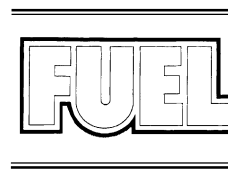


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Distribution and nature of organic/mineral bound elements in Assam coals, India[☆]

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Abstract

This study focuses on the determination and concentration of twelve elements (Na, K, Ca, Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd) occurring in sub-bituminous Assam coals and their geochemical association. Distribution of these elements between organic and mineral matters was studied. Comparison of the results of three coals has shown that three elements (Mg, Ca and Mn) are significantly organic bound, while five elements (Fe, Co, Ni, Cu and Zn) are significantly mineral bound; Cd is 50% bound to either organic or mineral matter. FTIR and XRD studies reveal qualitative information about the bonding pattern and nature of components of the mineral matters. The results obtained in this study have considerable geochemical and technological interests.

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1. Introduction

Industrial coal combustion plants such as coal-based power plants supply varieties of elements to the atmosphere. Huge deposits of coal and waste materials (after coal combustion) when dumped in open air are affected by wind and rain water leading to water and land pollution. These have been a great concern from last three decades. The United States Clean Air Act Amendments of 1990 identified Sb, As, Be, Cd, Cr, Co, Pb, Hg, Mn, Ni, Se and radionuclides as potentially hazardous air pollutants [1]. However, Finkelman [2] reported that besides these air pollutant elements, some other elements, e.g. Ba, B, Cl, Cu, F, Mo, P, Ag, Tl, Sn, V and Zn, are environmentally sensitive elements. The nature of enrichment of these elements in coal is prerequisite for efficient demineralisation.

Coal is an organic rock and it was formed by the bacterial decomposition of peat materials followed by other processes including metamorphic processes. The plant materials can contribute very trace amounts of metallic

elements while the major amounts could be from erosion and weathering products of soil, rocks, minerals, etc. The elements occur in coal, in two ways—organic bound and mineral bound. The organic bound includes ion-exchangeable, chelate and organometallic types, whereas, the mineral bounds are either discrete minerals or associated/adsorbed elements or both. Therefore, it is very important to understand the distribution pattern of elements in coals for their efficient removal. However, works on leaching of model minerals such as quartz and kaolinite [3], gypsum [4,5], pyrite [4], etc. as well as demineralisation of coals [6–8] have been reported. Also a large number of literature is known on the mode of occurrence of elements in varieties of coals [9–12].

Assam coal is a high sulphur coal and its total reserve is estimated to be 161.3 mt. Total annual production is about 1.3 mt and is mainly consumed in power plants, chemical industries, brick-fields, tea garden factories, etc. Although a few reports are available on metal association in Assam coals [13,14] but to our knowledge the literature on the distribution behaviour of the elements is very scanty. Since common alkali, alkaline earth and transition elements contribute majority of the ash content, their study is most important relative to the study on trace and rare elements so far as demineralisation of coal is concerned. In view of

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the lack of knowledge on the degree of occurrence and their nature of association, the present work is carried out to examine the distribution pattern of twelve metallic elements present in Assam coals. For this, three Assam coals are chosen from three different collieries of the same age (Tertiary) and rank (Sub-bituminous), and containing similar organic constituents and exhibiting similar mineralogy.

2. Experimental

2.1. Coal samples and their geology

Three Assam coal samples were obtained from 20 ft seam of the Tirap, Tikak, and Boragolai collieries of the Makum coal field (27°16' to 27°18'N and 95°43' to 95°55'E) of Upper Assam, North East India. The coalfield covers an area of 30 km long and 5 km wide, and is situated along the outermost flank of the Patkai range. The southern and southeastern sides of the field are hills, which rise abruptly to a height of 300–500 m from alluvial plains of the Burhidihing and the Tirap Rivers [15]. The coals of the Makum coal field have high sulphur content ranging generally from 2 to 6%. The basic compositional data for the coals are given in Table 1. Each coal sample was ground to size < 100 μm .

2.2. Mineralogical analysis

Coal contains a number of minerals but their quantities may vary from coal to coal. In this study, pyrite was detected (Table 1) from pyritic sulphur determined by the standard procedure for coal [16]. Melanterite and gypsum are responsible for sulphate sulphur in coal; these minerals were detected from sulphate sulphur determination by

standard procedure [16]. The values of sulphate sulphur for these coals are also given in Table 1. Each raw coal sample was made to ash by the low temperature ashing (LTA) method as reported by Miller et al. [17]. X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy were used for identification of mineral component and phases present in the coal samples.

2.3. Chemical fractionation

1N ammonium acetate solution, as used by the soil scientists for determining ion-exchangeable cations [18,19] was also used to extract the ion-exchangeable cations occurring in coal organic matter as recommended by Miller and Given [20]. Here, 500 mg air-dried coal sample was taken in a 100 ml beaker and 20 ml 1N ammonium acetate solution was added. The contents of the beaker were kept for an hour at 25 °C with constant stirring. The solid residue was separated by filtration, washed several times with 1N ammonium acetate solution. The filtrate and the washings were collected in a 100 ml volumetric flask.

It is true that 0.1N HCl extraction does not isolate chelated cations from the organic matter effectively because of high stability of the complexes; these could be unaffected in the weathering processes. However, this acid can dissolve carbonates, certain oxides and sulphides in addition to leaching adsorbed elements from the mineral surface and clays. Therefore, the 0.1N HCl extraction is mainly selective for mineral bound metal ions and was applied in this study.

The ammonium acetate treated (dry and weighed) sample was taken in a 100 ml beaker and 20 ml 0.1N HCl was added, the contents in the beaker was kept for an hour with constant stirring at 25 °C. The solid residue was removed by filtration, washed several times with 0.1N HCl and finally collected the filtrate and washings in a 100 ml volumetric flask.

After sequential extractions of 1N ammonium acetate solution and 0.1N HCl, the coal residue contains organic bound (i.e. chelated and/or organometallic) and mineral bound (i.e. discrete mineral) elements. A suitable organic solvent was searched for gravity separation of the minerals from coal. Carbon tetrachloride (CCl_4) being a common solvent with specific gravity 1.60 g/l in the laboratory, was selected for the gravity separation of minerals. Thus most of the minerals are removed by gravity separation using CCl_4 and the residue thus obtained is termed as mineral-free coal for our convenience. It is to be noted that the mineral-free coal may not be absolutely free from all the mineral matters.

The elements present in the mineral-free coal are resistant to 1N ammonium acetate and 0.1N HCl extractions, and therefore, a suitable reagent was searched for. Out of many reagents studied, viz. FeCl_3 , CoCl_2 , NiCl_2 , PdCl_2 and RuCl_3 ; ruthenium tri-chloride showed promising results for the leaching of minerals from the mineral-free coal; this reagent was selected for the present study.

Table 1
Basic compositional data for coal samples from Makum coal field

Analysis	Tirap coal	Tikak coal	Boragolai coal
Proximate (wt%)			
Moisture	1.90	1.30	2.10
Ash	10.30	12.40	12.70
Volatile matter	40.10	42.10	40.30
Fixed carbon	47.80	44.30	44.80
Ultimate ^a (wt%)			
Carbon	75.50	72.70	73.30
Hydrogen	4.90	5.00	4.90
Nitrogen	1.70	1.60	1.70
Sulphur (organic)	6.70	5.20	6.40
Oxygen (by diff.)	11.20	15.50	13.70
Sulphur			
Total sulphur	8.20	7.20	7.70
Pyritic sulphur	0.90	0.90	0.80
Sulphate sulphur	0.60	1.10	0.50

^a Air dry basis.

20 ml 0.01 M RuCl_3 solution was added to the dry and weighed mineral-free coal, taken in a 100 ml beaker. The content in the beaker was warmed at 60 °C for an hour with occasional stirring. After that, the beaker was cooled to room temperature and then filtered; the residue was washed several times with 0.01 M RuCl_3 solution. The filtrate and the washings were collected in a 100 ml volumetric flask.

2.4. Preparation of samples for analysis

The ammonium acetate extracts were mixed with 5.0 ml glacial acetic acid and diluted to 100 ml in volumetric flasks with 1N ammonium acetate solution. Similarly HCl and RuCl_3 extracts were made up to 100 ml with 0.1N HCl solution.

The weighed insoluble residue, obtained after RuCl_3 treatment, was ashed at 800 °C in a muffle furnace for an hour. The whole ash was mixed with concentrated HNO_3 (4 ml), HF (10 ml) and HClO_4 (1 ml) taken in Teflon lined bomb and heated up to 120 °C for an hour. On cooling, the solution and also the washings in the Teflon bomb were poured into a 100 ml beaker containing a warmed (~60 °C) solution of boric acid prepared by dissolving 5 g boric acid in 40 ml deionised water. The solution in the beaker was stirred well and then filtered. The filtrate and the washings were collected in a 100 ml volumetric flask and made up to 100 ml with 4.0% HNO_3 .

For the determination of total amount of each element, the feed coal was subjected to HNO_3 , HF and HClO_4 treatment and heated to 120 °C as above. The other procedures are same and the filtrate and washings were stored in 100 ml volumetric flask.

2.5. Preparation of standard solution and analysis

The cations present in different extracts were analysed by an atomic absorption spectrophotometer. Standards of 1–100 ppm were prepared from the stock solutions of 1000 ppm. The detection limit of the instrument is 1 ppm. For some elements, it was necessary to make further dilutions to obtain the strength of the solution to optimum measuring range of the instrument. Blank determination of all the reagents were made. All the determinations of

the elements were done thrice with correlation coefficient greater than 0.992.

3. Results and discussion

3.1. Elements in different extracts

The concentration of elements obtained from different methods of analysis for the Tirap coal is given in Table 2. Out of 12 elements studied here, it is observed that 9 elements could be extracted by the ammonium acetate solution. As three elements (K, Co and Cu) were not leached out by the reagent used, it seems likely that these elements are not present in this coal as ion-exchangeable elements occurring in coal organic matter. Calcium exhibits highest amount of extracted element in them while lowest is observed in case of Cd.

All the elements, except K, were leached out by dilute HCl suggesting that these elements are present in the coal either as carbonate, oxide, sulphide or as adsorbed species on mineral or clay surfaces. Highest amount is observed in Fe and the lowest is seen in case of Cd (Table 2). Since the extraction of RuCl_3 solution was done for mineral-free samples, the elements leached out by the reagent could be attributed to non-exchangeable organic bound elements. Thus nine elements are non-exchangeable organic bound, where Ca shows highest quantity and Cu represents lowest amount (Table 2). Three elements (Cr, Ni and Zn) seem to be of not much organic bound; however, these are occurring as ion-exchangeable elements and were extracted by the ammonium acetate solution. It is interesting to note that only three elements (Mg, Fe and Zn) were present in the ash prepared by heating the RuCl_3 solution treated mineral-free sample and could be assigned to complex organic bound elements. The occurrence of K in Tirap coal is very significant because this element was neither extracted by the ammonium acetate solution nor by HCl solution and also was not present in ash; however, this cation could be extracted by RuCl_3 solution. In general it is apparent that the elements which were not completely leached out by the sequential extractions with solutions of ammonium acetate

Table 2
Analysis of elements in Tirap Coal (in $\mu\text{g/g}$)

Analysis	Alkali elements		Alkanline earth elements		Transition elements							
	Na	K	Mg	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
Ammonium acetate extraction	258	ND	24	975	5	13	10	ND	18	ND	17	3
Dil. HCl extraction	431	ND	33	377	9	12	3680	15	34	12	45	6
RuCl_3 extraction	234	113	10	1030	ND	4	34	7	ND	3	ND	5
Ash	ND	ND	10	ND	ND	ND	1050	ND	ND	ND	7	ND

ND = Not detected (<1 $\mu\text{g/g}$).

Table 3
Analysis of elements in Tikak Coal (in $\mu\text{g/g}$)

Analysis	Alkali elements		Alkanline earth elements		Transition elements							
	Na	K	Mg	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
Ammonium acetate extraction	275	ND	34	3292	7	9	6	ND	ND	22	22	3
Dil. HCl extraction	313	ND	54	857	9	4	3380	13	23	59	39	7
RuCl ₃ extraction	67	ND	10	914	24	7	586	ND	ND	2	ND	4
Ash	ND	23	15	ND	ND	11	562	ND	ND	ND	7	ND

ND = Not detected ($<1 \mu\text{g/g}$).

and dilute HCl, were extracted by the RuCl₃ solution, thus revealing that RuCl₃ solution is an excellent leaching agent.

The quantity of elements extracted by the different procedures for the Tikak coal is given in Table 3. Highest amount is observed in Ca whereas lowest is seen in Cd in the extraction with the ammonium acetate solution. The reagent does not extract three elements (K, Co and Ni). In the HCl extraction, all the elements except K were leached out. Iron shows exceedingly high value while the lowest value is observed in Mn. Eight elements are occurring in this coal as non-exchangeable organic bound elements because these were extracted by the RuCl₃ solution. Presence of the elements in ash are K, Mg, Mn, Fe and Zn suggesting that these five elements are present in the organic matter of coal in such complex fashions that these could not be leached out by any of the reagents used in this study.

The concentration of elements obtained from different methods for the Boragolai coal is given in Table 4. Calcium is found to be the dominant element but the lowest concentration is observed in case of Cr and Cd in the ammonium acetate extraction, however, two elements (K and Ni) were not extracted. Concentration of Fe is quite high than the rest of the elements in the dilute HCl extraction, the lowest value is found in Cr. Only K was not leached out by the acid treatment. In the RuCl₃ extraction, highest concentration is observed in Ca, lowest in Cu while four elements (K, Cr, Ni and Zn) were not extracted. Out of twelve, eight elements were not found in the ash but Fe still shows highest concentration.

Comparison of Tables 2–4 reveal that K is not extracted by the dil. HCl; Ni and Zn by RuCl₃ solution and Na, Ca, Cr,

Co, Ni, Cu and Cd were not present in ash. The concentration of a particular element in each extraction is not same in all the coals, except Cd in ammonium acetate solution, although the coals have been of same age (Tertiary) and rank (Sub-bituminous) as well as from the same exploitation area (Makum coal). Thus the functional groups of coal organic matter, as well as presence of carbonate, sulphide and other minerals could largely be responsible for the uneven distribution of elements in coal. Therefore, it is very much essential to understand the distribution pattern of elements in coals. For this purpose a suitable relationship is drawn to calculate the concentration of organic bound elements in these coals.

3.2. Distribution of elements

A large number of literature is known for the determination of organic affinity of elements for different coals [2,10,21–29]; however, the equation for the geochemical distribution of trace elements proposed by Solari et al. [23] has been largely used.

In our recent work, we have used RuCl₃ solution as a special reagent for the extraction of gold from Assam coal [13]. The same reagent is used here for leaching non-exchangeable elements associated with the organic matter of coal. As discussed in Section 2.3, treatment of ammonium acetate solution can leach out ion-exchangeable elements bound to organic matter. Subsequent treatment with dil. HCl can dissolve some carbonates, oxides, sulphides, etc. in addition to adsorbed species; these can be referred to as mineral bound. The residue after acid

Table 4
Analysis of elements in Boragolai coal (in $\mu\text{g/g}$)

Analysis	Alkali elements		Alkanline earth elements		Transition elements							
	Na	K	Mg	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
Ammonium acetate extraction	297	ND	33	690	3	13	16	4	ND	8	17	3
Dil. HCl extraction	289	ND	40	374	4	12	3376	14	21	25	28	8
RuCl ₃ extraction	67	ND	21	848	ND	6	173	9	ND	2	ND	6
Ash	ND	36	13	ND	ND	ND	594	ND	ND	ND	6	ND

ND = Not detected ($<1 \mu\text{g/g}$).

treatment contains elements in the form of non-exchangeable organic bound and discrete minerals. Gravity separation by CCl_4 could remove most of the elements leaving the coal with predominant amounts of non-exchangeable organic bound elements. Subsequent leaching with RuCl_3 solution could remove a part of the organic bound elements while the rest amounts were present in the ash. Therefore, it is quite distinct to suggest that in each case, the total organic bound element can be calculated from the sum of the quantities obtained in the soluble extracts of ammonium acetate and RuCl_3 solutions with those found in ash. Thus,

$$\text{Total concentration of organic bound element} = \text{Quantity of element in (ammonium acetate extract} + \text{RuCl}_3 \text{ extract} + \text{ash)}$$

The distributions of organic bound elements for all coals are given in Tables 5–7. The standard deviation of all the metals studied here given in Tables 5–7 clearly manifests the degree of accuracy and precision. Comparison of Na concentration in the three coals reveals that the element occurs 49.35–53.02% in organic matter; thus almost similar participation of Na in both organic and mineral matter. However, it is apparent that a considerable amount of the element is associated with the mineral matter. According to Karayigit et al. [29], Na is commonly associated with the aluminium–silicon bearing minerals and halite. The results of K is interesting because it is 94.96% organic bound in the Tirap coal (Table 5) while in the Tikak coal (9.11%) and in the Boragolai coal (11.84%), it has exceedingly quite low values (Tables 6 and 7) and therefore, could be assigned to largely mineral bound element. It is known that K is present in K_2O -bearing minerals, mainly illite [29]. The occurrence of K in clay minerals, feldspar, etc. suggest detrital origin.

The percentage of organic bound Mg is 50.86–55.83% in all the coals. It is apparent that this element is slightly higher organic bound relative to the mineral bound. However, its association with mineral matter is known. It is commonly

Table 5
Distribution of elements in Tirap coal

Elements	Total ($\mu\text{g/g}$)	Organic bound ($\mu\text{g/g}$)	% Organic bound	Standard deviation
Na	928	492	53.02	0.1425
K	119	113	94.96	0.1650
Mg	84	44	51.76	0.0971
Ca	2388	2005	83.96	0.5115
Cr	60	5	8.33	0.3008
Mn	31	17	54.84	0.2324
Fe	5806	1094	22.76	0.2857
Co	22	7	31.82	0.0776
Ni	54	18	33.33	0.2770
Cu	20	3	15.0	0.3864
Zn	114	24	21.05	0.0896
Cd	16	8	50.0	0.7828

Table 6
Distribution of elements in Tikak coal

Elements	Total ($\mu\text{g/g}$)	Organic bound ($\mu\text{g/g}$)	% Organic bound	Standard deviation
Na	693	342	49.35	0.5632
K	395	36	9.11	0.4846
Mg	116	59	50.86	0.0344
Ca	5007	4206	84.0	0.3442
Cr	43	31	72.09	0.0259
Mn	32	27	84.38	0.0310
Fe	5008	1154	23.04	0.4741
Co	13	0	0	–
Ni	23	0	0	–
Cu	87	24	27.59	0.0232
Zn	80	29	36.25	0.0371
Cd	14	7	50.0	0.0098

associated with carbonates and clay minerals. The enrichment of Ca in organic matter is quite high, i.e. 78.91–84.01% in all the coals. Although this element seems to have low association with mineral matter but it is commonly found in the carbonate minerals.

The results of Cr is very confusing because it is 8.33% organic bound in the Tirap coal, 72.09% in the Tikak coal and 33.33% in the Boragolai coal. Since the total concentration of Cr is quite low (9–60 $\mu\text{g/g}$) in all the coals, its association with organic and mineral matters depends on the environmental conditions and nature of existence prior to its association with the organic matter. A proportional increase in concentration of the element with respect to the rank of the coal has already been reported [30]. Our results for the Tikak coal agrees with the work of Pires and Teixeira [26], who reported that Cr in general, has been found to be associated with the organic matter. Similar concentration of the element in organic and inorganic fractions of Candiotia coal has been known [26]. In the present study, two out of three coals have major amount of Cr in the mineral matter. Reports of Cr association in

Table 7
Distribution of elements in Boragolai coal

Elements	Total ($\mu\text{g/g}$)	Organic bound ($\mu\text{g/g}$)	% Organic bound	Standard deviation
Na	688	364	52.91	0.4742
K	304	36	11.84	0.2228
Mg	120	67	55.83	0.2196
Ca	1949	1538	78.91	0.5641
Cr	9	3	33.33	0.0219
Mn	33	19	57.58	0.0103
Fe	4759	783	16.45	0.4782
Co	28	13	46.43	0.0573
Ni	24	0	0	–
Cu	37	10	27.02	0.0335
Zn	59	23	38.98	0.0465
Cd	18	9	50.0	0.0478

mineral matter are largely known. It is present in high concentration in the sulphide mineral [26]. Ruppert et al. [31] reported that Cr might be related to the Cr-bearing minerals such as Cr-spinel and clay minerals. High concentration of Cr in coal have been found in chromite, FeCrO_4 [31]. According to Querol et al. [32], enrichment of Cr in Cayirhan lignite could be the result of synsedimentary activity. Therefore, the predominant occurrence of Cr in mineral matter is quite justified here.

The remarkable evidence of organic bound Mn is due to its association with the organic matter in the range of 54.84–84.38% for all the coals under study. Our result is strongly supported by the study of Swaine [9] who reported that substantial part of Mn could be organically associated. However, a significant part is also associated with the mineral matter. It is enriched with mostly the inorganic fraction of Candiota coal [26]. Moreover, frequent association of Mn in carbonate specially with siderite and ankerite is known [10,33]. It is interesting to note that the Mn enrichment in organic or mineral matters varies with the rank of coal. Most of the elements in bituminous coals occur in mineral matter (i.e. in carbonates) [29] but in low rank coals (lignite and brown coals), it is largely associated with the organic matter [9]. Thus predominant association of Mn in organic matter, observed in this study, could be due to low-rank coals, studied here.

In contrast, Fe is distinctly mineral bound because the organic bound contents vary from 16.45 to 23.04% only. This is quite logical since in the oxic environment of natural systems, soluble ferric iron is only possible nearly at pH 3.0, which at near neutral pH or in alkaline condition forms insoluble substances leading to low susceptible for association with organic matters. Presence of sulphides and disulphides (i.e. pyrite), carbonate (siderite) and iron-bearing minerals occurring in coal could be responsible for the high mineral bound Fe in coals under study.

An important point to note is that Fe is the dominant element in each coal sample. Besides its predominant association with mineral matter, its association with organic matter has been largely studied because its actual association with organic matter is remarkable. Metalloprotein like ferredoxin as well as iron–cystine complex present in carbonaceous systems [36] could be responsible for the enrichment of Fe in coal organic matter [37]. Identification of iron–porphyrin [38], Fe–N coordinated compound of octahedral symmetry [39,40] and Fe–S coordinated compound [41] in different coals have already been reported. Iron in compounds that could be to some extent represents the non-exchangeable organic bound element.

Like Fe, similar results of significant mineral bound are observed for four elements, viz. Co, Ni, Cu and Zn. These elements have low percentage of organic affinity: 0–46.43% for Co, 0–33.33% for Ni, 15.0–27.59% for Cu and 21.05–38.98% for Zn in these three coals (Tables 5–7). These elements are frequently concentrated in sulphides. Cobalt is related to the Cr-bearing mineral [29] while Ni is

associated with mineral clays and spinals. Moreover, nickel sulphide minerals reported to occur in coal are millerite, NiS; linnæite, $(\text{Co,Ni})_3\text{S}_4$; ullmannite, NiSbS [10] and its trace amount is found in galena, sphalerite, pyrite, clausthalite and other minerals in coals [34]. Copper-bearing chloride, known to occur in coal, is the important source of mineral bound copper. Moreover, copper pyrites, CuFeS_2 is generally found in most of the coals. On the other hand, sphalerite (ZnS) is the most common zinc containing mineral occurring in coal. The data for Cd is very interesting in the sense that it is 50.0% organic bound in all the coals; thus representing equal participation in both organic and inorganic matters. But a significant amount of the element in mineral matter is important so far as environmental pollution is concerned. Cadmium is commonly associated with Zn in the sphalerite mineral [33] and pyrite [9]. In German coals, Cd is found in clays and carbonates [35].

3.3. Infrared study

Infrared spectra of samples, prepared by low temperature ashing method, for all the three coals are given in Fig. 1. For the Tirap coal, the infrared bands at 3397, 1702, 1608, 1400, 1091, 751, 558 and 472 cm^{-1} have been observed. The bands at 3405, 1717, 1615, 1166, 1087, 798, 691, 513 and 469 cm^{-1} of the infrared spectrum of the Tikak coal have occurred; however, a new band at 1166 cm^{-1} appears in this coal instead of the band occurring at 1400 cm^{-1} for the Tirap coal. In the Boragoali coal, similar bands found in the Tirap coal are observed; the bands occurred at 3407, 1706, 1611, 1400, 1023, 773, 559 and 472 cm^{-1} . Table 8 summarises the typical assignments of the infrared bands in all the three coals under study. Interpretation of the infrared spectra of samples is given below for different types of minerals likely to be present in the coals studied here.

3.3.1. Sulphate minerals

The sulphate minerals in coal include mainly malenterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The report of the occurrence of Jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ in coal has also been known. Each sulphate mineral has tetrahedral SO_4^{2-} unit; it has four modes of vibration when it retains its full symmetry. According to Nakamoto [42], the fundamental frequencies of sulphate anion are occurred at 1105, 983, 611 and 450 cm^{-1} .

The vibration for gypsum occurs at 1160, 1140, 1115, 870, 680 and 605 cm^{-1} and for jarosite at 1190, 1100, 1028, 1018, 685, 638 and 482 cm^{-1} [43]. Out of these coal studied here, in the Tikak coal, a band at 1166 cm^{-1} is prominent suggesting the presence of sulphate minerals (e.g. gypsum) in this coal. Surprisingly, this band is not evident in the spectra of Tirap and Boragolai coals. Since varying amounts of sulphate sulphur is always present in a coal, therefore, its absence in Tirap and Boragolai coals cannot be possible. It could be true that the quantity of this type of mineral is comparatively high in the Tikak



Fig. 1. Infrared Spectra of Tirap coal (a), Tikak coal (b) and Boragolai coal (c).

coal relative to that of the other coals. This is strongly supported by the chemical analysis of sulphur as shown in Table 1.

It is an established fact that the bending mode is ascribed to the water hydrogen bonded to sulphate which is occurring at 1744 cm^{-1} [43]. Interestingly, all the three coals studied here have shown infrared band at $\sim 1700\text{ cm}^{-1}$, strongly suggesting the occurrence of sulphate minerals in three coals.

3.3.2. Carbonate minerals

The commonly occurring carbonates in each coal are calcite, CaCO_3 and siderite, FeCO_3 . The internal mode of frequencies of calcite are 1425 , 876 and 712 cm^{-1} and of siderite are 1422 , 866 and 737 cm^{-1} [43]. In carbonate, three strongly polarised bands are observed. The low frequency bands are the lattice modes. The bands at 1400 cm^{-1} in the Tirap and the Boragolai coals show the presence of carbonate mineral in these coals, however, such a band is not observed in the spectrum for the Tikak coal.

3.3.3. OH/H₂O bound minerals

In the region of OH stretching vibrations of a polycrystalline compound, one observes a complex adsorption band with intense components at 3554 , 3513 and 3408 cm^{-1} . Moreover, the deformation vibration of adsorbed water lies at 1630 cm^{-1} is characteristic of molecular H_2O . The symmetric and asymmetric stretching vibrations of adsorbed water give rise to a broad band centered at

3400 cm^{-1} , compared with $\sim 3700\text{ cm}^{-1}$ in the free molecule: the reduction in frequency reflecting the formation of moderately strong hydrogen bonds ($\text{OH}\cdots\text{O} \approx 2.94\text{ \AA}$). Occurrence of absorption bands at 3397 and 1608 cm^{-1} for the Tirap coal, at 3404 and 1614 cm^{-1} for the Tikak coal, and at 3404 and 1610 cm^{-1} for the Boragolai coal strongly suggest the OH stretching vibrations of coordinated H_2O and/or bonded OH groups present in the minerals of all these coals. The OH bending

Table 8
Assignment of infrared bands observed in Tirap, Tikak and Boragolai (LTA) coals

Infrared bands (cm^{-1})			Assignment
Tirap coal	Tikak coal	Boragolai coal	
3397	3405	3407	OH stretching vibration of coordinated water or bonded OH
1702	1717	1706	Hydrogen bonded sulphate
1608	1615	1611	OH stretching vibration of coordinated water or bonded OH
1400	–	1400	bonding carbonate
–	1166	–	bond for sulphate
1091	1087	1023	Si–O stretching vibration
751	798	778	OH bending vibration
–	691	–	band for sulphate
558	513	559	Si–O bending vibration
472	469	472	Si–O stretching vibration

vibrations occurring in the region of $750\text{--}800\text{cm}^{-1}$ in the spectra of coals studied here further supports this conclusion.

3.3.4. Sulphide minerals

Pyrite is the most common disulphide mineral in coal. It along with marcasite (both have same formula of FeS_2) is termed as pyritic sulphur. Other less common disulphide mineral in coal is cassiterite, SnS_2 [44]. The stretching vibration of S–S bond (for disulphide) is generally observed in the region of $400\text{--}500\text{cm}^{-1}$. Appearance of the bands at 471cm^{-1} for the Boragolai and Tirap coals, and at 468cm^{-1} for the Tikak coal, reveal the presence of disulphide minerals in these coals. This observation is strongly supported by the quantity of pyritic sulphur (Table 1) found in these coals.

Besides disulphides, coal contains minor quantities of some sulphides viz. sphalerite (ZnS), copper pyrite (CuFeS_2), galena (PbS) and cinnabar (HgS) [44]. The common band in these sulphides and also in disulphides is metal sulphur bond. The stretching vibration of metal–sulphur bond occurs below 400cm^{-1} (e.g. 340cm^{-1} for Fe–S [45]) is not observed here because the infrared spectra were recorded in the range of $400\text{--}4000\text{cm}^{-1}$.

3.3.5. Silicate minerals

Another most important mineral occurring in coal is silicates. Kaolinite and chlorite are generally observed. Both are layered silicates and contain the planar hexagonal silicon–oxygen (Si–O) network. The Si–O stretching vibrations lying in the region of $700\text{--}1200\text{cm}^{-1}$ are also weakly coupled with other vibrations of the structure. But Si–O bending vibrations lying between 150 and 600cm^{-1} are strongly coupled with vibration of the octahedral cations and with translatory vibrations of the hydroxyl groups. A band centered at $\sim 1050\text{cm}^{-1}$ is reported to be Si–O stretching vibration [43]. Occurrence of the band at 1090cm^{-1} for the Tirap coal, at 1087cm^{-1} for the Tikak coal, and at 1022cm^{-1} for the Boragolai coal suggests the presence of silicate minerals in these coals. The bands for the bending Si–O vibration between 513 and 558cm^{-1} in the coals under study further strengthen the presence of silicate minerals. Since major amounts of ash in coal is silica and therefore, considerable amounts of ash found in these coals, as given in Table 1, strongly reveals the occurrence of silicate minerals in the three coals.

It is known that chlorites containing a high proportion of dioctahedral sites occupied by aluminium give a distinctive three bonded hydroxyl stretching pattern [43]. The position of the band at $\sim 3400\text{cm}^{-1}$ does, however, appear to be unique. Surprisingly, this band is common in the spectra of all the three coals. Therefore, it can be strongly recommended that chlorites are the most common silicate minerals in these coals.

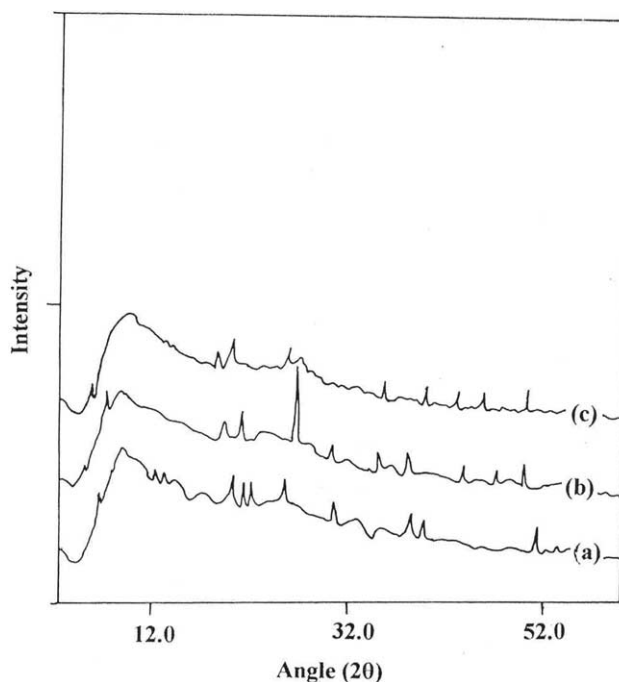


Fig. 2. X-ray diffraction spectra of Tirap coal (a), Tikak coal (b) and Boragolai coal (c).

3.4. X-ray diffraction study

X-ray diffraction study of low temperature ashing coal samples did not give prominent peaks for any mineral. No sulphate, carbonate, sulphide, etc. minerals were detected by the diffraction study; however, some significant peaks for silicate minerals are observed (Fig. 2).

The d -values normally appear for all the coals under study indicate presence of quartz ($d = 3.353\text{Å}$) as the dominant mineral constituent. However, the peak intensity for the quartz is much more prominent in Tikak coal than the Tirap and Boragolai coals. The Boragolai and Tirap coals also indicate the presence of dioctahedral chlorite ($d = 4.509\text{Å}$) as trace constituent. Similar observation have also been reported by Acharya [46] for the Talcher coals of India.

4. Conclusion

It is evident that the mode of occurrence of twelve elements in three sub-bituminous Assam coals studied here shows a distinct distribution pattern of organic bound and mineral bound elements. The nature of distribution of eight elements (Na, Ca, Mg, Mn, Fe, Cu, Zn and Cd) in all the coals are totally same; the other four elements (K, Cr, Co and Ni) do not behave similarly. FTIR and XRD studies have given a quantitative account of the nature of component minerals occurring in these coals. The results presented here would be significant for geochemical

distribution of elements and also be useful as a prerequisite for demineralisation of coal.

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