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GEOCHEMISTRY OF COAL AND COAL BEARING STRATA FROM THE UPPER CRETACEOUS MAMU FORMATION, SOUTHEASTERN NIGERIA: IMPLICATIONS FOR PALEOREDOX HISTORY

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Abstract: Thirteen coal samples from the Maastrichtian Mamu Formation in the Anambra Basin (SE Nigeria) were analysed for total organic carbon (TOC), major and trace elements using *LECO C-230* analyser and inductively coupled plasma-optical emission spectrometry (ICP-OES) in order to assess the paleoredox depositional conditions of sedimentation and the role of clastic input. TOC contents of up to 65% were recorded in the coal samples. The organic richness of the coals (average TOC = 34.7%) was due to high organic carbon flux resulting from high primary productivity and enhanced organic preservation. The chemical composition of the major oxides in the coals are dominated by SiO_2 (1.02–52.77%), Al_2O_3 (0.66 to 20.69%), TiO_2 (0.01-2.14%), Fe_2O_3 (0.04-2.01%) and K_2O (0.01-1.36%), indicating high detrital quartz and clay mineral content. The SiO_2/Al_2O_3 ratios (1.43 to 3.03), TiO_2/Al_2O_3 (0.01-0.11) and K_2O/Al_2O_3 (0.02-0.07) are consistent with limited clastic influx during coal formation. Ternary plots of TOC-S-Fe_2O_3 associations and redox-sensitive trace element ratios indicate dominantly oxic environment of deposition for the coal samples. Ni/Co and V/Cr ratios indicate mainly oxic environment and V/(V+Ni) ratios inferred variable paleoredox (oxic, anoxic and euxinic) conditions during accumulation of these coals.

Keywords: Anambra basin, coal, mamu formation, paleoredox history, trace elements

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Introduction

The coal-bearing Mamu Formation (Reyment, 1965) in the Anambra Basin (SE Nigeria) extends from Auchi/Agenebode area in the west to Ogboyoga in north, along the Awgu-Enugu Escarpment to Udi/Enugu area in the east of the basin (Fig. 1). The Mamu Formation host a 600m-thick sedimentary succession of Maastrichtian age (Simpson, 1954) comprising sandstones, shales, mudstones, sandy shales and coal seams. The coal seams range from a few centimeters to about 4 metres. This formation is exposed in coal mines at Ogboyoga, Okaba, Ezimo, Orukpa, Enugu, Udi and on the Enugu-Onitsha expressway and Awgu-Enugu Escarpment (Fig. 1).

The study area is located in the Anambra Basin in SE Nigeria within latitudes 6°15′ to 7°55′ N and longitudes 7°15′ to 8°00′E (Fig. 1). The evolution of the Anambra Basin in southeastern Nigeria is linked to the opening of the South Atlantic Ocean during Mesozoic Era (Burke *et al*., 1972; Murat, 1972; Nwachukwu, 1972). Sedimentation in the Anambra Basin began with the deposition of the marine Campanian-Maastrichtian Enugu/NkporoShales and its lateral equivalent- the deltaic Owelli Sandstones (Fig. 1). These basal units are overlain successively by the Lower Maastrichtian Mamu Formation (Lower Coal Measures), Middle Maastrichtian Ajali Sandstones (False-Bedded Sandstones) and the Maastrichtian-Paleocene Nsukka Formation (Upper Coal Measures; Fig. 1).

Agagu *et al*. (1985) studied the stratigraphy and sedimentation in the Senonian Anambra Basin and described the Mamu Formation as representing strandplain to deltaic environments, evolving into more open strandplain system. Akande *et al*. (1992) regarded the coals of the Mamu Formation as having accumulated in forest and reed marsh swamps within delta plain environments. Courel *et al*. (1991) investigated coal occurrence related to sedimentary dynamics and reported significant number of dinoflagellates below the coal-bearing part of the Mamu Formation, inferring a lower delta plain environment of deposition for these beds. Several organic geochemical studies have been carried out on coals and source rocks of Mamu Formation (Akaegbobi *et al*., 2000; Obaje *et al*., 2004; Akande *et al*., 2007; Ogala, 2011; Ogala and Akaegbobi, 2014). However, the depositional conditions that favoured the accumulation of coals in the Anambra Basin during the Upper Cretaceous are not well understood. According to Davies *et al*. (2006), coal seams are highly sensitive indicators of changes in accommodation and organic productivity. In this study, samples of coals from the Maastrichtian Mamu Formation were analysed in order to investigate the environmental conditions that permitted the accumulation and preservation of organic rich sediments and to assess the depositional environment of the coals.

Materials and Methods

Thirteen coal samples from eleven cores drilled by the Nigerian Coal Corporation (NCC) in five coal fields (Enugu, Ezimo, Ogboyoga, Orukpa and Okaba) in the Anambra Basin were sampled (Fig. 2). Major and trace elements were determined at Activation Laboratory, Ontario, Canada, using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Loss on ignition (LOI) measurements were performed using gravimetric analysis by weighing a 2 g sample before and after ignition at 1050°C. Limits of detectable measurement (LDM) for major elements are 0.01% for SiO_2, Al_2O_3, Fe_2O_3(T), P_2O_5, K_2O, Na_2O, CaO and MgO; 0.001% for TiO_2 and MnO and 0.01% for S. LDM for trace elements are 2 ppm for Te, Bi, Zr, Sr and Ba; 1 ppm for Zn, Ni, Mo, Li, Hg, Ga, Cu, Cr, Co, Be, Sc and Y; 5 ppm for W, Tl, Sb and V; 0.3 for Cd and Ag; 10 ppm for U; 3 ppm for Pb and As. Total organic carbon (TOC) analysis were conducted after treatment of the samples with concentrated hydrochloric acid to remove carbonates using a LECO C-230 analyzer at Humble Geochemical Services, Texas, USA. The enrichment factor (EF; Tribovillard *et al*., 2006) were calculated for trace elements (Ti, Fe, Zr, V, Cr, Co, Ni, Cu, Zn, Mo and U) using the composition of average upper continental crust (UCC; Rudnick and Gao, 2003) as reference: [$EF_{element}$= $(Element/Al)_{sample}/(Element/Al)_{UCC}$; Tribovillard *et al*., 2006]. Values of $EF_{element}$ greater than one (>1) and less than one (<1) indicate enrichment and depletion, respectively of element relative to its concentration in average upper continental crust. According to Liu *et al*. (2015), enrichments are due to hydrothermal or authigenic inputs of materials to the sediment. The degree of pyritization (DOP; Berner, 1970; Raiswell *et al*., 1988) was employed in this study in order to understand the paleoenvironmental conditions that prevailed during sediment accumulation. Degree of pyritization is defined as the ratio of pyritized iron to the total amount of reactive iron: (DOP = Fe_{pyrite}/Fe_{total}; Berner, 1970; Raiswell and Berner, 1986; Raiswell *et al*., 1988; Algeo and Maynard, 2008); where total iron (total-Fe) is the sum of pyrite iron (pyrite-Fe) plus HCl-soluble Fe. The values of DOP in this study were approximated using total degree of pyritization (DOP_T) which is defined as the ratio of pyrite-Fe (based on total sulphur) to total-Fe (DOP_T; Algeo and Maynard, 2008). DOP_T can be used in place of true DOP, if pyrite sulphur composes the bulk of total sulphur and reactive iron composes the bulk of total iron (Algeo and Maynard, 2008).

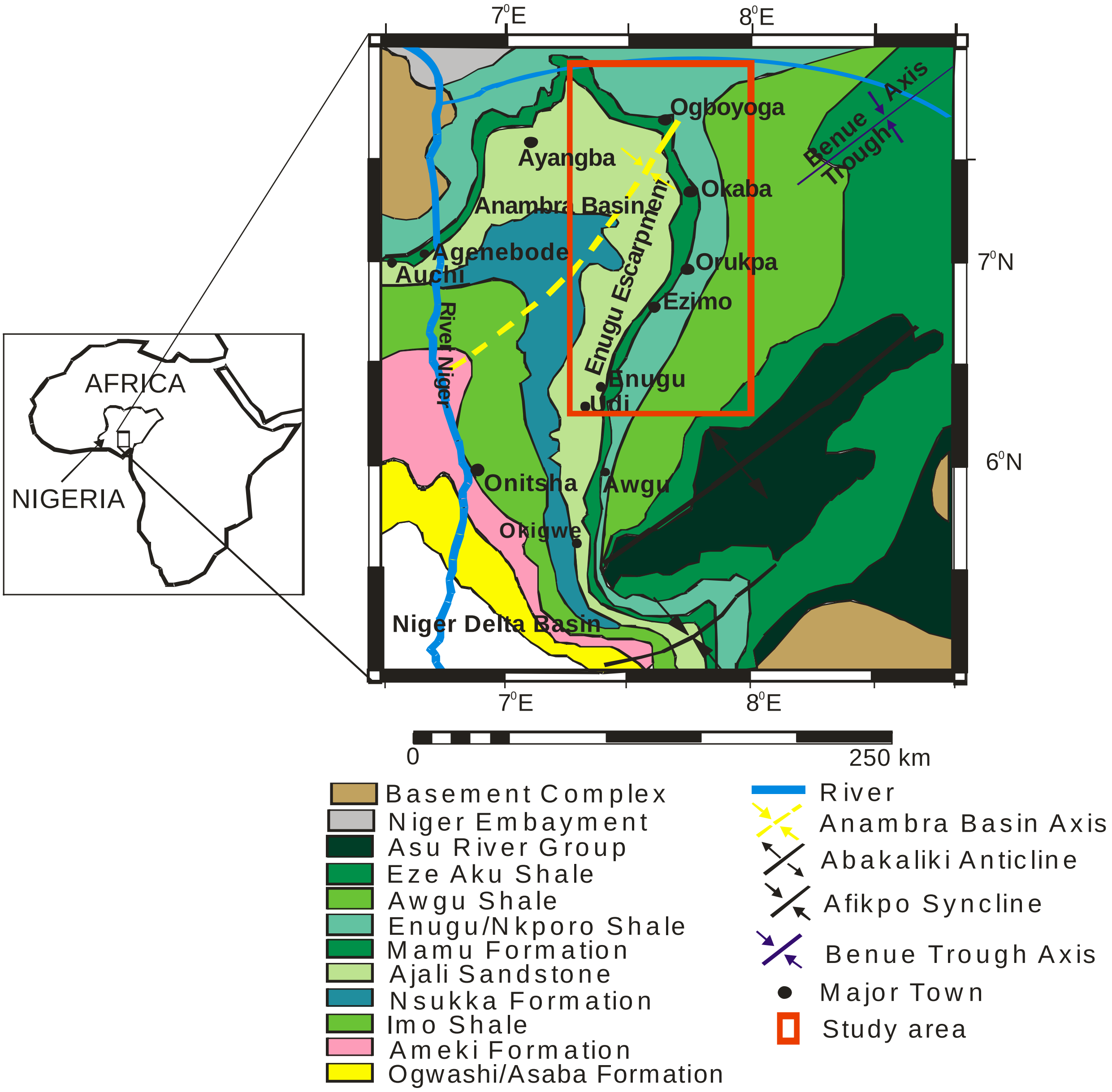


Fig. 1: Map of Nigeria showing the location of the study area

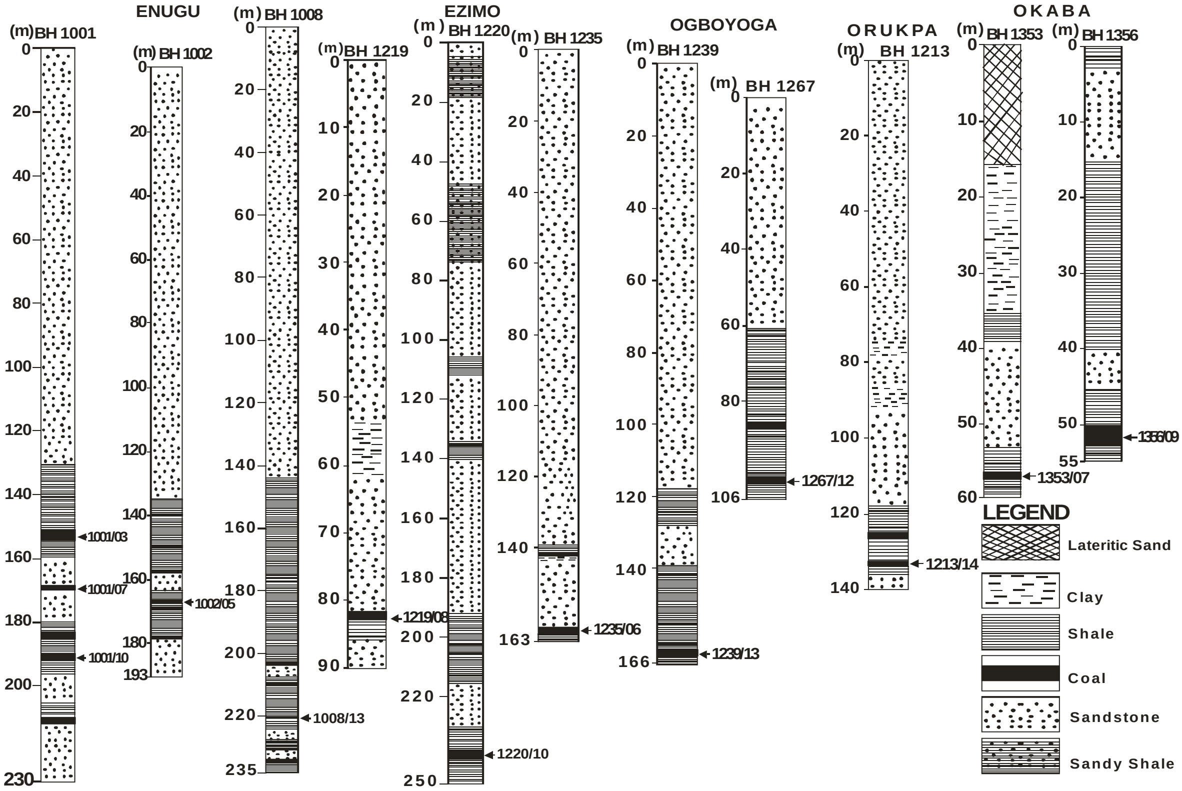


Fig. 2: Lithologic profiles of sampled boreholes in the study area

Results and Discussion

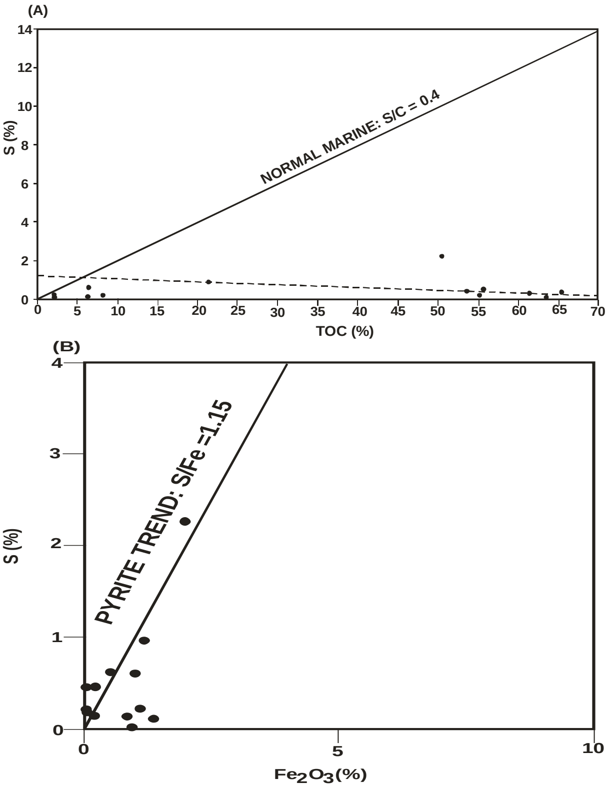
Geochemistry

Major elements, LOI, TOC and sulphur contents for the studied coal samples from the Mamu Formation are listed in Table 1. The results of the chemical analysis revealed that SiO_2 (1.02-52.77 %), Al_2O_3 (0.66-20.69%), Fe_2O_3(T) (0.04-2.01%), TiO_2 (0.01-2.14%) and K_2O (0.01-1.36%) were the dominant oxides in all the coal samples (Table 1). The contents of MnO, MgO, CaO, Na_2O and P_2O_5 are all <1.0%. The sulphur content of the coal is low (0.09-0.97%) for all the samples except sample 1267/12 (2.29%; Table 1). The TOC content of the coal samples range from 2.33 to 65.19% averaging 34.73% (Table 1). The most abundant trace elements in the coal samples are Ba (mean~207 ppm), Zr (157 ppm), Cr (45 ppm), V (42 ppm), Sr (34 ppm), Zn (32 ppm), Ni (17 ppm), Cu (16 ppm), Pb (15 ppm) and Y (14 ppm). Scandium, Be, Ag, As, B, Cd, Co, Ga, Hg, Mo, Sb, and Te) have average values between 0.4 and 9 ppm while Bi, Tl, U and W showed values below the detection limit (Table 2). These concentration values are generally lower than the average values of Post Archean Australian Shale (PAAS; Taylor and McLennan, 1985) and Upper Continental Crust (UCC; Rudnick and Gao, 2003).

Total organic carbon-sulphur-iron relationships

The TOC-S-Fe_2O_3 distributions for all strata are dominated by organic carbon contribution (Table 1). The dominance of organic carbon is prominent in the coal strata where Fe_2O_3 and S values are very low (Figs. 3a and b; Table 1). Leventhal (1979) and Berner and Raiswell (1983) suggested that the amount of reduced sulphur in sediment is linked with the organic carbon content. They concluded that with increasing amounts of organic carbon, a larger amount of organic matter is metabolizable and more sulfide is produced.

On a sulphur versus TOC diagram (Fig. 3a), all samples plot below the normal marine line. The coal samples show a variable distribution and no covariance of TOC and sulphur was observed in the samples. The TOC-Sulphur plot shows no correlation and a line fit through the data produces a positive intercept at 1.4 (Fig. 3a). This result is similar and comparable with those of Rimmer (2004) and Rimmer *et al.* (2004). The lack of correlation between organic carbon (TOC) and sulphur (*r*=0.194) is an indication that sulphur is present not only in sulphide form but also as organic and sulphate sulphur (Ogala *et al*., 2010).



Figs. 3: Plots of (a) organic carbon versus sulphur and (b) Fe_2O_3versus sulphur. Solid line shows typical S/C and S/Fe ratios for normal marine sediments (Dean and Arthur, 1989)

The relationships between sulphur and Fe_2O_3 are shown in Figure 3b. A positive correlation between S and Fe_2O_3 (r=0.608) was observed in the studied coal samples. The positive correlation between S and Fe_2O_3 concentrations in the samples strongly suggests that authigenic iron enrichment was linked to pyrite formation. Saez *et al*. (2011) observed that in normal marine environments, the presence of non-sulfide iron can reflect the existence of non-reactive Fe-bearing minerals and low availability of reduced sulphur during sedimentation and diagenesis. They concluded that such low sulphur availability may inhibit the consumption of all available Fe for pyrite formation. On the S versus Fe_2O_3 diagram (Fig. 3b), six samples plot below the pyrite line (S/Fe = 1.15; Fig. 3b), indicating that a significant portion of iron is associated with non pyrite (Johnson *et al*., 2010); while the other seven samples follow the trend of data for pyrite line proposed by Dean and Arthur (1989).

Ternary plot of TOC-S-Fe_2O_3 could be used to approximate the degree of pyritization (Dean and Arthur, 1989). On the TOC-S-Fe_2O_3 ternary diagram (Fig. 4), six samples plot within the normal marine (oxic trend; S/C=0.4) whereas the other seven samples tend to cluster at the TOC-pole and defines a trend that passes through the origin along the line having S/Fe ratio =1.15, suggesting that the Fe is reactive and fixed as pyritic sulphur (Rimmer *et al*., 2004) and also practically the entire carbon budget comes from organic sources (Saez *et al*., 2011). Iron and sulphur concentrations are extremely low (Fig. 4 and Table 1). The organic richness of the coal is due to high primary productivity and enhanced organic preservation. The DOP_T values of the studied coal ranges from 0.07-8.40 (Table 4), indicating variable conditions during accumulation of these coals.

Table 1: Major elements, LOI, TOC and sulfur content (concentrations in %) of coal samples from Mamu Formation

	SiO_2^a	$Al_2O_3^a$	$Fe_2O_3(T)^a$	MnO^a	MgO^a	CaO^a	Na_2O^a	K_2O^a	TiO_2^a	$P_2O_5^a$	LOI^b	Total	TOC^c	S^d
DL	**0.01**	**0.01**	**0.01**	**0.001**	**0.01**	**0.01**	**0.01**	**0.01**	**0.001**	**0.01**	**0.01**	**0.01**		**0.01**
1267/12	5.74	2.19	2.01	0.011	0.02	0.07	0.06	0.05	0.093	< 0.01	88.42	98.66	50.16	2.29
1239/13	4.72	1.79	0.91	0.024	0.03	0.11	0.05	< 0.01	0.141	< 0.01	90.9	98.65	2.40	0.09
1356/09	15.35	7.86	1.08	0.009	0.15	0.23	0.08	0.23	0.416	0.03	73.16	98.6	6.45	0.59
1353/07	3.28	1.61	0.49	0.009	0.03	0.09	0.09	0.03	0.087	< 0.01	93.87	99.59	55.55	0.62
1213/14	1.98	1.18	0.20	0.005	< 0.01	0.02	0.05	0.03	0.022	< 0.01	95.36	98.85	63.45	0.14
1235/06	1.02	0.66	0.04	< 0.001	< 0.01	< 0.01	0.06	< 0.01	0.011	< 0.01	97.3	99.01	65.19	0.19
1219/08	7.25	4.14	0.26	0.003	0.02	0.02	0.03	0.06	0.326	0.01	86.56	98.67	53.61	0.45
1220/10	49.65	20.69	1.36	0.009	0.16	0.02	0.1	0.45	1.919	0.10	24.59	99.04	6.11	0.10
1001/03	52.77	19.60	1.24	0.007	0.25	0.08	0.13	1.36	2.142	0.09	22.78	100.4	21.57	0.97
1001/07	48.59	16.02	0.85	0.007	0.14	0.03	0.07	0.56	1.376	0.05	31.1	98.79	8.17	0.16
1001/10	2.94	2.05	0.05	< 0.001	< 0.01	0.01	0.07	< 0.01	0.02	< 0.01	93.63	98.74	61.42	0.42
1008/13	3.34	1.40	0.05	< 0.001	< 0.01	< 0.01	0.07	0.07	0.047	< 0.01	93.7	98.70	55.07	0.19
1002/05	42.37	18.58	1.15	0.007	0.19	0.03	0.08	0.61	1.404	0.14	35.67	100.20	2.33	0.15

DL: detection limit; ^{a}: concentrations determined by using FUS-ICP; ^{b}: concentrations determined by using Gravimetry; ^{c}:concentrations determined by using LECO TOC analyzer; ^{d}: concentrations determined by using TD-ICP

Table 2: Trace elements (in ppm) and sulphur (%) content of coal samples from the Mamu Formation

Element	D.L.	1267/12	1239/13	1356/09	1353/07	1213/14	1235/06	1219/08	1220/10	1001/03	1001/07	1001/10	1008/13	1002/05
Ba^a	**2**	161	227	255	147	20	< 2	64	452	388	218	12	12	733
Sr^a	**2**	15	19	46	15	4	< 2	15	66	83	54	3	2	130
Y^a	**1**	4	2	7	3	< 1	< 1	4	30	54	28	< 1	< 1	48
Sc^a	**1**	1	1	5	2	< 1	< 1	2	14	17	11	< 1	< 1	15
Zr^a	**2**	22	21	56	22	2	2	28	335	739	486	5	6	319
Be^a	**1**	1	2	2	< 1	2	< 1	3	2	4	3	< 1	< 1	5
V^a	**5**	14	10	49	17	< 5	< 5	27	99	138	89	< 5	< 5	96
Ag^d	**0.3**	< 0.3	< 0.3	0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.1	0.8	1.1	< 0.3	< 0.3	0.4
As^d	**3**	< 3	< 3	< 3	5	< 3	< 3	< 3	< 3	4	4	3	4	3
B^d	**1**	< 1	< 1	< 1	< 1	1	3	2	1	1	1	2	2	3
Bi^d	**2**	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Cd^d	**0.3**	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.3	< 0.3	0.6	0.5	0.4	< 0.3	< 0.3	0.5
Co^d	**1**	15	< 1	6	2	3	3	3	21	22	20	2	3	13
Cr^d	**1**	46	8	58	29	5	4	37	96	107	81	8	10	89
Cu^d	**1**	12	1	21	14	2	4	22	27	36	25	6	5	30
Ga^d	**1**	11	1	14	3	1	2	10	17	16	16	4	3	21
Hg^d	**1**	3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1	2	< 1	< 1	3
Mo^d	**1**	1	< 1	< 1	< 1	< 1	< 1	1	2	2	1	< 1	< 1	1
Ni^d	**1**	27	1	18	5	5	9	8	30	39	40	4	4	29
Pb^d	**3**	10	< 3	23	9	< 3	4	12	32	31	22	3	7	31
Sb^d	**5**	7	< 5	6	< 5	5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Te^d	**2**	< 2	< 2	< 2	< 2	< 2	< 2	< 2	2	4	3	< 2	< 2	< 2
Tl^d	**5**	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
U^d	**10**	< 10	< 10	< 10	< 10	< 10	< 10	< 10	10	< 10	< 10	< 10	< 10	< 10
W^d	**5**	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Zn^d	**1**	20	5	17	6	9	17	14	58	69	67	6	8	115

^{a}: concentrations determined by using FUS-ICP; ^{d}: concentrations determined by using TD-ICP

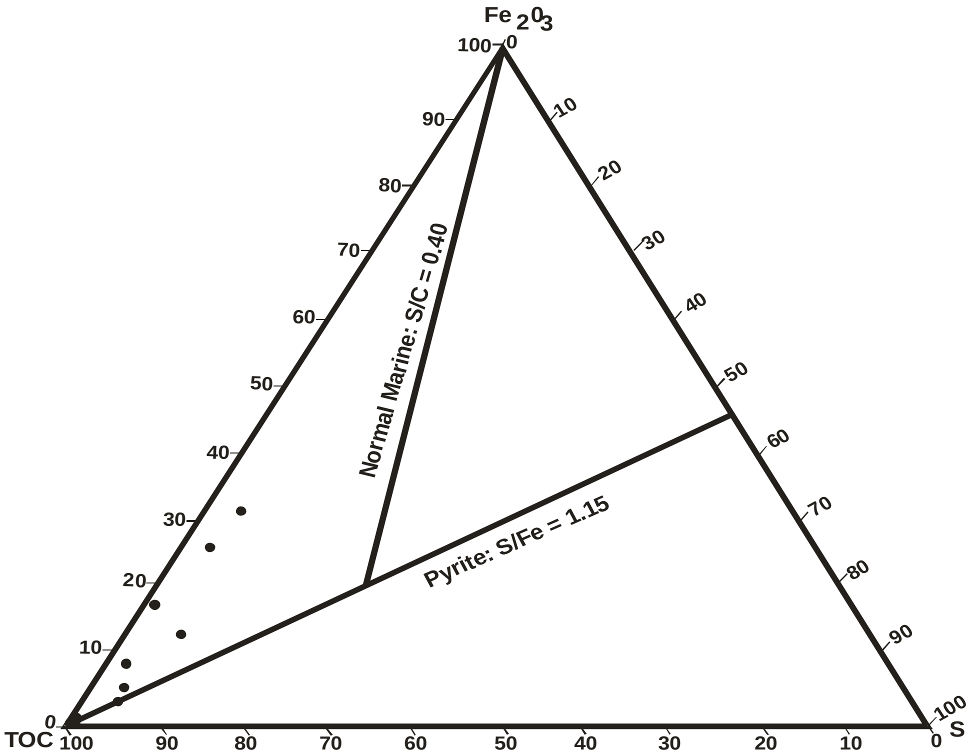


Fig. 4: Ternary diagram showing TOC-S-Fe_2O_3 relationships of coals from Mamu Formation

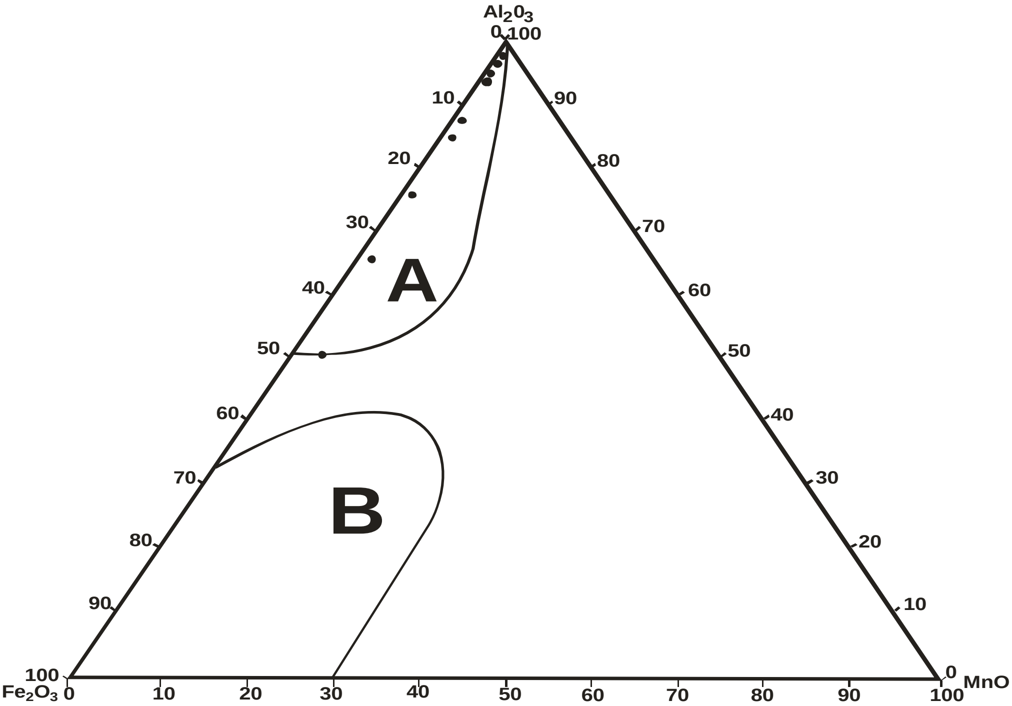


Fig. 5: Ternary plot of Al_2O_3-Fe_2O_3-MnO for coal samples from the Maastrichtian Mamu Formation. A = non-hydrothermal: B = hydrothermal (after Adachi *et al*., 1987)

Paleoredox depositional conditions

Trace element concentrations in coal have been used by different authors (Hart and Leahy, 1983; Swaine, 1983; Orem and Finkelman, 2003) as indicators of depositional environments. Chou (1984) and Goodarzi (1987, 1988) studied the geochemistry, concentration and elemental distribution in coal seams and cited elements such as Mo, Mg, B, Cl, Br, Na, Y and U as indicators of marine influence.

Redox-sensitive elements Mo, U, V, Cr, Fe, Mn, Ni, Co, Ba, Pb, Cd, Zn, Cu and their ratios have been used to assess paleoredox depositional conditions in sedimentary rocks (Algeo and Maynard, 2004, Rimmer *et al*., 2004; Tribovillard *et al*., 2006; Saez *et al*., 2011). In this study, V/(V+Ni), V/Cr, Ni/Co, V/Ni, Cu/Zn, TOC-S-Fe_2O_3 relationships, DOP_T and Fe_2O_3/Al_2O_3 ratios were used to evaluate the paleoredox conditions of depositional environments during sediment accumulation. According to Jones and Manning (1994), Ni/Co ratios < 5 and V/Cr ratios < 2 suggest oxic conditions; 5-7 and 2-4.25 (dysoxic conditions) and > 7 and > 4.25 (suboxic to anoxic conditions) respectively. The Ni/Co and V/Cr ratios of the studied samples ranges from 1.01-3.0 and 0.3-1.29 respectively (Table 5), indicating mainly oxic depositional environment. Hatch and Leventhal (1992) compared V/(V+Ni) ratios to geochemical indices and DOP_T, and proposed V/(V+Ni) ratios > 0.84 for euxinic conditions, 0.54 – 0.82 (anoxic waters) and 0.46 – 0.60 (dysoxic conditions). Therefore, V/(V+Ni) can be related to redox conditions in source rocks depositional environment (Moldowan*et al*., 1986; Hatch and Leventhal, 1992; Killops and Killops 2005; Peters *et al*., 2005). Low V/(V+Ni) porphyrin ratios in marine Toarcian rocks reflects oxic-suboxic conditions, while high ratios reflect anoxic sedimentation (Moldowan et al., 1986; Killops and Killops 2005).

The concentrations of vanadium in the coals of the Mamu Formation ranges from < 5 to 138 ppm (mean~41.61 ppm) as shown in Table 2. The low vanadium content of the coal suggests a low mature and marine/terrestrial sourced coal (Adedosu *et al*., 2007). Low V/Ni ratios (< 0.5) are expected for petroleum derived from marine organic matter, with high to moderate sulphur content, while V/Ni ratios (1-10) are expected from petroleum derived from lacustrine and terrestrial organic matter (Barwise, 1990). The value of V/Ni ratio of the studied coal ranges from 0.52 to 10.00 (Table 3). The source rock depositional environment determines the proportionality of vanadium to nickel. The closeness of chromium (mean~44.46 ppm) and nickel (mean~16.85 ppm) contents as well as V/Ni ratios (0.52-10; Table 3) for the coal samples suggest the same depositional environment. Also, plots of V/Cr and Ni/Co ratios (Table 3 and Fig. 6a; Jones and Manning, 1994) indicate predominantly oxic conditions during sediment accumulation. Based on Hatch and Leventhal (1992) published thresholds, the V/(V+Ni) ratios for the studied samples (Table 3; Fig. 6b) indicate a relatively wide range of conditions, from oxic, to anoxic, to possibly euxinic. However, V/(V+Ni) ratios predict lower oxygen bottom-water conditions (anoxic) than either Ni/Co or V/Cr (Peters *et al*., 2005). The V/(V+Ni) ratio can be linked to redox condition in source rock and low ratios reflect oxicity while high ratios (> 0.9) reflect anoxic condition in the depositional environment of coal (Peters *et al*., 2005). The low V/(V+Ni) ratio (0.34-0.91; Table 3) shows that the coal samples are deposited under oxic condition. This is typical of coal depositional environment and in agreement with earlier work done by Akande *et al*. (1992).

The degree of pyritization (DOP) and the ratios of Fe_2O_3/Al_2O_3 are good indicators of paleoredox conditions (Raiswell *et al*., 1988; Rimmer *et al*., 2004; Algeo and Maynard, 2004; Lyons and Severmann, 2006). According to Raiswell *et al*. (1988), DOP values are typically low for oxic depositional environments. Rimmer *et al*. (2004) suggested that DOP values < 0.42 indicate aerobic (normal marine) conditions while values > 0.75 point to conditions with absence of oxygen (anoxic) and presence of H_2S (euxinic conditions). They also observed that DOP values between 0.42 and 0.75 suggest dysoxic conditions (previously referred to as restricted) but Raiswell *et al*. (1988) previously referred to conditions linked with DOP values greater than 0.75 as inhospitable. Hatch and Leventhal (1992) noted that DOP values between 0.67 and 0.75 indicate a less strongly stratified water column while values > 0.75 indicate a strongly stratified anoxic water column. Lyons and Severmann (2006) suggested that DOP values < 0.2-0.3 and Fe_2O_3/Al_2O_3 ratios < 0.5 is indicative of oxic to suboxic conditions while DOP values > 0.6 and Fe_2O_3/Al_2O_3 ratios > 0.5 suggest euxinic conditions. Of the thirteen coal samples studied, four samples (1239/13, 1220/10, 1001/07 and 1002/05) had DOP_T values < 0.3, two samples (1356/09 and 1213/14) between 0.42 and 0.75, and seven samples (1267/12, 1353/07, 1235/06, 1219/08, 1001/03, 1001/10 and 1008/13) > 0.75, respectively (Table 3), which suggests deposition under variable conditions ranging from oxic, to dysoxic and euxinic depositional environments. The high DOP_T values and the corresponding high TOC contents of the coal is indicative of an iron limited environment (Raiswell and Berner, 1985), and also the main sulphur sink is organic matter rather than pyrite (Bein *et al*., 1990). This assertion is supported by the positive correlation between Fe_2O_3 and S (*r*=0.608). Majority of the studied coal samples have Fe_2O_3/Al_2O_3 ratios between 0.4 and 0.5 with exception of two samples (1239/13 and 1267/12) having Fe_2O_3/Al_2O_3 ratios > 0.5 (Table 3), suggesting dominantly aerobic (oxic) conditions for these coals (Algeo, 2004; Lyons and Severmann, 2006; Algeo and Maynard, 2008).

Berner and Raiswell (1983) and Rimmer *et al*. (2004) used TOC-S relationships to differentiate between normal marine from euxinic depositional environments during organic matter accumulation. No relationship was observed in the TOC versus S plots (Fig. 3a). The lack of correlation between TOC and S (*r*=0.194) and the positive intercept at 1.4 on the TOC versus S plot (Fig. 3a) is indicative of accumulation under anoxic conditions. This result is in agreement with those of Rimmer (2004) and Rimmer *et al*. (2004). This interpretation is also supported by TOC-S-Fe_2O_3 (Fig. 4) associations which suggest variable conditions ranging from oxic to dysoxic and anoxic depositional environments during coal accumulation.

Hallberg (1976) proposed that Cu/Zn ratios reflects redox conditions. High Cu/Zn ratios suggest reducing depositional conditions whereas low Cu/Zn ratios point to oxidising conditions (Hallberg, 1976). The coal samples had Cu/Zn ratios (0.20-2.23; Table 3), indicating more oxidising conditions during sediment accumulation.

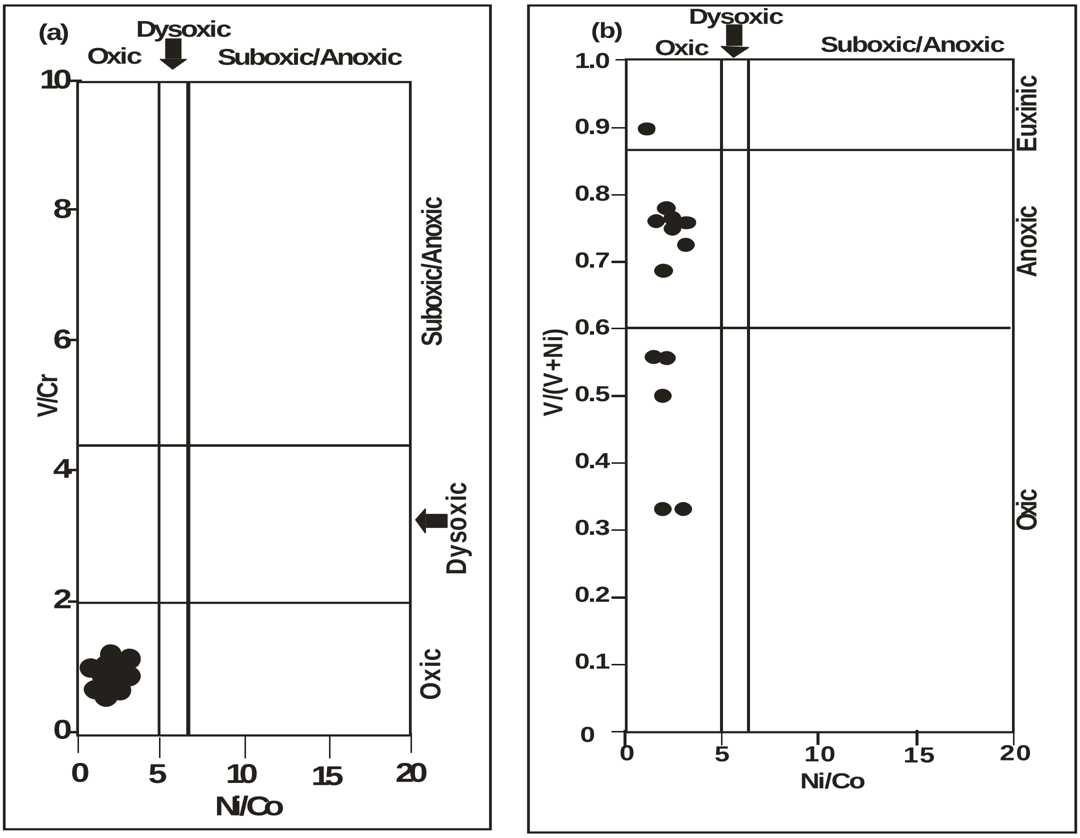
The enrichment factors (EFs) for the trace elements analyzed in the coal samples are listed in Table 4. Among the trace metals, Mo shows the greatest enrichment ($EF_{\mathbf{Mo}}$ mean~2.36; range 0.75-6.39) and Fe the smallest enrichment ($EF_{\mathbf{Fe}}$ mean~0.63; range 0.11-2.8; Table 4). In all the samples, most trace elements are equal to or depleted in relation to the average upper continental crust (UCC; Taylor and McLennan, 1985; Rudnick and Gao, 2003). Despite the relative enrichment, the concentration of Mo in the coal samples are extremely low (<1-2 ppm; Table 2) indicating that conditions were not strongly anoxic (Rimmer et *al*., 2004; Von Mann *et al*., 2006). According to Tribovillard *et al*. (2006), molybdenum and uranium shows strong authigenic enrichment under reducing depositional conditions. As a result, high U/Mo ratios greater than 2 are indicative of suboxic bottom water conditions (Liu *et al*., 2015). The concentrations of uranium in the studied samples are below detection limit in all samples except for one sample (1220/10; U=10) with U/Mo ratio of 5. Furthermore, it is obvious that depositional conditions changed during accumulation of these coals, the less-organic-rich coal beds (1239/13,1220/10, 1001/07 and 1002/05) were probably deposited under aerobic (oxic) conditions while the high-organic-rich coal strata (1267/12, 1356/09, 1353/07, 1213/14,1235/06, 1219/08, 1001/03, 1001/10, 1008/13) were deposited in dysoxic-anoxic environment. The enrichments of uranium (EF_U=2.86), vanadium (EF_V=1.02-1.68) and molybdenum (EF_{MO}=1.35-6.39) together with enrichments in nickel (EF_{Ni}=1.02-4.47) and copper (EF_{Cu}=1.01-4.79) suggests that anoxia is accompanied by a high organic flux. Also the enrichments of iron in samples (1267/12 and 1239/13; Table 4) is indicative of anoxic conditions during the precipitation as pyrite (Algeo and Maynard, 2008).

Table 3: Geochemical indices applied to evaluate the coal samples

Parameter	1267/12	1239/13	1356/09	1353/07	1213/14	1235/06	1219/08	1220/10	1001/03	1001/07	1001/10	1008/13	1002/05
TiO_2/Al_2O_3	0.04	0.08	0.05	0.05	0.02	0.02	0.08	0.09	0.11	0.09	0.01	0.03	0.08
Al_2O_3/TiO_2	23.55	12.7	18.89	18.51	53.64	60.00	12.70	10.78	9.15	11.64	102.5	29.79	13.23
K_2O/Al_2O_3	0.02		0.03	0.02	0.03		0.02	0.02	0.07	0.04		0.05	0.03
SiO_2/Al_2O_3	2.62	2.64	1.95	2.04	1.68	1.55	1.75	2.40	2.69	3.03	1.43	2.39	2.28
Fe_2O_3/Al_2O_3	0.92	0.51	0.14	0.30	0.17	0.06	0.06	0.07	0.06	0.05	0.02	0.04	0.06
Fe_2O_3/TiO_2	21.61	6.45	2.60	5.63	9.09	3.64	0.8	0.71	0.58	0.62	2.5	1.06	0.82
$Al_2O_3/(Al_2O_3+Fe_2O_3)$	3.01	1.91	2.08	1.49	1.20	1.04	1.26	2.36	2.24	1.85	1.05	1.05	2.15
Zr/Al_2O_3 (10^{-3})	1.01	1.17	0.71	1.37	0.17	0.30	0.68	1.62	3.77	3.03	0.24	0.43	1.72
TOC/P_2O_5			215				5361	61	240	163			16.64
S/TOC	0.05	0.04	0.09	0.01	0.002	0.003	0.008	0.02	0.05	0.02	0.007	0.004	0.06
Cu/Zn	0.60	0.20	1.24	2.33	0.22	0.24	1.57	0.47	0.52	0.37	1.00	0.63	0.26
V/Ni	0.52	10.00	2.72	3.40	0.998	0.55	3.38	3.30	3.54	2.23	1.25	1.25	3.31
Ni/Co	1.80	1.01	3.00	2.50	1.67	3.00	2.67	1.43	1.77	2.00	2.00	1.33	2.23
V/Cr	0.30	1.25	0.85	0.59	1.00	1.25	0.73	1.03	1.29	1.10	0.62	0.50	1.08
V/(V+Ni)	0.34	0.91	0.73	0.77	0.50	0.36	0.77	0.77	0.78	0.69	0.56	0.56	0.77
DOP_T	1.14	0.10	0.55	1.27	0.70	4.75	1.73	0.07	0.78	0.19	8.40	3.80	0.13

Table 4: Enrichment factors of coal samples from the Mamu Formation

Sample number	EF_{Ti}	EF_{Fe}	EF_{Zr}	EF_V	EF_{Cr}	EF_{Co}	EF_{Ni}	EF_{Cu}	EF_{Zn}	EF_{Mo}	EF_U
1267/12	1.02	2.80	0.80	1.02	3.52	6.23	4.04	3.01	2.1	6.39	
1239/13	1.90	1.55	0.94	0.89	0.75		0.18	0.31	0.64		
1356/09	1.25	0.42	0.57	0.99	1.24	0.69	0.75	1.47	0.5		
1353/07	1.27	0.93	1.09	1.68	3.02	1.13	1.02	4.78	0.86		
1213/14	0.44	0.52	0.14		0.71	2.31	1.39	0.93	1.75		
1235/06	0.39	0.19	0.24		1.02	4.12	4.47	3.33	5.92		
1219/08	1.85	0.19	0.54	1.04	1.5	0.66	0.63	2.92	0.78	3.38	
1220/10	2.18	0.20	1.29	0.76	0.78	0.92	0.48	0.72	0.64	1.35	2.86
1001/03	2.57	0.19	3.01	1.12	0.91	1.02	0.65	1.01	0.81	1.43	
1001/07	2.02	0.16	2.42	0.88	0.85	1.13	0.82	0.86	0.96	0.87	
1001/10	0.23	0.75	0.20		0.65	0.88	0.64	1.61	0.67		
1008/13	0.79	0.11	0.34		1.2	1.94	0.94	1.96	1.31		
1002/05	1.78	0.19	1.37	0.82	0.8	0.63	0.51	0.89	1.42	0.75	



Figs. 6: Cross plots of (a) V/Cr versus Ni/Co and (b) V/(V+Ni) versus Ni/Co (Ranges forV/Cr and Ni/Co are from Jones and Manning (1994) while V/(V+Ni) are from Hatch and Leventhal (1992)

Role of clastic input

Elemental concentrations (Si, Ti, Al and K) and their ratios have been used as proxy for detrital influx (Nesbitt *et al*., 1980; Taylor and McLennan, 1985; Tribovillard *et al*., 1994; Cox *et al*., 1995; Caplan and Bustin, 1998). The high concentrations of SiO_2 (1.02-57.77%) and Al_2O_3 (0.66-20.69%) with SiO_2/Al_2O_3 ratio (1.43-3.03; Table 3) is indicative of high detrital quartz and clay mineral content in the coal samples. The positive correlation between SiO_2 and Al_2O_3 with MgO, Na_2O, K_2O, TiO_2, P_2O_5, Fe_2O_3, Ba, Sr, Y, Sc, Zr, Be, V, Ag, Cd, Co, Cr, Cu, Ga, Mo, Ni, Pb, Te and Zn, implies that these elements were derived from detrital sources. Various authors have used the ratio of TiO_2/Al_2O_3 as proxies for clastic influx and consequently rate of sedimentation (Caplan and Bustin, 1998), and also as an indicator of grain size and paleo-wind strength (Boyle, 1983; Rimmer *et al*., 2004). The TiO_2/Al_2O_3 ratios of the studied samples vary from 0.01 to 0.11 (Table 3), suggesting that clastic starvation contributed to the elevated organic carbon (TOC) concentrations and preservation (Rimmer *et al*., 2004). This trend is observed in coal beds (1267/12, 1353/07, 1213/14, 1235/06, 1219/08, 1001/10 and 1008/13) with very high organic carbon while other beds (1239/13, 1356/09, 1220/10, 1001/03, 1001/07 and 1002/05) with lower organic carbon contents display variable trend. The ratio of K_2O/Al_2O_3 can be used as a geochemical indicator for the study of sediments original composition and intensity of chemical weathering (Cox *et al*., 1995). The K_2O/Al_2O_3 ratios of alkali feldspar varies from 0.4 to 1, illite (≈0.3) and clay minerals nearly zero (Cox *et al*., 1995). K_2O/Al_2O_3 ratios > 0.5 point to the dominance of alkali feldspar and < 0.4 is indicative of minimal alkali feldspar in the sediment original composition. The K_2O/Al_2O_3 ratio in the studied sample varies from 0.02-0.07 (average = 0.03; Table 3), suggesting a minimal contribution of fine-grained K-feldspar during accumulation of the Mamu coals.

Calvert and Pedersen (2007) proposed Zr/Al ratios as proxy for aeolian inputs to marine sediments. According to Liu *et al*. (2015) zircon and aluminum are highly immobile in the burial environment and as such Zr/Al ratios are well preserved. The Zr/Al ratios of the studied samples range from $0.24\text{-}3.77\times10^{-3}$(mean~$1.17\times10^{-3}$; Table 3), suggesting a lack of aeolian input. The Zr/Al ratios of the coal strata are comparable to the upper continental crust values of 2.36 (UCC; McLennan, 2001) and Post-Archean Australian Shale of 2.1 (PASS; Nance and Taylor, 1976). The Al_2O_3/TiO_2 ratio is generally used to differentiate between mafic and felsic source rocks (Hayashi *et al*., 1997). Al_2O_3/TiO_2 ratios < 8 indicate mafic while > 21 point to felsic igneous rocks. The Al_2O_3/TiO_2 ratios for the studied coals vary from 9.15 to 102.5 (Table 3), inferring an intermediate and felsic source rocks.

Hydrothermal influences on the Mamu Formation

According to Hamade *et al*. (2003), three sources (detrital, biogenic and hydrothermal) are responsible for the presence of silica in marine and sedimentary rocks. These sources can be differentiated by geochemical indices. Liu *et al*. (2015) suggested that high enrichment of iron and manganese in cherts are linked to a hydrothermal source while enrichment of aluminum and titanium is associated with detrital source. Bostrom *et al*. (1973) reported that Al/(Al+Fe) ratio less than 0.4 and Fe/Ti ratio greater than 20 suggest hydrothermal source while Al/(Al+Fe) ratio greater than 0.4 and Fe/Ti ratio less than 20 point to a terrestrial source. These ratios can be supported by using a ternary diagram of Fe-Al-Mn (Adachi *et al*., 1986). The studied coal samples from the Mamu Formation had Al/(Al+Fe) ratio greater than 0.4 in all samples while Fe/Ti ratio are less than 20 except for one sample (1267/12; Table 3). These values suggest that the coals are derived mainly from detrital source. Ternary diagram of Fe-Al-Mn (Fig. 5) shows that all samples plot within the region "A", inferring a detrital input during coal accumulation.

Paleoproductivity influences in the Mamu Formation

Holland (1978) and Rimmer *et al*., (2004) reported that the presence of nutrients such as nitrogen (N) and phosphorus (P_2O_5) in surface waters controls primary productivity on organic matter accumulation. Rodriguez and Philp (2012) suggested that organic matter enrichment in marine sediments are influenced by productivity. The P_2O_5 contents of the coal ranges from 0.01-0.14 (Table 1). The TOC/P_2O_5 ratios for the studied samples vary from 16.64 to 5361 averaging 1009 (Table 3). These ratios (TOC/P_2O_5) are comparable with those reported by Rimmer *et al*. (2004). The TOC/P_2O_5 ratios for data obtained by ICP-OES (Table 3) versus XRF technique of Rimmer *et al*. (2004), show reasonably good agreement. The TOC/P_2O_5 ratios for the coal samples from the Mamu Formation are higher than typical C/P ratios for marine phytoplankton (106C:1P; Redfield, 1958) with average TOC/ P_2O_5 ratios of 1009 (Table 3). These ratios are similar with those reported originally for anoxic laminated black shales from the Illinois Basin (Ingall *et al*., 1993). However, two samples (1220/10 and 1002/05) with lower total organic carbon intervals exhibit much lower TOC/P_2O_5 ratios (<100; Table 3), which is similar with average values reported originally for toxic bioturbated shales (Ingall *et al*., 1993). Nickel, copper, zinc and barium are good elemental paleoproductivity proxies and can be used to establish bottom water oxygenation and organic carbon sinking flux (Piper and Perkins, 2004; Tribovillard *et al*., 2006; Griffith and Paytan, 2012). The negative correlation of TOC with Ba (r=-0.792), Zn (r=-0.628), Ni (r=-0.578) and Cu (r=-0.578) suggests that these elements (Ba, Zn, Ni and Cu) resides in organic matter and also indicate that primary productivity rates were an important influence on organic carbon enrichment of the coals (Liu *et al*., 2015).

Conclusion

The geochemistry of organic rich coal beds from eleven boreholes penetrating the Maastrichtian Mamu Formation were investigated in order to evaluate the paleoredox depositional conditions. The elemental composition of the coal shows that SiO_2, Al_2O_3 and Fe_2O_3(T) accounts for over 75% composition. The high SiO_2/Al_2O_3 ratios and the relatively low TiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios are indicative of restricted detrital input during accumulation of these coals. Geochemical ratios, including Fe_2O_3/Al_2O_3, Ni/Co, V/Cr and V/ (V+Ni), also indicate variable paleoredox conditions for the studied coals, ranging from oxic, anoxic, to possibly euxinic.

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