coal-bearing unit in the Lower Gondwana formations. The coal seams intercalate with the sandstone and shale beds. This formation is thicker in the northern and the western parts of this basin, while it becomes thinner towards the east and south. It has a maximum thickness of 750 m.

Raniganj Formation

The Raniganj Formation consists of a large number of regionally developed coal seams of commercial importance. The Raniganj Formation is characterized by a sequence of sandstone-shale-coal sequence in which different lithology exhibits broad fining upward cycles. The sandstones in this formation are fine-grained and of uniform character compared to that in the Barakar Formation. The sandstones are associated with micaceous siltstone, sandy shales, dark grey shales, and coal seams. The Raniganj Formation attains a maximum thickness of 1150 m at the Surajnagar area located south-east of Asansol in the western part of the Raniganj Basin (GSI 2003).

2.2 Jharia Basin

Jharia Basin (Fig. 2; following Fox 1930, Mishra and Cook 1992) comprises a large reserve of bituminous coking coals that can be used in the metallurgical industries (Mishra and Cook 1992). This basin extends between 23° 37' – 23° 52' N and 86° 06' – 86° 30' E with a total area of 456 km², and this basin forms a half-graben structure (Basu and Shrivastava 1981; Mishra and Cook 1992). The basal axis has a plunge towards the west with an east-west trend. Meanwhile, the southern boundary fault had deformed the southern flank of this basin with a throw of around 1500 m (GSI 1977; Mishra and Cook 1992;

Verma 1983). The stratigraphic successions of this basin are depicted in Table 2 (following Chandra 1992, Fox 1930, GSI 1977). The bituminous coal samples were collected from the Barakar and the Raniganj Formation of the Jharia Basin. Short discussions of these two formations are manifested below:

Table 2
Stratigraphic successions of the Jharia Basin (following Chandra 1992, Fox 1930, GSI 1977)

Age	Epoch	Formation	Lithology	Thickness (m)
Jurassic or Tertiary			Dolerite dykes	—
Lower Jurassic			Mica lamprophyre dykes and sills	—
Upper Permian	Lopingian (260 to 252.2 Ma)	Raniganj	Fine-grained feldspathic sandstone, shales with coal seams	800
Middle Permian	Gaudalupian (271 to 260 Ma)	Barren Measures	Buff colored sandstones shales and carbonaceous shales	730
Lower Permian	Cisularianan (299 to 271 Ma)	Barakar	Buff colored coarse and medium- grained feldspathic sandstones, grits, shales, carbonaceous shales and coal seams	1250
		Talchir	Greenish shale and fine-grained sandstones	245
Precambrian			Metamorphic rocks	—

Barakar Formation

The Barakar Formation comprises fluvial sediments, and this is the most important coal-bearing formation with an areal extent of 210 square kilometers. This formation consists of coarse-grained sandstones, conglomerates, siltstones, fireclays, carbonaceous shales, and coal seams. The coal seams in this formation are thick and may indicate the slow sinking of this basin.

Raniganj Formation

The Raniganj Formation is exposed in an oval basin with an areal extent of 58 square kilometers and has a maximum thickness of 800 m (Chandra 1992). This formation is the uppermost coal-bearing unit in the Jharia Basin. The Raniganj Formation consists of coarse- to fine-grained sandstones, shales, carbonaceous shales, and coal seams. Fox (1930) had recognized three regional coal seams in Mohuda, Bhurungiya, and Pathargaria and eight local seams in the Raniganj Formation. Sengupta (1980) had identified thirteen coal seams and numbered them from 0 to XII. The 0 seam corresponds to the Mohuda Bottom seam, and the XII (XIIA and XIIB) is assigned to the Telmucha seams.

2.3 Sikkim Himalayan fold-thrust belts

Sikkim state extending from 27° 05' N to 28° 08' N and 88°10' E to 88° 55' E is bordered by the southern ranges of the Eastern Himalayan mountain belts with 7096 km² area (GSI 2012). The tectonic compressional stress had deformed the preceding thrust systems and developed the Himalayan fold-thrust belts (Valdiya 1980; Gansser 1964; Ray 1995; Bhattacharyya and Mitra 2009). The Teesta and Rangit rivers acted as the erosion agent in this area and shaped the 'Teesta half window' (Schwan 1980). The 'Lesser Himalayan Sequence' uncovers greenschist facies metamorphic rocks at this half window (Bhattacharyya and Mitra 2011). Buxa and Daling lithology, along with the Gondwana sequences, exhibited multiple repetitions in this sequence, a portion of which is exposed as the Rangit duplex at the Rangit window (Fig. 3; following Bhattacharyya and Mitra 2009) lying within the Teesta half window (Bhattacharyya et al. 2006). The intense tectonism had influenced the microstructural characteristics of the Gondwana lithology and enhanced the rank of the coal to the anthracite A (Ghosh et al. 2018). The general stratigraphic layout within the Sikkim Himalayan fold-thrust belts (following GSI 2012) is shown in Table 3. A brief of the Damuda Formation, from which the coal samples were collected is demonstrated below:

Table 3
Stratigraphic successions of the Himalayan fold-thrust belts (following GSI 2012)

Age	Group/Formation	Lithology
Upper Pleistocene-Holocene	Sesela Formation	Variiegated clay, fine and medium-grained sand, pebble bed
	Intrusive	Tourmaline/biotite leuco-granite, schroll rock/pegmatite, apatite (undifferentiated)
Triassic	Tso Lahmo Formation	Fossiliferous sandstone, limestone, shale
Carboniferous-Permian	Lachi Formation	Boulder bed, fossiliferous sandstone, limestone, shale
	Damuda Group	Sandstone, shale, carboniferous shale and coal
	Rangit pebble slate Groups	Pebble/boulder slate, conglomerate, phyllite
Ordovician	Everest Limestone Formation	Fossiliferous limestone with quartzite
	Lingste Granite Gneiss	Phyllite, quartzite, biotite gneiss
	Sill	Amphibolite
	Buxa Formation	Dolostone, ortho-quartzite, chert, purple phyllite
	Reyang Formation	Ortho-quartzite, pyritiferous balck slate, meta-greywacke, variegated chert, phyllite
	Proterozoic (Undifferentiated)	Daling Group/Gorubathan Formation
	Kanchenjunga Gneiss/Darjeeling Gneiss (undifferentiated)	Migmatite, augen (garnet) biotite gneiss, sillimanite with palaeosomes ofstaurolite, kyanite, mica schist, sillimanite gneiss, granite gneiss
	Chungthang Formation	Quartzite, garnet-kyanite-sillimanite-biotite schist, calc-silicates

Damuda Formation

The Damuda Formation shows prominent exposure in the Rangit Window and outcrops on Naya Bazar – Legship road section, Jorethang-Namchi road section, and adjoining areas. The Damuda Formation comprises sandstone, calcareous sandstone, shale, carbonaceous shale, and coal seams. The sandstones are intercalated with carbonaceous slate, fissile black slate, and in places with coal seams. The coal seams had lost a lot of volatile matter and turned into anthracite rank. The coal deposits exhibit pinching and swelling structures. They are found almost in the pulverized state due to brittle failure of the grains originated from intense tectonism of the Himalayas (GSI 2012). They have also shown evidence of thermo-stress coupling on their microstructure driven by the Himalayan orogeny (Ghosh et al. 2018, 2020).

3 Materials And Methods

3.1 Sampling

A total of fifteen (15) coal samples were collected from the Raniganj and the Jharia Basins as well as from the Sikkim Himalayan fold-thrust belts (FTBs) of India to carry out this study (Table 4). A total of eight (8) coals from these basins were collected through channel sampling procedure, following the guidelines mentioned in ISO 14180 (2017). CG1671 and CG1672 samples belong to the Raniganj and the Barakar Formations of the Raniganj Basin, respectively. CG1674 belongs to the Raniganj Formation of the Jharia Basin, while CG1673 and CG1675–CG1679 samples were collected from the Barakar Formation of the Jharia Basin (Anwita et al. 2020; Ghosh et al. 2020). Besides, a total of seven (7) coal samples were collected from road cut sections, which traverse through Jorethang-Namchi- Nayabazar- Legship- Sikkip- Reshi towns of the west and south Sikkim (Table 4). CG3300, CG3301, and CG3302 samples were picked up from the Jorethang area and CG3303 was collected near Namchi at the south Sikkim. Sample CG3304 was sampled from the north of the Kamling village (Ghosh et al. 2018, 2020). Furthermore, CG3305 and CG3306 were collected near the Reshi Khola in the Reshi town (Ghosh et al. 2018, 2020). These coals belong to the Damuda Group of the Gondwana Supergroup. CG3300, CG3301, and CG3302 samples outcropped on the foreland dipping Jorethang horse of the Rangit duplex in the south of the Rangit window, whereas CG3303 outcropped on the Namchi horse. CG3304, CG3305, and CG3306 samples were collected from the hinterland dipping horses of the Rangit duplex in the north of the Rangit window. As these areas are extremely close to international borders, detailed information of sample locations is kept confidential. All the coal samples were preserved within high-quality bags that protected the samples from contamination, additional moisture, and sample loss. At the laboratory, the samples were air-dried at 40°C for 3 h following the standard guidelines mentioned in ISO 18283 (2006).

Table 4
Sampling sites of coals from the Raniganj and the Jharia Basins as well as from Himalayan fold-thrust belts of Sikkim, India (following Ghosh et al. 2020)

Sample No.	Name of colliery	Seam No.	Formation/Group	Basin/Area	State
CG1671	Satgram	Rotibati-G4, Ghusik A seam	Raniganj Formation	Raniganj Basin	West Bengal
CG1672	Satgram	Kuardih, Seam No. 14	Barakar Formation	Raniganj Basin	West Bengal
CG1673	Brindabanpur	BP seam (top section)	Barakar Formation	Jharia Basin	Jharkhand
CG1674	Barari	VII bottom seam	Raniganj Formation	Jharia Basin	Jharkhand
CG1675	Maheshpur	IX top seam	Barakar Formation	Jharia Basin	Jharkhand
CG1676	Lohapatti	XIV seam	Barakar Formation	Jharia Basin	Jharkhand
CG1677	Damagoria	Salaspur 'C' seam	Barakar Formation	Jharia Basin	Jharkhand
CG1679	Dahibari- Basantimata	Gopinathpur bottom seam	Barakar Formation	Jharia Basin	Jharkhand
CG3300	—	—	Damuda Group	Jorethang	Sikkim
CG3301	—	—	Damuda Group	Jorethang	Sikkim
CG3302	—	—	Damuda Group	Jorethang	Sikkim
CG3303	—	—	Damuda Group	Namchi	Sikkim
CG3304	—	—	Damuda Group	Kamling	Sikkim
CG3305	—	—	Damuda Group	Reshi	Sikkim
CG3306	—	—	Damuda Group	Reshi	Sikkim

3.2 X-ray fluorescence (XRF)

The samples were ground and sieved to -72 BS size and were kept within open crucibles in a furnace at $815 \pm 10^\circ\text{C}$ temperature for 1 hour to obtain the ash yield. The ash yield values in the analytical state were calculated following ASTM (2015) standard. After that, 5 mg of the ash samples were mixed thoroughly with a drop of paraffin for making a compact mixture. Then, that mixture was spread as a 3 mm thick layer over a very thin layer of boric acid (H_3BO_3). After that, a pressing machine was employed to press the mixtures with 20 tons weight for 1 minute. Mylar foils of 1 micron thickness were used to cover the pellets, and then, the covered samples were placed inside the X-ray fluorescence (XRF) instrument. The authors had carried out the X-ray fluorescence study of these ash samples at the R&D Centre for Iron and Steel (RDCIS), Ranchi, India, with the aid of a Rikako Koyama XRF instrument.

3.3 Fourier Transform Infrared (FTIR) Spectroscopy

To carry out the FTIR spectroscopy, the coal samples were treated following the methodologies described by (Painter et al. 1981). The pellets were dried in a vacuum oven for 48 hours to minimize the influence of water on the spectra. The spectra were recorded within $4000\text{--}400\text{ cm}^{-1}$ wavenumber region in absorbance mode using a Bruker 3000 Hyperion Microscope compounded with a Vertex 80 FTIR system at the Sophisticated Analytical Instrument Facility in Indian Institute of Technology, Bombay (IITB) in Mumbai, India. The Fityk 1.3.1 software with the Gaussian function was used to fit the curve of the raw spectra.

4 Results

4.1 Major elemental oxide distributions in the ash yield of the studied coal samples

Table 5 represents the ranges of the concentrations of the major elemental oxides in the ash yield of the studied samples. In the ash yield, the silica (SiO_2) content varies from 48.65 to 65.09 wt% in bituminous coal samples, while it ranges from 35.92 to 50.11 wt% in the anthracite samples. The ranges of the Al_2O_3 exhibit a steady variation between 25.07 and 29.84 wt% in bituminous coal samples and 23.97 to 31.22 wt% in the anthracite samples. The CaO content is drastically low in the ash yield of the anthracite samples (0.06 to 0.49 wt%) in comparison to the bituminous coal samples (0.68 to 4.49 wt%) (Fig. 4a). The K_2O content, on the other hand, shows a higher concentration anthracite samples (4.78 to 7.41 wt%) compared to that in the ash yield of the bituminous coal samples (0.88 to 2.54 wt%) (Fig. 4b). The Na_2O and P_2O_5 contents vary from 0.09 to 0.39 wt% and 0.08 to 4.29 wt%, respectively, in the bituminous coal samples, while 0.08 to 0.97 wt% and 0.05 to 3.22 wt%, respectively, in the anthracite samples. Further, the FeO, MgO, and MnO concentrations in the ash yield range from 4.49 to 6.45 wt%, 0.47 to 2.04 wt% and 0.01 to 0.063 wt%, respectively in the bituminous coal samples, whereas from 1.72 to 12.43 wt%, 0.50 to 2.79 wt% and 0.02 to 0.12 wt%, respectively, in the anthracite samples. The TiO_2 content ranges between in the anthracite 1.31 and 2.32 wt% in the anthracite samples compared to that in the bituminous coal samples (1.54 to 4.22 wt%). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio varies from 6.97 to 17.02 in the bituminous coal samples, whereas 10.33 to 20.06 in the anthracite samples. Further, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio ranges from 0.03 to 0.09 in the ash yield of the bituminous coal samples, whereas between 0.16 and 0.27 in the anthracite samples. The index of compositional variation (ICV) values exhibit variation from 7.00 to 15.14 in the ash yield of the bituminous coal samples, whereas from 5.91 to 10.57 in the ash yield of the anthracite samples. Moreover, the plagioclase index of alteration (PIA) and the chemical index of alteration (CIA) values vary from 76.94 to 98.91 and 73.73 to 95.66, respectively, in the bituminous coal samples, while from 93.20 to 98.29

and 75.79 to 81.52, respectively, in the anthracite samples. Finally, the palaeohumidity factor (PHF) varies from 0.56 to 1.75 in the bituminous coal samples, whereas between 0.25 and 1.50 in the anthracite samples.

Table 5
Rank, disposition of major elemental oxides, their ratios as well as the indices computed from those disposition within the ash yield of the s

Serial No.	Sample No.	R _r (%)	Rank	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	MgO	Fe ₂ O ₃	MnO	TiO ₂	P ₂ O ₅	Al ₂ O ₃ /TiO ₂	K ₂ O/Al ₂ O ₃
1	CG1671	0.65	Bituminous C*	59.22	25.07	0.39	2.19	2.48	2.04	5.07	0.04	1.56	1.44	15.99	0.09
2	CG1672	0.58	Bituminous D*	60.71	26.19	0.18	0.68	2.06	1.57	6.45	0.03	1.53	0.08	17.03	0.078
3	CG1673	0.95	Bituminous C*	48.65	29.43	0.18	4.44	1.37	0.80	5.97	0.06	4.22	3.71	6.97	0.04
4	CG1674	1.09	Bituminous B*	64.09	28.07	0.09	0.80	1.05	0.49	1.49	0.01	3.03	0.10	9.24	0.03
5	CG1675	0.90	Bituminous C*	60.63	28.01	0.14	0.68	2.10	0.88	3.81	0.03	2.73	0.20	10.24	0.07
6	CG1676	0.76	Bituminous C*	57.50	26.02	0.21	2.54	2.01	1.73	5.71	0.04	1.94	1.60	13.41	0.07
7	CG1677	1.00	Bituminous B*	61.13	29.84	0.12	1.22	0.88	0.53	2.50	0.01	2.94	0.17	10.12	0.02
8	CG1679	1.00	Bituminous B*	55.60	27.86	0.09	3.87	2.54	0.46	2.36	0.01	2.14	4.29	13.02	0.09
9	CG3300	5.12	Anthracite A#	47.73	25.07	0.12	0.06	6.39	1.51	12.42	0.09	1.30	0.05	19.18	0.25
10	CG3301	4.94	Anthracite A#	48.95	29.11	0.96	0.08	4.78	1.41	7.70	0.10	1.45	0.19	20.07	0.16
11	CG3302	5.15	Anthracite A#	46.99	26.78	0.44	0.35	4.88	2.79	10.16	0.09	1.35	0.17	19.78	0.18
12	CG3303	5.36	Anthracite A#	47.14	28.44	0.20	0.48	6.59	2.12	7.20	0.11	1.76	0.20	16.15	0.23
13	CG3304	4.11	Anthracite A#	50.11	31.21	0.15	0.36	5.70	0.76	2.94	0.02	1.84	0.29	16.89	0.18
14	CG3305	4.15	Anthracite A#	35.92	23.97	0.08	0.32	6.41	1.48	9.25	0.02	2.31	3.22	10.34	0.26
15	CG3306	4.73	Anthracite A#	44.13	28.02	0.17	0.16	7.41	0.50	1.72	0.03	1.96	0.06	14.28	0.26

4.2 Fourier transform infrared (FTIR) spectroscopy

The fitted Fourier transform infrared peaks are assigned following the works of Djomgoue and Njopwouo (2013), Saikia and Parthasarathi (2010), and Varma et al. (2018) and the representative fitted curves from the bituminous (CG 1674), and the anthracite samples (CG3303) are displayed in Fig. 5 (a-f). The fitted spectra in the bituminous coal samples exhibit the stretching frequencies of kaolinite at around 3620, 3651, 3671, and 3691 cm⁻¹ (Fig. 5a), where the first one is related to the inner -OH stretching vibrations of the kaolinite structure and the last three peaks correspond to the vibrations of the surface hydroxyls (Saikia and Parthasarathi 2010). Additionally, the peak near 3420 cm⁻¹ (Fig. 5a) may be attributed to the H-O-H stretching mode of water present within the montmorillonite clay (Djomgoue and Njopwouo 2013). Moreover, the peaks near 1008 and 1030 cm⁻¹ (Fig. 5b) may represent the presence of quartz and feldspar (Varma et al. 2018) in these samples. Besides, the -OH bending vibrations of the kaolinite (Fig. 5c) are found around 940 cm⁻¹ (surface -OH bending), 913 cm⁻¹ (inner surface -OH bending), and 754 cm⁻¹ (surface -OH bending) (following Saikia and Parthasarathi 2010). Further, the -OH bending vibration of montmorillonite is observed near 695 cm⁻¹. The Si-O-Si inter-tetrahedral bridging bonds in SiO₂ (Fig. 5c) are observed near 780 and 798 cm⁻¹ (Saikia and Parthasarathi 2010).

On the other hand, the hydroxyl stretching peaks of kaolinite exhibit irregular appearances in the anthracite samples except the inner hydroxyl stretching intensity around 3620 cm⁻¹ (Fig. 5d). The -OH stretching frequency of illite near to 3600 cm⁻¹ is observed in these samples (Fig. 5d) (Djomgoue and Njopwouo 2013). The peaks of quartz and feldspar (Fig. 5e) along with that of the Si-O-Si inter-tetrahedral bridging bonds of SiO₂ are also observed in the anthracite samples (Fig. 5f). Apart from these peaks, the bending intensities of kaolinite are observed around 754 cm⁻¹ and 912 cm⁻¹, corresponding to the surface hydroxyl and inner surface -OH bending vibrations (Fig. 5f).

5 Discussions

5.1 Major elemental oxides

5.1.1 Inorganic parent rock composition

The SiO₂ content in the ash yield of the studied samples may imply intermediate igneous source rocks with slight inputs from the mafic and felsic ends as well. However, the variation in silica concentrations in the two sample sets may be due to the disparities in its origin from the source minerals (quartz, feldspars, and clays). The sum of MgO and Fe₂O₃ contents vary from 1.99 wt% to 8.02 wt% in the ash yield of the bituminous coal samples, while in the ash yield of the anthracite samples, the range is between 2.23 wt% and 13.95 wt%. The range of the sum of these two major elemental oxides may, further, imply the input from igneous rocks of intermediate composition. Additionally, the ratio of Al₂O₃ to the TiO₂ (Al₂O₃/TiO₂) can discriminate the source rock characteristics of the clastic sediments. The range of this ratio from 3 to 8 implies the mafic igneous rocks; 8 to 21 indicates intermediate igneous rocks, and 21 to 70 for felsic rocks (Hayashi et al. 1997). The range of this ratio (Table 5) in the bituminous coal samples may indicate the dominant input from intermediate igneous rocks with a little influence from the mafic igneous rocks (Fig. 6a). This ratio may additionally suggest that the minerals in the anthracite samples would have also derived from the igneous rocks of intermediate composition with a little influence from felsic sources (Fig. 6a).

The P₂O₅ and the CaO are strongly correlated ($r = 0.97$) in the bituminous coal samples (Fig. 6b), which may indicate the formation of apatite. In the anthracite samples, these two parameters show a moderate correlation ($r = 0.65$) (Fig. 6b). CG3305 contains a large amount of P₂O₅, which leads to the exclusion of this particular sample from the bivariate plot of the P₂O₅ and CaO for the anthracite samples.

5.1.2 Palaeohumidity

The distribution and abundance of some chemical elements may provide imperative clues regarding the palaeoenvironmental conditions that prevailed during the sediment deposition (Moradi et al. 2016; Worash 2002) in the peatland. The humid climatic condition enriches Fe, Mn, Cr, V, Ni, and Co (Cao et al. 2012). On the other hand, under arid condition, the rate of evaporation overcomes the rate of precipitation, enhancing the alkalinity of water, which in turn, leads to the enrichment of Mg, Ca, Na, K, Ba and Sr. Cao et al. (2012), Moradi et al. (2016) and Zhao et al. (2007) among others had applied the C-value (Eq. (1)) as a proxy to document the transformations in palaeoclimate:

$$C = (\text{Fe} + \text{Mn} + \text{Cr} + \text{Ni} + \text{V} + \text{Co}) / (\text{Ca} + \text{Mg} + \text{Sr} + \text{Ba} + \text{K} + \text{Na}) \dots\dots\dots (1)$$

However, the trace elements are not detected in this study. Therefore, a new index, termed as palaeohumidity factor (PHF), is proposed in this study, which considers only the Fe, Mn, and Ti in the numerator, while Ca, Mg, Na, and K in the denominator. All the concentrations are considered as elemental weight percentages. The PHF is calculated (Eq. (2)) as follows:

$$\text{PHF} = (\text{Fe} + \text{Mn} + \text{Ti}) / (\text{Ca} + \text{Mg} + \text{K} + \text{Na}) \dots\dots\dots (2)$$

The range of the PHF in the bituminous coal samples lies between 0.56 and 1.75, whereas in the anthracite A samples, this parameter ranges from 0.25 to 1.50 (Table 5). Most of the samples may indicate the sub-humid to humid climatic conditions (Fig. 7).

5.1.4 Clay mineral composition

K₂O/Al₂O₃ ratio

Cox et al. (1995) had observed the ratio of K₂O to Al₂O₃ (K₂O/Al₂O₃) lies between 0 and 0.3 in clay minerals, while between 0.3 and 0.9 in feldspars and close to zero in the sediments comprising a large amount of kaolinite, montmorillonite, saponite, and halloysite, etc. In illite-rich sediments, this ratio varies from 0.2 to 0.3 (Cox et al. 1995). The range of this ratio (Table 5) in the bituminous coal samples may imply the presence of an abundant amount of kaolinite (most dominant), vermiculite, montmorillonite clays (Fig. 8a). In the anthracite samples, this ratio (Table 5) may indicate the presence of kaolinite, montmorillonite, and illite (Fig. 8a).

Index of compositional variation (ICV)

In complementary, the index of compositional variation (ICV; Eq. (5)) proposed by Cox et al. (1995) can differentiate the characters of the source rocks based on the concentration of the major elemental oxides:

$$\text{ICV} = (\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO} + \text{Na}_2\text{O} + \text{MgO} + \text{MnO} + \text{TiO}_2) / \text{Al}_2\text{O}_3 \dots\dots\dots (5)$$

This index measures the concentration of alumina with respect to the other major elemental oxides, and it excludes SiO₂ to avoid the problems of quartz dilution (Cox et al. 1995). The non-clay silicates comprise comparatively smaller amounts of alumina than in clay minerals and hence, show larger ICV values than the clay minerals. Additionally, the amphiboles and the pyroxenes exhibit larger ICV values as they are more prone to chemical weathering on the earth's crust, while relatively stable mineral-like alkali feldspar shows lower ICV. This index further lowers in montmorillonite and illite and becomes the lowest in the kaolinite minerals (Cox et al. 1995). In the present study, the ICV values in the bituminous and the anthracite samples range from 0.25 to 0.58 and 0.38 to 0.87, respectively (Table 5). The range of the ICV in the bituminous coal samples may imply the mixed abundance of kaolinite and montmorillonite clays (Fig. 8b), whereas, in the anthracite samples, this index may suggest mainly the presence of illite (Fig. 8b) mixed with kaolinite.

5.1.5 Weathering extent of the inorganic parent rocks

The Plagioclase index of alteration (PIA) was calculated (Eq. (6)) following Fedo et al. (1995) to document the degree of chemical weathering of the plagioclase feldspar.

$$PIA = 100 \times [(Al_2O_3 - K_2O) / \{(Al_2O_3 - K_2O) + CaO^* + Na_2O\}] \dots \dots \dots (4)$$

Here, the major element concentrations are considered in mol%. CaO* reports the CaO concentration in silicates. CaO* is obtained from the method described by McLennan et al. (1993). According to this concept, if the CaO value after the correction for the apatite ($CaO_{corrected} = \{CaO - (3.33 \times P_2O_5)\}$) remains $> Na_2O$, then CaO* equals the value of Na₂O. But CaO* equals the concentration of CaO if CaO_{corrected} is less than the concentration of Na₂O. This index shows the variation from 76.94 to 98.91 and from 93.19 to 98.29 (Table 5) in the bituminous and the anthracite samples, respectively. Therefore, these values may imply the moderate to intense chemical weathering of plagioclase feldspar in both sample sets. The smaller values of this ratio in CG1671, CG1673, and CG1679 would have resulted possibly due to the presence of reasonable amounts of smectite class of clay, which includes, especially, the montmorillonite.

The chemical index of alteration (CIA) proposed by McLennan et al. (1993) may potentially indicate the degree of chemical weathering on the earth's crust that the parent rocks had experienced, which may, in turn, point towards the palaeohumidity conditions. The high CIA values may indicate strong chemical weathering triggered by warm and moist climate, while the low CIA values may imply weak chemical weathering under cold and arid conditions. The CIA is calculated (Eq. (7)) as below:

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100 \dots \dots \dots (7)$$

Here, CaO* is obtained from the method described by McLennan et al. (1993) and in the same method mentioned for the calculation of PIA. The CIA values for the bituminous coal samples vary from 73.73 to 95.66 (Table 5). CG1671, CG1673, and CG1679 samples have comparatively lower CIA values and plot near the smectite field of the A-CN-K diagram (Fig. 9a). This may suggest the presence of considerable amounts of montmorillonite (a subclass of smectite) that would have led to plot these three samples along the A-CN axis. The rest of the bituminous coal samples show larger CIA values indicating strong chemical weathering under hot and humid climatic conditions and consequently a large amount of kaolinite that might have caused the samples to lie at the Al₂O₃ apex (Fig. 9a).

5.1.6 Epigenetic potassium metasomatism

The chemical index of alteration (CIA) parameter ranges between 75.79 and 81.52 in the anthracite samples (Table 5), which may imply, apparently, moderate chemical weathering under warm and moist conditions. Interestingly, these samples cluster along the A-K axis near the illite field within the A-CN-K diagram and plot a bit offset from the traditional weathering trend in the A-CN-K diagram (Fig. 9b), which may suggest the plausible influence of potassium metasomatism (K-metasomatism) in the anthracite samples. Fedo et al. (1995) had reported the effects of K-metasomatism of sandstone. Coal contains low interconnected porosity than sandstone, and in the anthracite rank, the aromatic layers tend to align parallel to one another, reducing the interlayer spacing for the hydrothermal fluids to penetrate deep into the stable microstructural framework. The enhancement in aromatic condensation and stacking make the pathway more hydrophobic, reducing the flow of the hydrothermal fluids. However, the labile network reacts with the fluids and exhibits transformations in chemistry. The K-metasomatism either may transform the aluminous clay minerals like kaolinites to illites or converse the plagioclase feldspar to K-feldspar (Fedo et al. 1995). However, the ICV values and the K₂O/Al₂O₃ ratio may imply the presence of illite mixed with kaolinite and montmorillonite in dominance rather than the K-feldspar in these samples (Fig. 8a and b).

Therefore, the epigenetic K-metasomatism is assumed, here, to take place in the first way, i.e., through conversing the kaolinites into illites. Ghosh et al. (2018) had reported that these anthracite samples were at the onset of greenschist facies metamorphism. Therefore, the K-metasomatism at that pressure-temperature condition would have acted as an epigenetic phenomenon to alter the clay mineralogical characteristics of these anthracite samples. However, all the kaolinites might not have been converted to illite.

In this study, the CIA has been plotted against the PIA to observe whether these two proxies can jointly determine the degree of chemical weathering of the source rocks. These two parameters, in the bituminous coal samples, are highly correlated ($r = 0.98$) (Fig. 10), which may imply that these two weathering indices are in good agreement in revealing the intensity of chemical weathering of the parent inorganic rocks. Interestingly, in the anthracite samples, these two proxies show inverse correlation ($r = -0.52$) (Fig. 10), suggesting the plausible influences of the epigenetic mineralogical alterations on these weathering indices. Although the PIA values reveal the strong chemical weathering of the plagioclase feldspar, the epigenetic K-metasomatism may offset these samples from the common weathering trend as reflected from the A-CN-K diagram and the CIA values, and that's why the CIA inversely correlates with the PIA. Therefore, the above discussion may suggest that the K-metasomatism would have altered substantial amounts of kaolinite to illite in the anthracite samples, which is in good agreement with the K₂O/Al₂O₃ ratio and the ICV values.

5.1.7 Estimation of quartz and kaolinite in the samples

The high-temperature chemical transformations of minerals like silicate, carbonate, sulfide, sulfate, oxides, etc., produce the ash in the coal. X-ray fluorescence spectroscopy of high-temperature ash (HTA) obtained from the bulk coal samples can be used to calculate the quartz content in bituminous and anthracite samples based on the observations that quartz remains unaltered during ashing at high degree, unlike many minerals that undergo crystallographic or chemical alterations (Bandopadhyay 2010). The oxides like silica (SiO₂) and alumina (Al₂O₃) found in the X-Ray fluorescence spectroscopy of high-temperature coal-ash can be employed to estimate the quartz content in the bulk coal. The quartz content in high temperature-ash yield of coal samples can be calculated from the SiO₂ and Al₂O₃ contents from an empirical formula proposed by (Raask 1985) and later modified by (Bandopadhyay 2010) for Indian coals (Eq. (8)):

$$(\text{SiO}_2)_Q = (\text{SiO}_2)_t - 1.3 \times (\text{Al}_2\text{O}_3) \dots\dots\dots(8)$$

Where $(\text{SiO}_2)_Q$ is the percentage of silica in ash-yield, $(\text{SiO}_2)_t$ is the percentage of total silica obtained in XRF analysis and Al_2O_3 represents the weight-percentage of alumina derived from XRF analysis of the coal samples. Further, following the work of (Bandopadhyay 2010), the quartz content in bulk coal was computed from Eq. (9):

$$Q_C = 0.01 \times A^a \times (\text{SiO}_2)_Q \dots\dots\dots(9)$$

Where, Q_C = Quartz content in bulk coal sample; A^a = Ash yield of coal in analytical state and $(\text{SiO}_2)_Q$ = Percentage of silica in ash-yield.

Kaolinite content in the coal ash can also be determined from SiO_2 , Al_2O_3 , K_2O , potassium aluminosilicates, and quartz content following Raask's method (Raask 1985):

The potassium aluminosilicate ($K_{\text{Al-Si}}$) present within the coal mineral matter can be calculated from the following Eq. (10):

$$K_{\text{Al-Si}} = \text{K}_2\text{O}/0.11 = 9.1 \times \text{K}_2\text{O} \dots\dots\dots(10)$$

Then, the kaolinite content in the ash yield (Kaol_{ash}) is determined by (Eq. (11)):

$$\text{Kaol}_{\text{ash}} = [(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}) - \{(\text{SiO}_2)_Q + K_{\text{Al-Si}}\}] \dots\dots\dots(11)$$

After that, the kaolinite in bulk coal sample (Kaol_C) can be estimated as (Eq. (12)):

$$\text{Kaol}_C = 0.01 \times A^a \times \text{Kaol}_{\text{ash}} \dots\dots\dots(12)$$

The quartz content in bituminous coal samples varies from 1.45 to 7.88 wt%, while in the anthracite samples, it ranges between 2.39 and 7.65 wt% (Table 6). On the other hand, the kaolinite content in the bituminous coal samples is placed between 5.47 and 15.99 wt%, whereas in the anthracite samples, the kaolinite content exhibits variation from 1.61 to 13.45 wt% (Table 6). Moreover, the kaolinite to quartz ratio (Kaol_C/Q_C) in the bulk bituminous coal samples varies from 1.41 to 5.44, while in the anthracite samples, this ratio ranges from 0.39 to 2.69 (Table 6).

Table 6
Ash yield (in the analytical state), amounts of quartz and kaolinite in ash yield and bulk coal samples along with amounts of potassium aluminosilicates present in the mineral matter of the studied samples and ratio of total kaolinite to quartz contents in the bulk coal samples

Sample No.	Ash yield ^a	(SiO ₂) _Q	Q _C	K _{Al-Si}	Kaol _{ash}	Kaol _C	Kaol _C /Q _C
CG1671	14.57	26.63	3.88	22.63	37.53	5.47	1.41
CG1672	18.00	26.66	4.80	18.82	43.50	7.83	1.63
CG1673	13.97	10.39	1.45	12.52	56.56	7.90	5.44
CG1674	28.54	27.60	7.88	9.58	56.05	16.00	2.03
CG1675	29.77	24.22	7.21	19.17	47.37	14.10	1.96
CG1676	21.00	23.67	4.97	18.32	43.56	9.15	1.84
CG1677	15.96	22.34	3.57	8.04	61.49	9.82	2.75
CG1679	27.40	19.38	5.31	23.13	43.50	11.92	2.24
CG3300	50.54	15.14	7.65	58.24	5.83	2.95	0.39
CG3301	47.62	11.10	5.29	43.50	28.24	13.45	2.54
CG3302	51.88	12.17	6.32	44.48	22.01	11.42	1.81
CG3303	50.97	10.16	5.18	59.98	12.04	6.14	1.18
CG3304	50.27	9.53	4.79	51.89	25.62	12.88	2.69
CG3305	50.26	4.76	2.39	58.33	3.21	1.61	0.67
CG3306	49.02	7.70	3.78	67.44	4.43	2.17	0.58

The variation in the quartz content in both sample sets may imply the variable input concentrations of quartz from the source igneous source rocks as the metamorphic influences on quartz concentration are negligible. Extremely low quartz content in CG1673 and CG 3305 may be associated with the very poor derivation of quartz from the source rocks. The Kaol_C/Q_C ratio in CG1673 is overestimated due to this low quartz content. The ratio, in the rest of the bituminous coal samples, exhibits almost a stable variation and has the values > 1, which may imply the dominance of kaolinite over quartz content in the bulk coal (Fig. 11). However, in the case of anthracite samples, this ratio shows unstable variation, possibly due to molecular breakdown of kaolinite structure at high temperature (325.02°C to 387.89°C; Ghosh et al. 2018) as well as epigenetic transformations of kaolinite to illite by plausible epigenetic K-

metasomatism. Surprisingly, in CG3300, CG3305, and CG3306, the kaolinite/quartz ratio declines to less than 1, which may correspond to the lowering of the kaolinite content through epigenetic alterations compared to the stable quartz grains (Fig. 11).

5.2 Spectral evidence of potassium metasomatism

The presence of four hydroxyl (–OH) stretching peaks of kaolinite in the bituminous coal samples (Fig. 5a) may suggest the preservation of molecular ordering of the kaolinite structure, which in turn may low metamorphic temperature and relatively unaltered mineralogical framework in these samples. Moreover, the presence of –OH stretching vibrations of montmorillonite in the bituminous coal samples may support the discussion based on the K_2O/Al_2O_3 ratio and the ICV values regarding the clay composition. Also, this substantiates the presence of the sericite class of clay present in these samples observed from the A-CN-K diagram (Fig. 9a).

The inconsistencies of the hydroxyl stretching peaks in the anthracite samples may be the consequences of the dehydroxylation and removal of OH^- ions from the kaolinite structure. The high thermal maturity (R_r : 4.11–5.36 %) of the anthracite samples would have resulted in the molecular disordering of the kaolinite structure and led to the dehydroxylation process. In contrast, the consistent appearance of the inner hydroxyl stretching frequency may correspond to relatively strong hydrogen bond energy compared to the surface hydroxyls. Additionally, the irregular appearances of the kaolinite stretching peaks may also provide a clue to the K-metasomatism of kaolinites to illites, apart from the dehydroxylation. The appearance of the hydroxyl stretching frequency of illite in these samples (Fig. 5d) may strengthen this clue of the epigenetic K-metasomatism in the anthracite samples influencing the kaolinite molecular structure. This observation is, hence, in good agreement with the interpretations of the A-CN-K diagram (Fig. 9b). The absence of the other two –OH bending peaks of kaolinite (Fig. 5f) may be in good agreement with the thermal decomposition and K-metasomatism of kaolinites. The hydroxyl bending vibration of montmorillonite has not been observed in these samples.

From the deconvoluted FTIR spectra, the total hydroxyl stretching and bending intensities of the kaolinite and the intensities of quartz and feldspar are calculated (Table 7). The total kaolinite intensity (TI_K) is always less than the intensity of the quartz and feldspar (TI_{Q-F}). Further, the ratio of these total intensities (TI_K/TI_{Q-F}) in the anthracite samples is found to decline from the bituminous coal samples (Fig. 12a), which may support the thermal decomposition and the K-metasomatism of the kaolinites to illites. For additional confirmation, this ratio has been correlated with the R_r values, and it is observed that this ratio forms clusters within the reflectance range of the two sample sets (Fig. 12b) and varies non-linearly with the thermal maturity. This non-linear correlation of these two variables may suggest that the thermal maturity solely did not affect this ratio; instead, it was also influenced by epigenetic K-metasomatism to a significant extent.

Table 7
Total relative intensities of kaolinite, quartz, and feldspar along with their ratio of the studied samples

Sample No.	TI_K	TI_{Q-F}	TI_K/TI_{Q-F}
CG1671	0.06	0.13	47.50
CG1672	0.34	0.57	60.86
CG1673	0.09	0.18	50.12
CG1674	0.39	0.50	78.34
CG1675	0.27	0.32	85.65
CG1676	0.42	0.69	61.61
CG1677	0.19	0.31	61.29
CG1679	0.16	0.23	69.68
CG3300	0.10	0.25	40.84
CG3301	0.03	0.14	21.91
CG3302	0.24	0.73	32.86
CG3303	0.43	0.91	47.50
CG3304	0.39	0.98	39.26
CG3305	0.26	1.19	21.85
CG3306	0.17	0.69	24.95

6 Conclusions

The inorganic geochemical findings from the ash yield of the studied bituminous and anthracite samples have provided insights into the clay mineralogical framework and its alteration at the anthracite rank. The bituminous coal samples comprise kaolinite mixed with montmorillonite, while the anthracite coal samples are enriched in illite associated with kaolinite. Besides, the anthracite samples are clustered near the field of illite and are a bit offset from the weathering trends of parent rocks in the A-CN-K diagram, which may suggest plausible influences of epigenetic potassium metasomatism that would have

converted some of the kaolinite to illite. The tectonic deformation episodes of the Himalayas brought about greenschist facies metamorphism in these anthracite samples and surrounding lithology. In this metamorphic realm, the K-metasomatism occurred as an epigenetic phenomenon altering the clay mineralogical characteristics of these anthracite samples. The influence of the epigenetic K-metasomatism on the clay mineral framework of the anthracite samples is further confirmed from the ratio of kaolinite/quartz content in coal, and the declination of TI_K/TI_{Q-F} values from that observed in the bituminous coal samples. The presence of hydroxyl stretching intensity of the illite found in the FTIR spectra of the anthracite samples may further strengthen the K-metasomatic effects.

Declarations

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Conflicts of interest/Competing interests

The authors declare no conflict of interest for the publication of this manuscript.

Availability of data and material (data transparency)

The data will be made available on request.

Code availability (software)

Not applicable

Authors' contributions

Santanu Ghosh: Conceptualization; Writing: Original draft

Anwita Ojha: Formal analysis; Data treatment

Atul Kumar Varma: Supervision; Writing: Review & Editing

Ethics approval (include appropriate approvals or waivers)

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Consent to participate (include appropriate statements)

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Figures

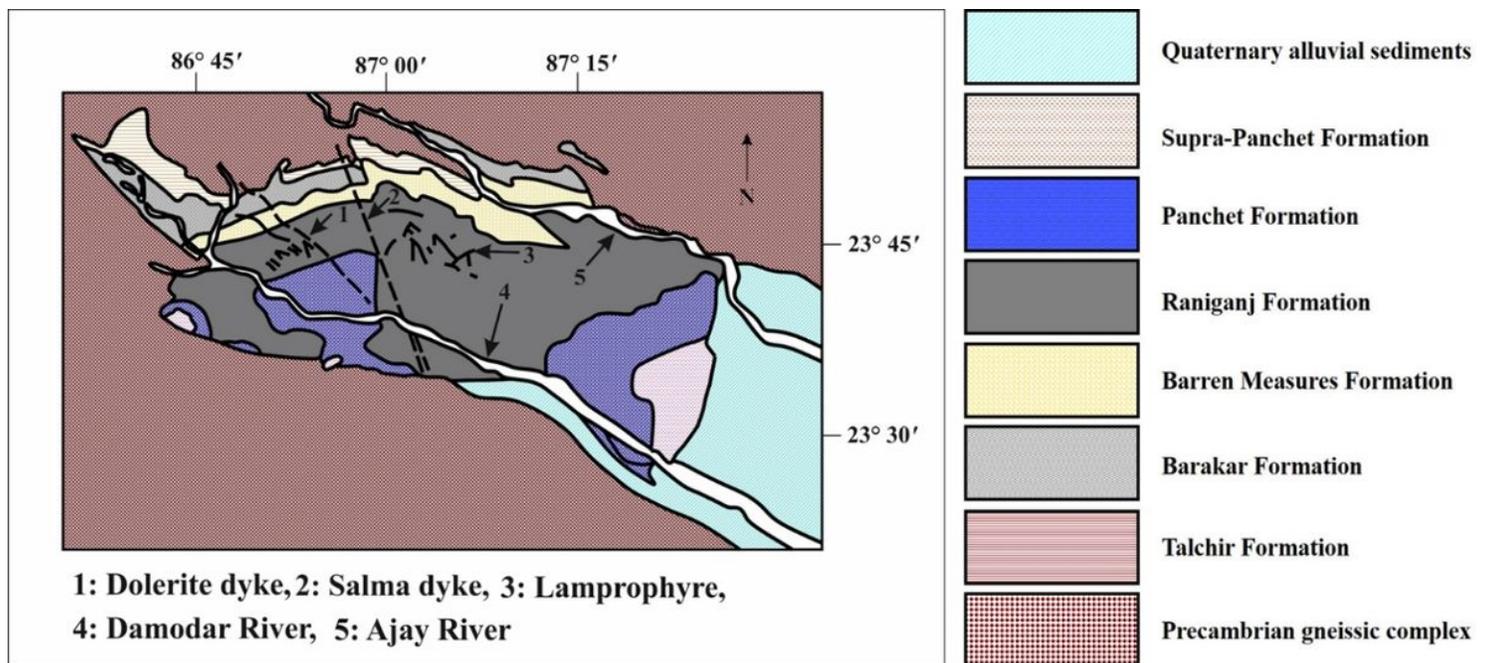


Figure 1

Map of the Raniganj Basin, India (following Gee 1932).

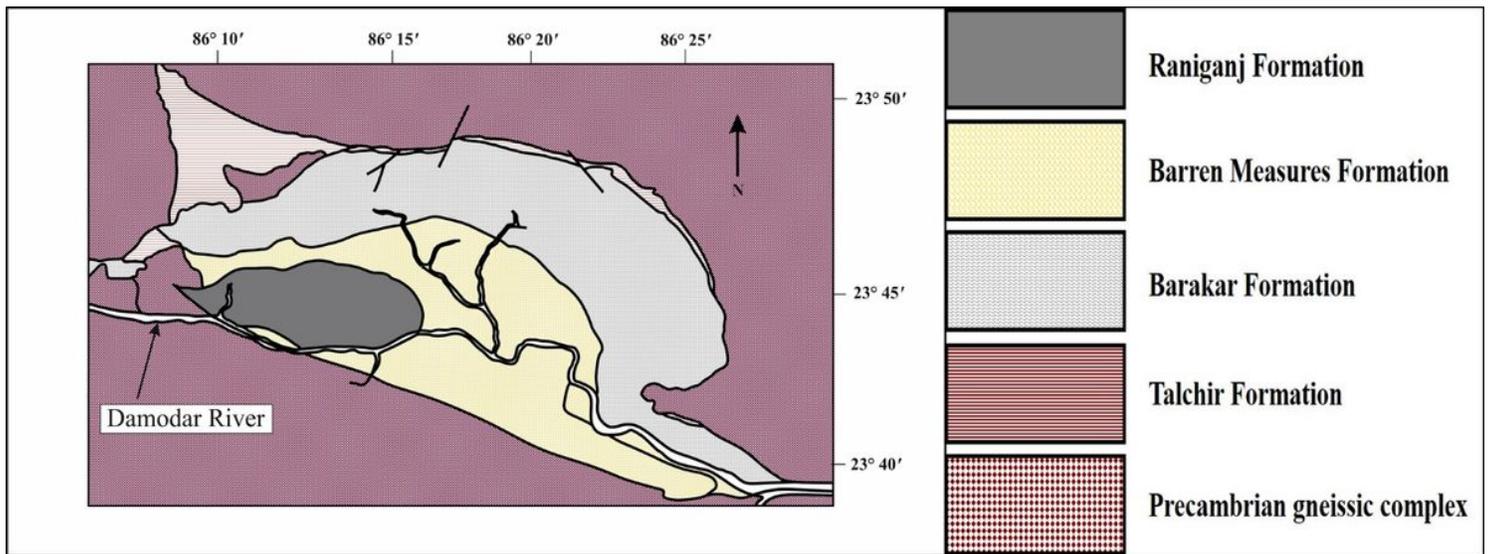


Figure 2

Map of the Jharia Basin, India (following Fox 1930, Mishra and Cook 1992).

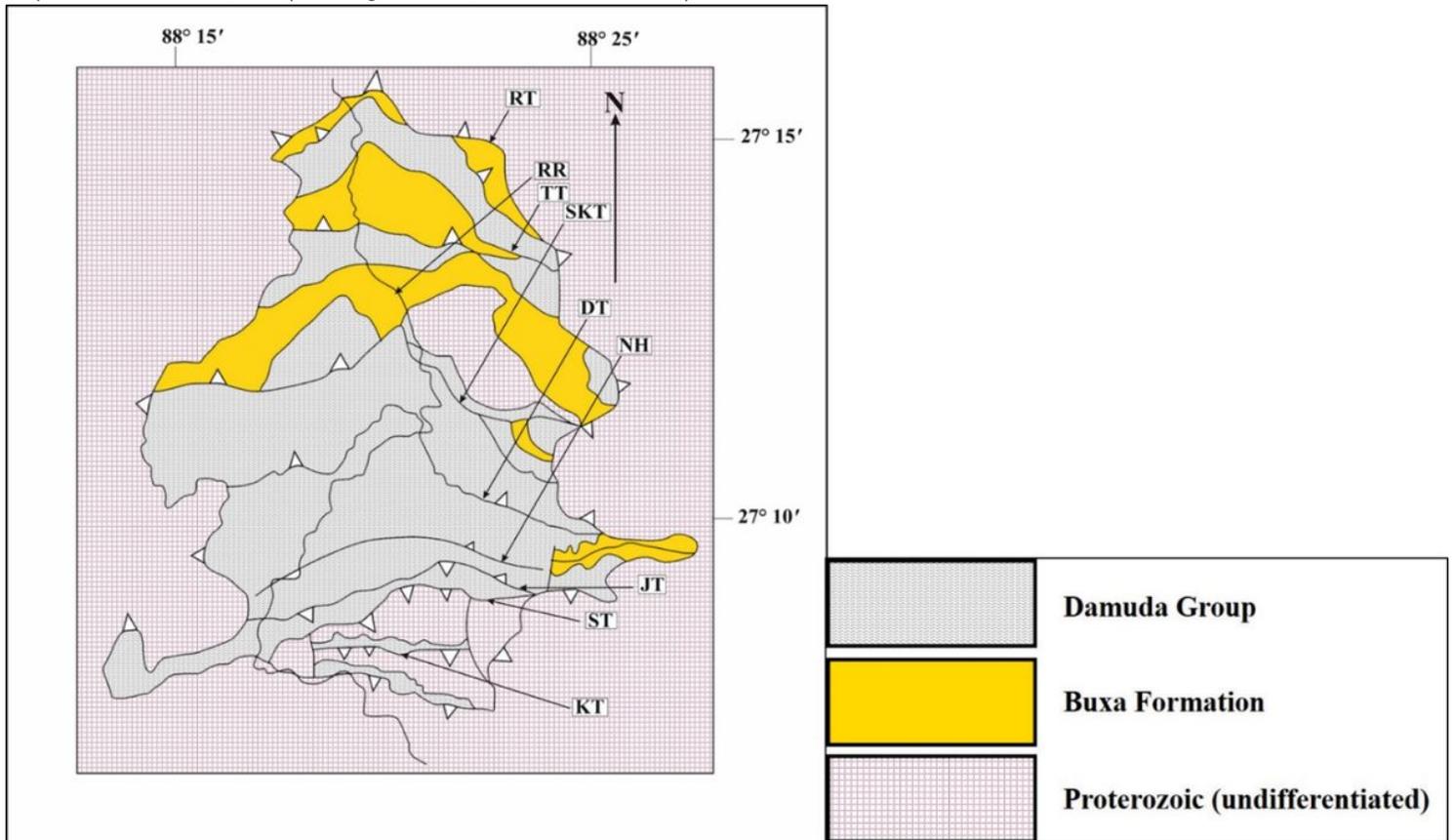
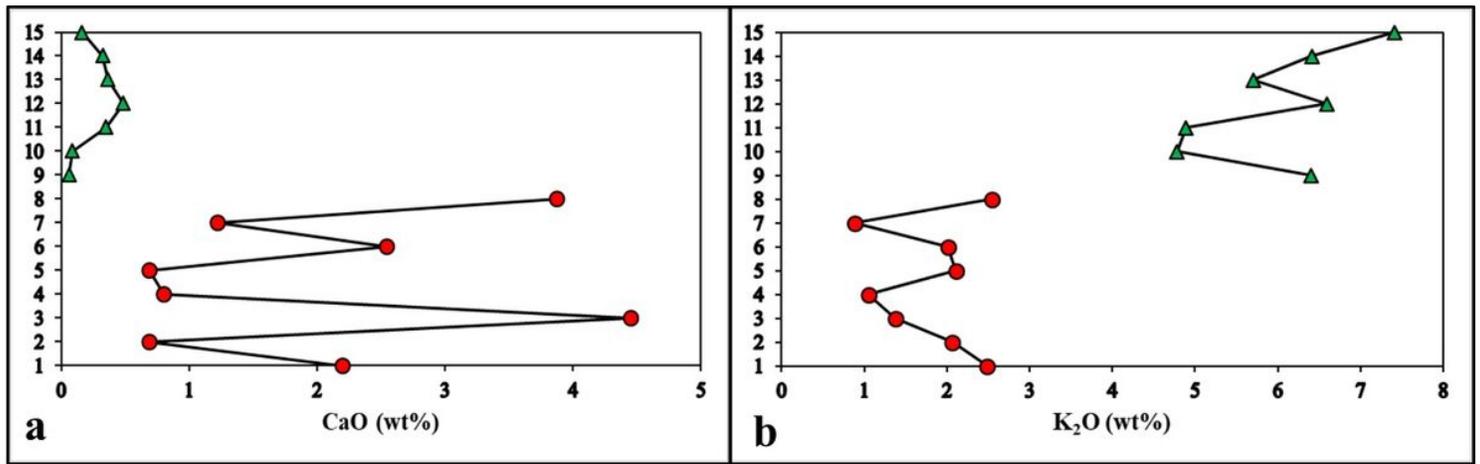


Figure 3

Map of the Rangit window, Sikkim Himalayan fold-thrust belts of India (following Bhattacharyya and Mitra 2009). Explanations: RT = Ramgarh Thrust; TT = Tatapani Thrust; SKT = Sikip Thrust; DT = Dong Thrust; JT = Jorethang Thrust; ST = Sorok Thrust; KT = Kitam Thrust; NH = Namchi Horse; RR = Rangit River.



● Bituminous coal samples

▲ Anthracite samples

Figure 4

(a) Low CaO content, and (b) high K₂O content in the anthracite samples. Explanations: The Y-axis in both of the plots represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.

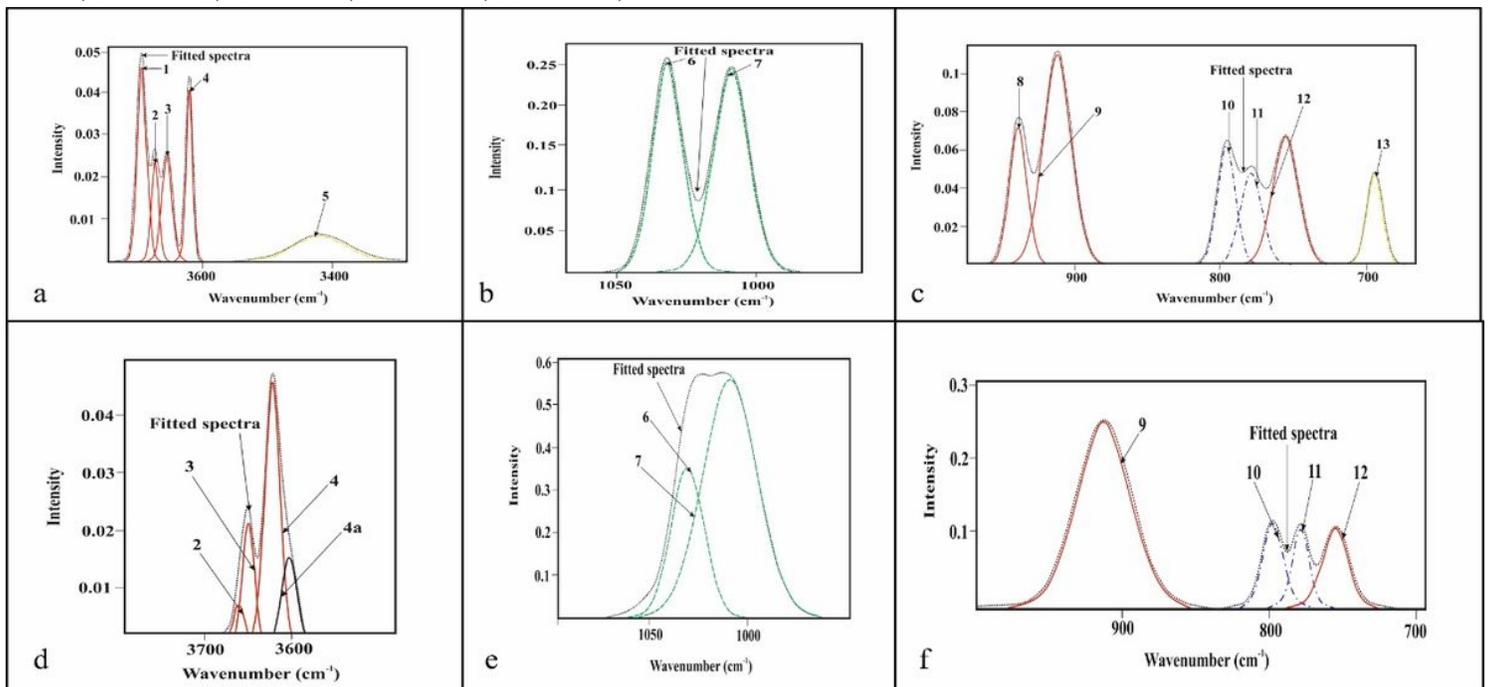


Figure 5

(a) –OH stretching vibrations of kaolinite and montmorillonite, (b) Vibrational frequencies of quartz and feldspar, (c) –OH bending vibrations of kaolinite and montmorillonite as well as Si-O-Si inter-tetrahedral bridging bonds of SiO₂ in CG1674 (representative sample of the bituminous coal sample set), (d) –OH stretching vibrations of kaolinite and illite, (e) Vibrational frequencies of quartz and feldspar, (f) –OH bending vibrations of kaolinite as well as Si-O-Si inter-tetrahedral bridging bonds of SiO₂ in CG3303 (representative sample of the anthracite sample set). Explanations: 1 = Surface –OH stretching vibration of kaolinite, 2 = Surface –OH stretching vibration of kaolinite, 3 = Surface –OH stretching vibration of kaolinite, 4 = Inner surface –OH stretching vibration of kaolinite, 5 = H-O-H stretching vibrations of water within montmorillonite, 6 = Quartz, 7 = Quartz, and feldspar, 8 = Surface –OH bending vibration of kaolinite, 9 = Inner surface –OH bending vibration of kaolinite, 10 = Si-O-Si inter-tetrahedral bridging bonds of SiO₂, 11 = Si-O-Si inter-tetrahedral bridging bonds of SiO₂, 12 = Surface –OH bending vibration of kaolinite, 13 = –OH bending vibration of montmorillonite. Peaks are assigned following the works of Djomgoue and Njopwouo (2013), Saikia and Parthasarathi (2010) and Varma et al. (2018).

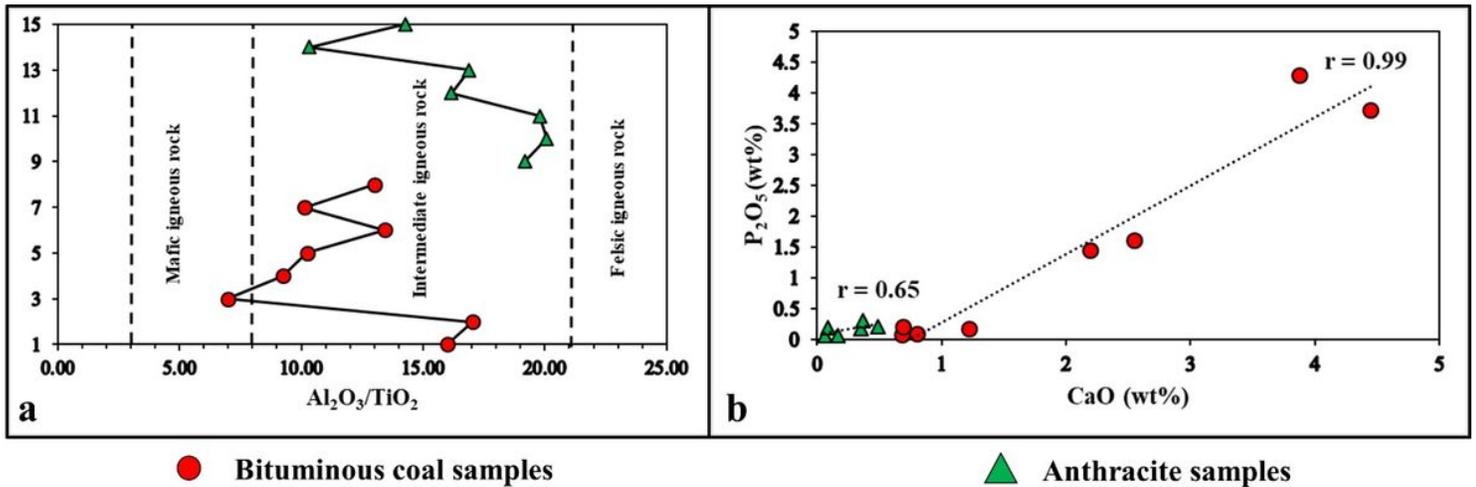


Figure 6

(a) Al_2O_3/TiO_2 ratio of the studied samples showing the source rock composition, (b) CaO vs P_2O_5 plot showing formation of apatite in the samples. Explanations: CG3305 is excluded from Fig. 6b due to the high P_2O_5 content, which was influencing the correlation. The Y-axis in Fig. 6a represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.

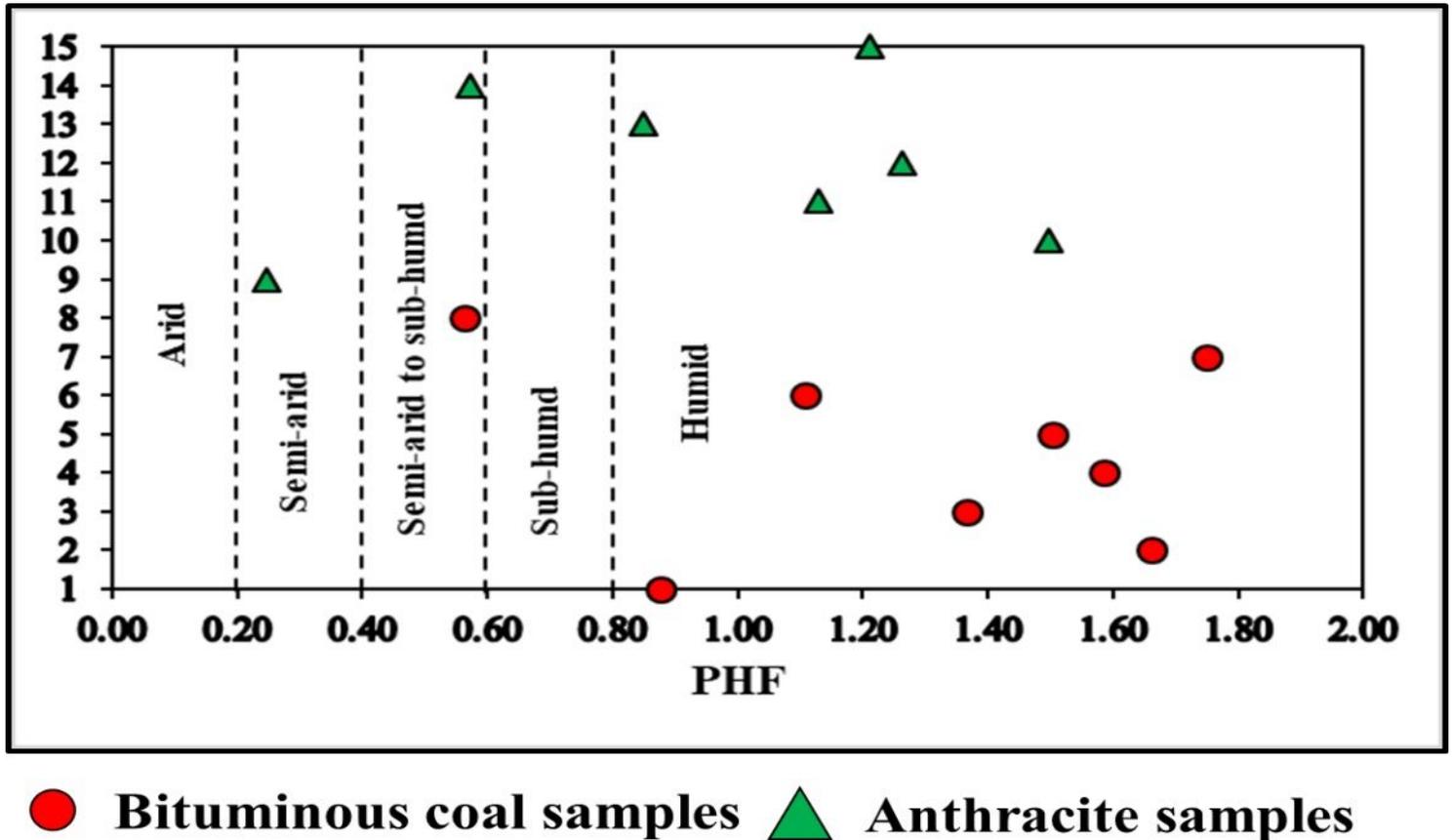


Figure 7

Palaeohumidity factor (PHF) showing sub-humid to humid climatic conditions. Explanations: The Y-axis in this plot represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.

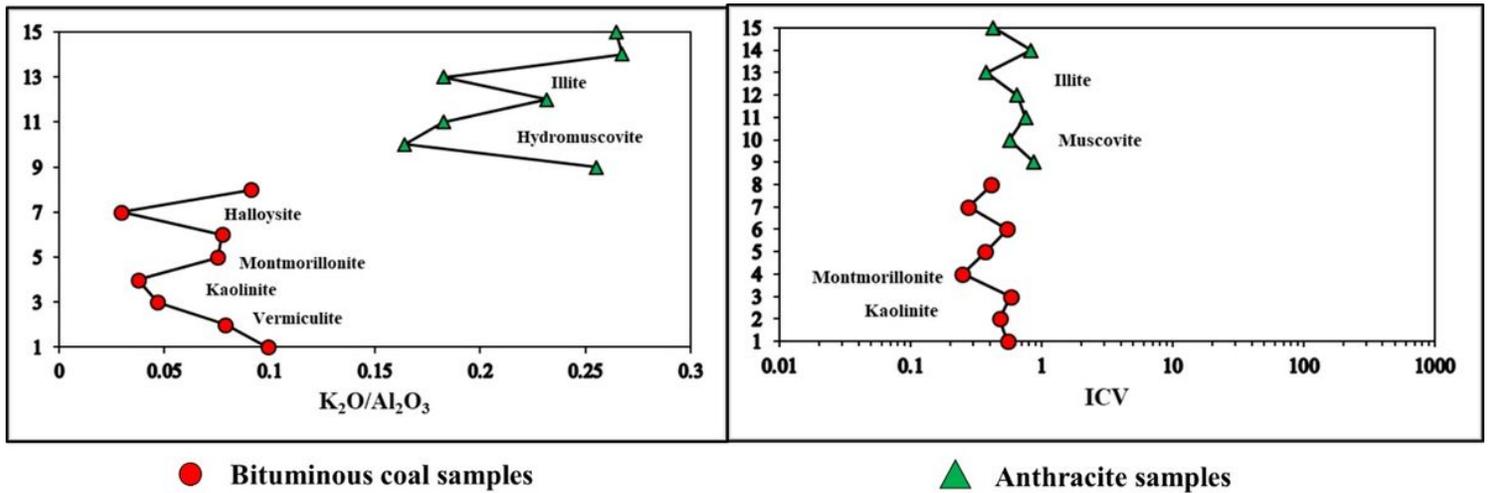


Figure 8
 (a) Relation between the K₂O and Al₂O₃ contents, (b) Index of compositional variation (ICV) discriminating the type of clay mineral present in the samples. Explanations: The ranges of the K₂O/Al₂O₃ and the ICV values have been mentioned following Cox et al. (1995). The Y-axis in both of the plots represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.

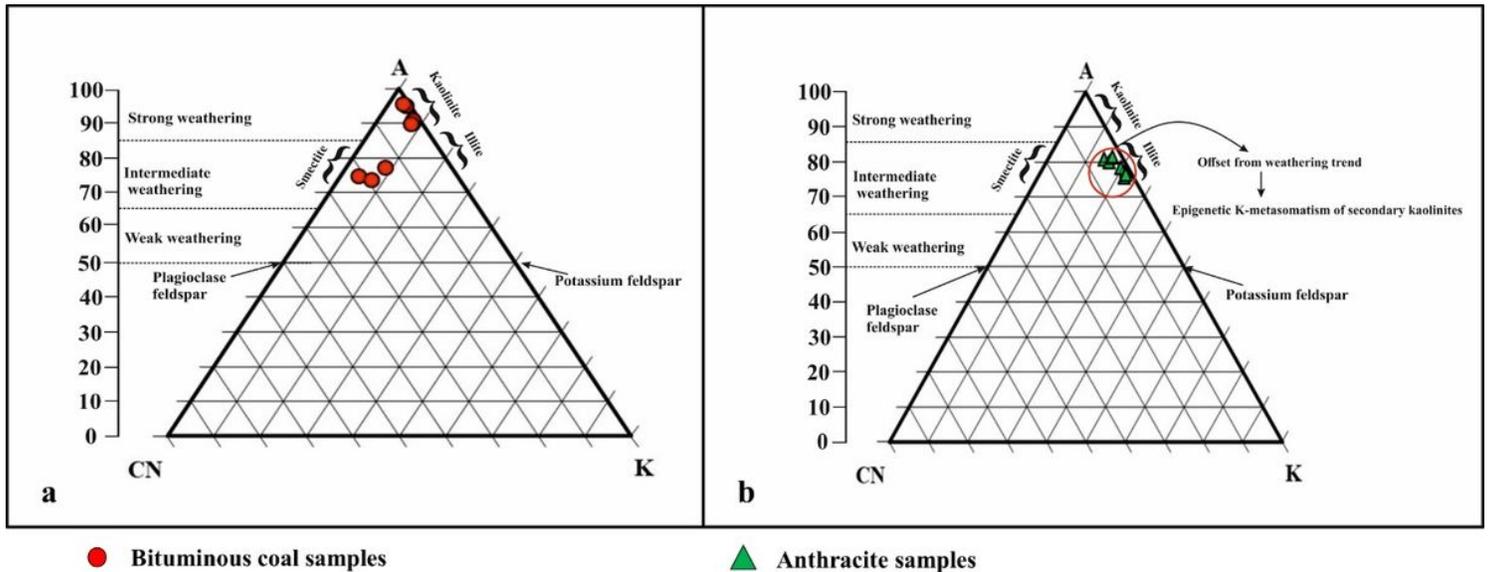
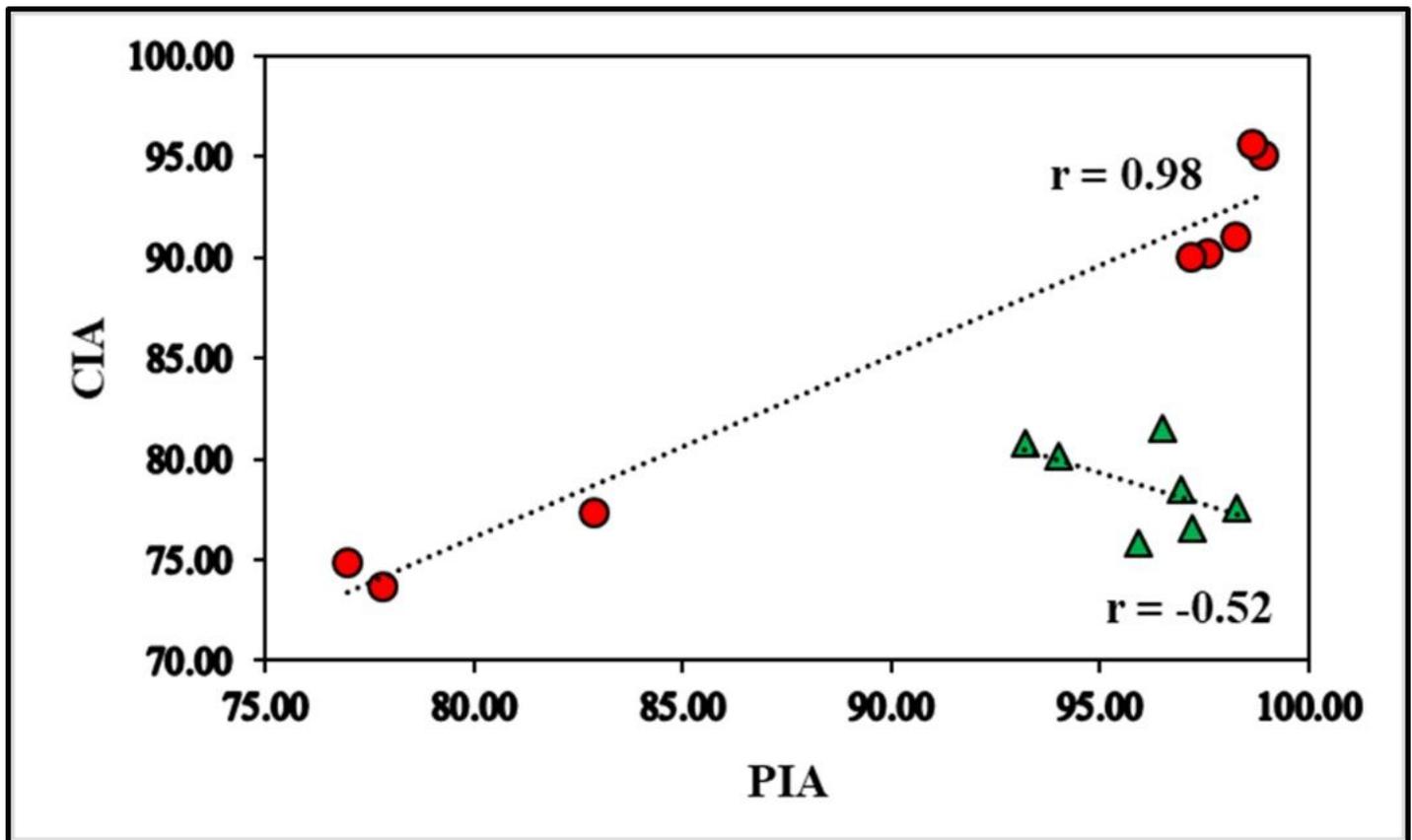


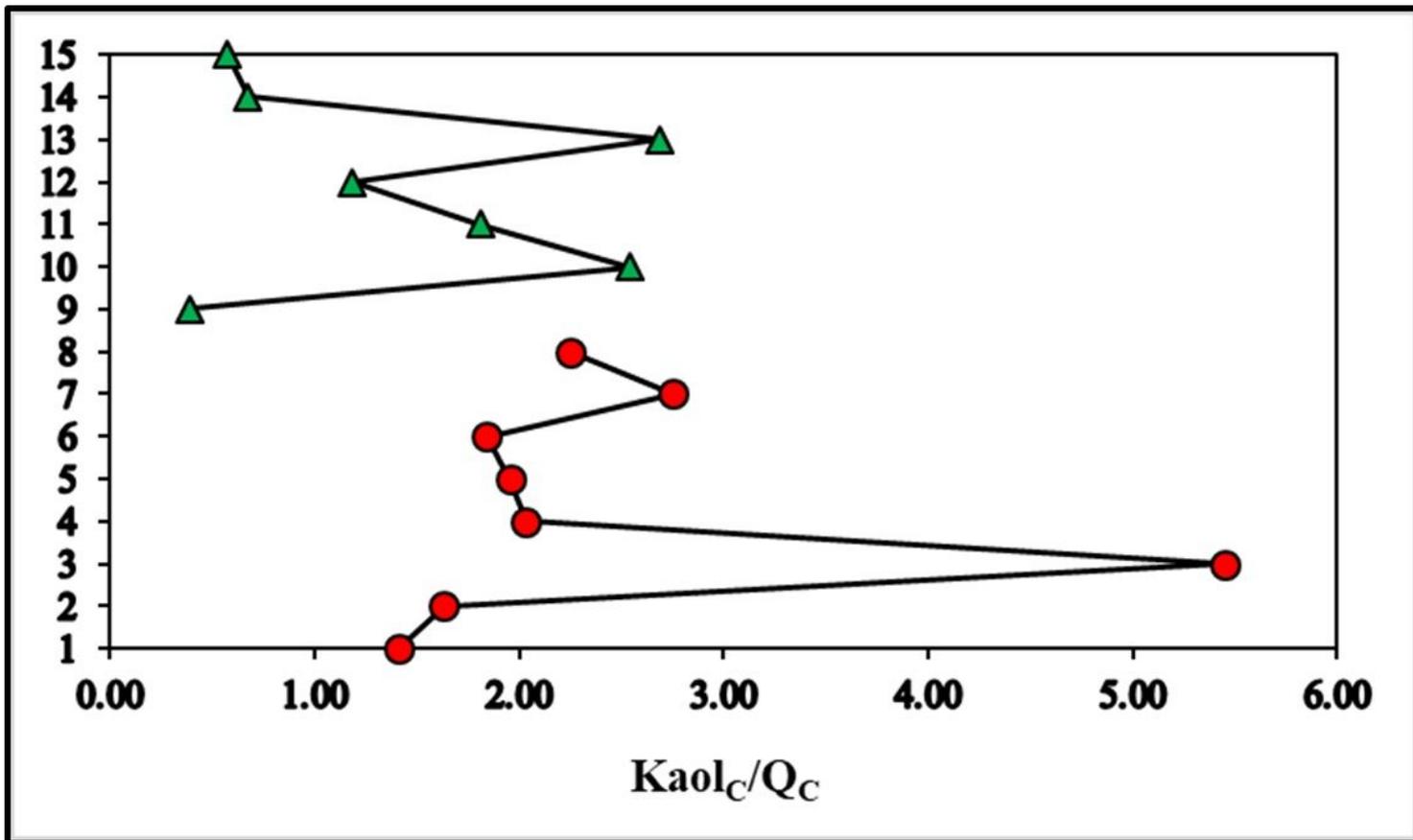
Figure 9
 (a) Bituminous coal samples are plotted in the A-CN-K (Al₂O₃-CaO*+Na₂O-K₂O) diagram with three samples (CG1671, CG1673, and CG1679) lying near smectite (montmorillonite) field, (b) Anthracite samples are plotted in the A-CN-K (Al₂O₃-CaO*+Na₂O-K₂O) diagram near the field of illite showing offset from the common weathering trend and the plausible influence of potassium-metasomatism (K-metasomatism) (adapted from Bai et al. 2015).



● Bituminous coal samples ▲ Anthracite samples

Figure 10

Relation between the chemical index of alteration (CIA) and the plagioclase index of alteration (PIA) of the studied samples.



● Bituminous coal samples ▲ Anthracite samples

Figure 11

Ratio of total kaolinite to quartz contents within the bulk coal samples Explanations: The Y-axis in this plot represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.

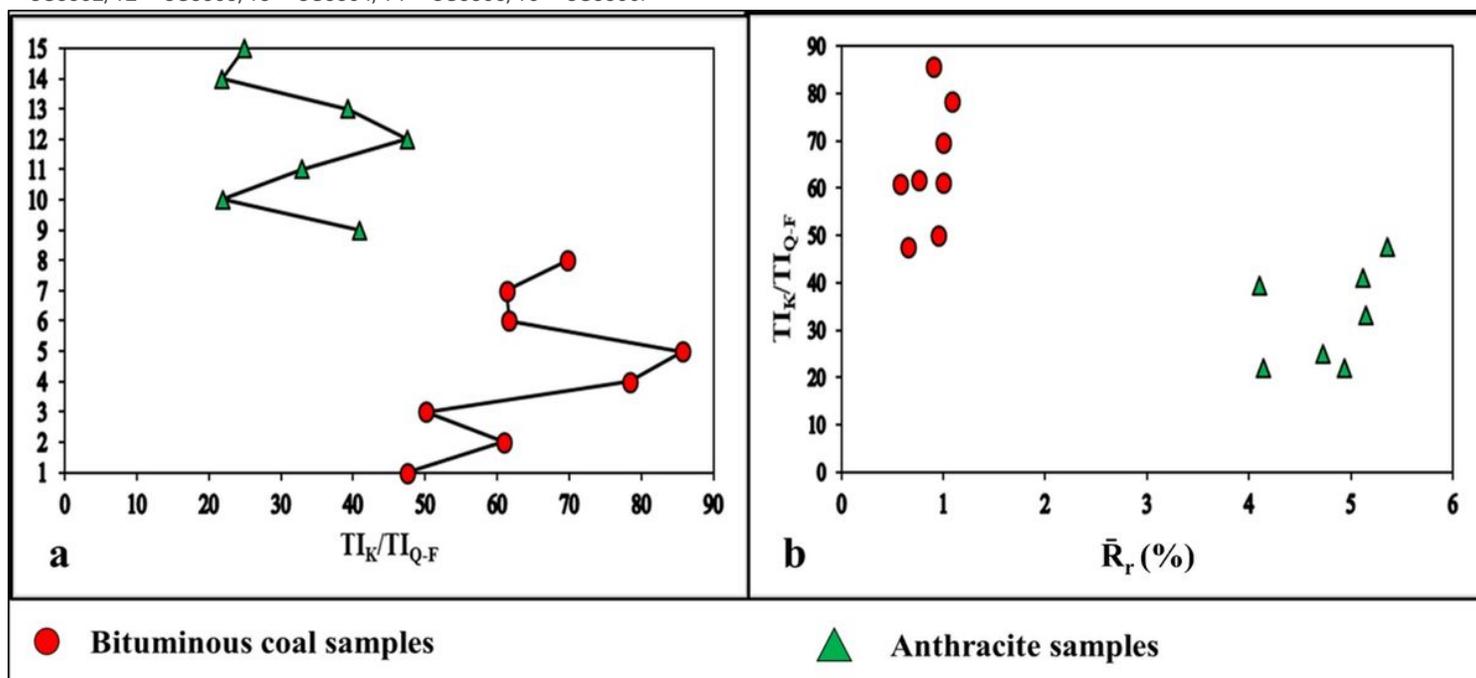


Figure 12

(a) Ratio of total relative intensities of kaolinite to the sum of the relative intensities of the quartz and the feldspar (TIK/TIQ-F) showing depletion towards the anthracite samples from the bituminous samples, (b) Relation between the mean random vitrinite reflectance (R_r) and the total relative intensities of kaolinite to the sum of the relative intensities of the quartz and the feldspar (TIK/TIQ-F) Explanations: The Y-axis in Fig. 12a represents the serial number of the samples mentioned in Table 5. 1 – CG1671, 2 – CG1672, 3 – CG1673, 4 – CG1674, 5 – CG1675, 6 – CG1676, 7 – CG1677, 8 – CG1679, 9 – CG3300, 10 – CG3301, 11 – CG3302, 12 – CG3303, 13 – CG3304, 14 – CG3305, 15 – CG3306.