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Abstract: Eighteen tar sand samples were collected from a vast bituminous sand deposit in Dahomey Basin, Southwestern Nigeria. The tar sand samples were heated at 475°C for 24 h producing 18 ash samples. The chemical compositions (major, trace and rare earth elements) of the ash products were determined using FUS-ICP (Fusion-Inductively Coupled Plasma) and FUS-MS (Fusion-Mass Spectrometry) analytical techniques. SiO₂, Al₂O₃ and Fe₂O₃ are the dominant oxides in the ash samples. The high concentrations of SiO₂ (1.69-89.21%), Al₂O₃ (0.22-18.87%) and Fe₂O₃ (0.06-6.81%) was due to quartz, feldspars and pyrite which constitute the main mineral phases of the ash bituminous sediment samples. Zr, V, Zn, Ba and Cr were found to be the most abundant trace elements with mean values of 289.3, 32.94, 31.39, 30.22 and 28.28 ppm, respectively. Furthermore, the correlation matrix result including factor analysis showed that the great majority of elements detected have a common source and also the chemistry of the bituminous sediments was influenced by the associated aluminosilicate minerals that constitute the matrix.

Keywords: Bituminous sediments, ashing products, geochemistry, Afowo formation, Dahomey Basin

Introduction

The Turonian-Maastrichtian Afowo Formation (Omatsola and Adegoke, 1981) is an extensive stratigraphic unit in the surface/subsurface of much of the Dahomey Basin. The formation consists of medium to coarse grained sandstones, some of which are tar-bearing, interbedded with organic rich shale beds, siltstones and claystones. Vast extensive deposit of bituminous sand occur in the Eastern Dahomey Basin along an East-West belt, stretching over 120 km long and 5-8 km wide across Edo, Ondo, Ogun and parts of Lagos States in southwestern Nigeria (Fig. 1; Adebiyi *et al.*, 2005; Adegoke, 1980; Enu, 1985). Proven bitumen reserves in Nigeria is estimated at 41 billion barrels of oil (Enu, 1985).

Bituminous sands (tar sands) are loose sands or partially consolidated sandstones containing a naturally occurring mixture of sand, clay, water and bitumen. Bitumen deposits occur in many countries, such as Canada, Venezuela, Kazakhstan, Russia and Nigeria. Proven worldwide reserve of natural bitumen are estimated at 249.67 Gbbl, of which 176.8 Gbbl (70.8%) are in Alberta, Canada (Smardych and Kueneman, 2010).

Several aspects of bituminous sand deposits in Nigeria have been investigated by previous workers. Adegoke (1980) and Enu (1985) studied and reported the occurrence, distribution, textural characteristics and reserve estimates of bituminous sand deposits in southwestern Nigeria. Ekweozor and Nwachukwu (1989) investigated the origin of tar sands of southwestern Nigeria. Adebiyi *et al.* (2005) studied the trace element and physico-chemical characteristics of the sand and water fractions of Nigerian bituminous sands. Olabanji *et al.* (1994), Obiajunwa and Nwachukwu (2000) and Adebiyi *et al.* (2008) employed different analytical techniques (Proton Induced Gamma-ray Emission, Proton Induced X-ray Emission and Total Reflection X-ray Fluorescence) to determine the elemental compositions (major, minor and trace elements) of Nigerian tar sands. Fasasi *et al.* (2003) and Akimmosin *et al.* (2009, 2016) used Gamma-ray spectrometric analysis and Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) to examine the presence and level of natural radioactivity of selected radionuclides in bituminous sand deposits in southwestern Nigeria.

Tar sands are currently exploited in Nigeria as sources of asphaltic materials for road surfacing and

construction works (Olabanji *et al.*, 1994, Obiajunwa and Nwachukwu, 2000). Furthermore, the prospects of Nigerian tar sands as a potential alternative energy sources cannot be over emphasized. The Nigerian tar sands can be used in the petrochemical industry and also as refinery feedstock for the production of lube oil. Tar sands are a major source of unconventional oil and their extraction contributes elements toxic at low concentration. The extraction of tar sands can affect the land, water resources, fragment wildlife habitat, increase the risk of soil erosion and the air due to the release of carbon dioxide and other emissions. According to Obiajunwa and Nwachukwu (2000) and Smardych and Kueneman (2010), trace elements (e.g., vanadium, lead, nickel, mercury, cobalt, iron, manganese, copper, selenium, arsenic, cadmium and chromium) are naturally present in tar sands and may be concentrated by the extraction process. The concentration of these heavy metals in the tar sands may pose environmental pollution problems (Obiajunwa and Nwachukwu, 2000).

None of the works so far carried out by previous workers has addressed the elemental composition of ash products of Nigerian bituminous sediments (tar sands). This study therefore concerns the investigation of the chemical composition (major, trace and rare earth elements) of the ashing products of the Nigerian tar sands using FUS-ICP (Fusion-Inductively Coupled Plasma) and FUS-MS (Fusion-Mass Spectrometry) analytical techniques.

Geology of Study area

The study area (Afowo Formation) is located in the eastern Dahomey Basin, southwestern Nigeria within latitudes 6° 33' and 6° 52'N, and longitudes 3° 58' to 5° 15'E (Fig. 1). Regionally, the Afowo Formation is underlain by the Ise Formation and overlain by the Araromi Formation (Fig. 1). The Dahomey Basin is the eastern part of the sedimentary basin that extends for about 450 km from the Volta Delta in Ghana to the Okitipupa Ridge in Nigeria (Omatsola and Adegoke, 1981). The Okitipupa Ridge is a subsurface high which separates the Dahomey Basin from the sedimentary sequence of the Niger Delta (Fig. 1). The geology and stratigraphy of the Dahomey Basin have been discussed by different authors (Jones and Hockey, 1964; Reament, 1965; Fayose, 1970; Murat, 1972; Omatsola and Adegoke, 1981;

Billman, 1982). According to Burke et al. (1971) and Nwachukwu (1972), the origin and tectonic evolution of the Dahomey Basin is associated with the opening of the South Atlantic Ocean consequent upon the break-up of the South American plate from the African continent during Early Cretaceous time. The rocks in the Dahomey Basin range from late Cretaceous to Recent in Age. The stratigraphic successions in the eastern Dahomey Basin from oldest (bottom) to youngest (top) includes: Ise Formation

((Neocomian, probably Valanginian-Barremian), Afowo Formation (Turonian-Maastrichtian), Araromi Formation (Maastrichtian-Paleocene), Ewekoro Formation (Paleocene), Akinbo Formation (Paleocene-Eocene), Oshosun Formation (Eocene), Ilaro Formation (Eocene) and the Miocene-Recent Benin Formation previously known as "Coastal Plain Sands" (Fig. 1).

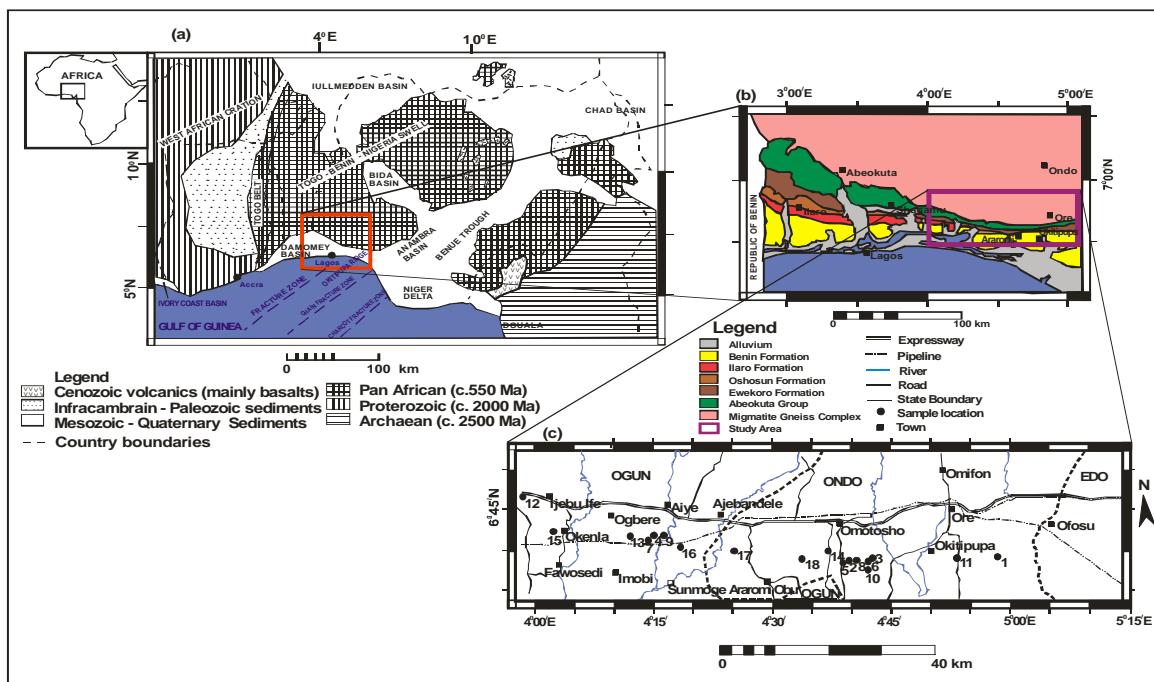


Fig. 1(a) Regional geological map of western Africa showing the location of the Dahomey Basin (modified after Wright *et al.*, 1985), (b) and (c) Geological map of Dahomey Basin showing sampling locations (modified after Billman, 1992).

Sampling and methods

Eighteen tar sand samples were heated at 475°C for 24 h producing 18 ash samples. The 18 ash samples produced were chemically analyzed for major, trace and rare earth elements using Fusion-Inductively Coupled Plasma (FUS-ICP) and Fusion-Mass Spectrometry (FUS-MS) analytical techniques (Adamidou *et al.*, 2007) at the Activation Laboratories, Ontario, Canada. Loss on ignition (LOI) was determined by gravimetric analyses at 1000°C.

The samples were ashed and then analyzed applying the technique described in detail by Adamidou *et al.* (2007). The samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt was immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30 min). The samples were analysed using a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP and a Perkin Elmer Scienx ELAN 6000. Calibration was performed and accuracy checked using USGS and CANMET certified reference materials.

Statistical analyses (Davis, 1986) was carried out using the IBM® SPSS® Statistics version 20. Samples with minimum values below detection limit (Bi and In) were excluded from further statistical treatment.

Results and Discussion

Chemical composition of ash

The chemical composition (major, trace and rare earth elements) of the ashing products of the bituminous sediment

samples are presented in Tables 1, 2 and 3. Silica (SiO_2), Al_2O_3 and Fe_2O_3 were the dominant oxides in all the samples analysed. The high concentrations of SiO_2 (1.69-89.21%), Al_2O_3 (0.22-18.87%) and Fe_2O_3 (0.06-6.81%) is due to quartz, feldspars and pyrite which constitute the main mineral phases of the bituminous sediment samples (Adamidou *et al.*, 2007). Loss on ignition display relatively high values ranging from 0.03-22.53% (Table 1) suggesting that the major elements are enriched in the ash samples. The concentrations of TiO_2 , K_2O , CaO , MgO , P_2O_5 , and MnO are all less than one percent (<1%). The major oxides are enriched in the ash samples (Table 1). Using the geochemical classification diagram (Fig. 2) proposed by Herron (1988), the studied samples are classified as Fe-shale (#2 and #6), Fe-sand (#1, #3, #4, #5, #8, #9, #10, #12, #13, #15, #16 and #18), litharenite (#7), sublitharenite (#14) and quartz arenite (#11 and #17). Table 4 compares the results of chemical composition of bituminous sand samples obtained in this study with those of previous workers in Nigeria (Adebisi *et al.*, 2008; Ipinmoroti and Aiyesanmi, 2001; Obiajuruwa and Nwachukwu, 2000; Olabanji *et al.*, 1994; Oluwole *et al.*, 1987) and Athabasca (Tissot and Welte, 1984; Jacob and Filby, 1982) while Table 5 presents the descriptive statistics (minimum, maximum, mean and standard deviation) of the bituminous sediment samples. However, the results obtained in this study using FUS-ICP and FUS-MS techniques are similar and also in close agreement with those of other workers on Nigerian and Athabasca tar sands (Table 5).

The most abundant trace element is Zr, with a mean value of 289.3 ppm. Vanadium, Zn, Ba and Cr follow with mean values of 32.94 ppm, 31.39 ppm, 30.22 ppm and 28.28 ppm,

respectively (Tables 2 and 5). The mean values of Sc, Be, Ga, As, Rb, Nb, Mo, Ag, Sn, Cs, Hf, Sr, Y, Co, Ta, W, Pb, Th and U range between 0.65 and 7.22 ppm. Nickel, Ge, Sb, Cu and Tl concentrations were below detection limits in some samples while Bi and In concentrations were below detection limits in all samples (Tables 2 and 5). The average mean values of the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) ranged from 0.30–32.11 ppm. These concentrations of major, trace and rare earth elements were generally lower than the average Upper Continental Crust (UCC) values (Taylor and McLennan, 1985, 1995).

The chondrite-normalized rare earth element (REE) abundances of the studied samples are shown in Fig. 3(a & b). The analyzed tar sand samples from Dahomey Basin show lower REE contents except for samples (#2, #6, #15, and #18) which displays relatively high REE content. The chondrite-normalized REE patterns of samples (#2, #6, #15, #17 and #18) are similar to those of typical Upper Continental Crust (Taylor and McLennan, 1985).

Table 1: Major elements (%) of the ash bituminous sediment samples from Dahomey Basin

Elements	SiO ₂ ^a	Al ₂ O ₃ ^a	Fe ₂ O ₃ (T) ^a	MnO ^a	MgO ^a	CaO ^a	Na ₂ O ^a	K ₂ O ^a	TiO ₂ ^a	P ₂ O ₅ ^a	Total	LOI ^b
DL	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01	0.01	
#1	18.27	0.67	0.51	0.01	0.04	0.14	0.03	0.07	0.085	0.03	19.86	1.62
#2	36.88	18.87	6.42	0.02	0.12	0.06	0.04	0.36	0.933	0.06	63.76	19.29
#3	66.5	2.55	2.77	0.01	0.04	0.08	0.02	0.05	0.317	0.06	72.39	0.73
#4	57.43	3.38	4.19	0.016	0.05	0.07	0.03	0.05	0.704	0.11	66.04	1.15
#5	26.52	1.75	0.49	0.005	0.03	0.06	0.02	0.06	0.247	0.03	29.22	1.36
#6	35.42	17.28	6.81	0.021	0.11	0.05	0.03	0.32	0.865	0.06	60.97	22.53
#7	1.69	0.22	0.06	0.002	0.03	0.06	< 0.01	0.05	0.039	0.02	2.17	
#8	58	2.29	0.85	0.006	0.03	0.04	0.03	0.04	0.329	0.02	61.62	0.74
#9	30.37	0.86	0.66	0.009	0.02	0.11	0.03	0.05	0.336	0.02	32.46	0.71
#10	14.08	1.47	0.66	0.003	0.02	0.03	0.02	0.09	0.132	0.01	16.52	2.08
#11	89.21	0.33	0.59	0.007	0.01	0.05	< 0.01	0.04	0.058	0.04	90.33	0.03
#12	81.09	2.34	1.51	0.005	0.01	0.02	0.03	0.03	0.173	0.02	85.23	1.89
#13	21.19	0.61	0.58	0.006	0.03	0.16	0.02	0.04	0.262	0.03	22.92	1.49
#14	80.33	2.63	0.54	0.004	0.02	0.02	0.02	0.14	0.19	0.01	83.9	0.37
#15	55.53	6.16	2.54	0.009	0.03	0.05	0.02	0.08	0.845	0.03	65.28	4.93
#16	81.99	2.41	1.8	0.009	0.02	0.02	0.02	0.03	0.406	0.01	86.72	0.48
#17	80.75	0.68	1.05	0.011	0.02	0.02	0.01	0.03	0.565	0.02	83.15	0.15
#18	58.24	4.4	1.85	0.011	0.04	0.04	< 0.01	0.07	0.717	0.05	65.42	2.73

^a: concentrations determined by using FUS-ICP; ^b: concentrations determined by using Gravimetry; **DL** = Detection limit

Table 2: Trace elements (ppm) of the ash bituminous sediment samples from Dahomey Basin

Elements	DL	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17	#18	
Sc ^a	1	< 1	14	3	5	1	15	< 1	2	2	< 1	< 1	2	< 1	2	7	2	2	5	
Be ^a	1	< 1	3	< 1	< 1	< 1	3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1	< 1	< 1	< 1	1	
V ^a	5	19	82	51	80	21	86	14	28	20	17	13	12	11	12	49	17	21	40	
Ba ^a	3	11	102	16	26	20	90	6	14	16	20	28	17	19	37	46	25	17	34	
Sr ^a	2	6	40	11	20	13	37	3	8	8	6	10	13	9	7	23	12	7	12	
Y ^a	2	3	25	18	12	11	25	< 2	12	8	5	12	19	6	14	28	12	17	26	
Zr ^a	4	88	198	347	666	274	155	34	316	234	126	82	122	440	223	533	276	646	448	
Cr ^c	20	< 20	80	50	140	< 20	80	< 20	20	< 20	< 20	< 20	< 20	50	< 20	< 20	40	< 20	< 20	30
Co ^c	1	2	13	2	2	1	15	2	1	2	1	< 1	2	2	1	8	3	2	6	
Ni ^c	20	< 20	30	< 20	< 20	< 20	30	30	< 20	< 20	< 20	< 20	< 20	20	< 20	< 20	< 20	< 20	< 20	
Cu ^c	10	< 10	20	< 10	< 10	< 10	20	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	
Zn ^c	30	< 30	50	< 30	30	< 30	50	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	
Ga ^c	1	1	24	5	7	3	24	< 1	5	2	2	< 1	5	2	4	11	4	3	7	
Ge ^c	1	< 1	1	< 1	< 1	< 1	1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1	< 1	< 1	< 1	1	
As ^c	5	< 5	< 5	< 5	6	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	
Rb ^c	2	3	16	< 2	3	3	15	< 2	< 2	< 2	3	< 2	< 2	< 2	4	3	< 2	< 2	< 2	
Nb ^c	1	2	18	7	10	5	17	2	6	4	3	< 1	2	3	5	9	4	7	7	
Mo ^c	2	< 2	4	2	3	< 2	4	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	
Ag ^c	0.5	< 0.5	0.6	0.9	2.7	1.1	0.6	1.2	0.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.7	0.7	2.1	1.2	
In ^c	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	
Sn ^c	1	< 1	3	1	1	3	3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1	< 1	< 1	< 1	1	
Sb ^c	0.5	< 0.5	< 0.5	0.6	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	
Cs ^c	0.5	< 0.5	2	< 0.5	< 0.5	0.5	1.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	
Hf ^c	0.2	2.1	4.5	7.7	15.8	6.7	4.3	0.8	7.6	5.8	3.1	1.9	3	9.1	4.9	11.6	6.1	14	10.5	
Ta ^c	0.1	0.2	1.4	1.4	1.5	0.5	1.3	< 0.1	0.9	0.5	0.3	0.1	0.2	0.6	0.8	1.1	0.5	0.8	1	
W ^c	1	< 1	2	< 1	< 1	1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	
Tl ^c	0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
Pb ^c	5	< 5	18	6	8	< 5	17	< 5	< 5	< 5	< 5	< 5	< 5	< 5	7	10	< 5	< 5	9	
Bi ^c	0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	
Th ^c	0.1	2	12.2	4.4	6.5	3.6	13.4	1.3	3.8	4.1	2.9	0.7	1.8	2.3	6.1	8.9	3.4	10.8	7.7	
U ^c	0.1	0.4	12.2	2.2	3.4	1.1	13.2	0.2	1.5	0.9	0.8	0.4	9.3	0.7	2	2.9	0.9	1.3	2.6	

DL: Detection Limit; ^a: concentrations determined by using FUS-ICP; ^c: concentrations determined by using FUS-MS

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Table 3: Concentrations of rare earth elements (ppm) of the ash bituminous sediment samples from Dahomey Basin

Elements	La ^c	Ce ^c	Pr ^c	Nd ^c	Sm ^c	Eu ^c	Gd ^c	Tb ^c	Dy ^c	Ho ^c	Er ^c	Tm ^c	Yb ^c	Lu ^c	Eu/Eu*
DL	0.1	0.1	0.05	0.1	0.1	0.05	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.04	
#1	4.9	9.5	1.03	3.3	0.6	0.08	0.5	< 0.1	0.5	0.1	0.3	0.05	0.3	0.05	0.43
#2	57.1	110	12.9	45.9	8.2	1.79	6.5	1	5.3	1	2.9	0.44	2.8	0.41	0.72
#3	17.3	33.1	3.7	12.7	2.5	0.41	1.7	0.3	1.8	0.4	1.1	0.19	1.3	0.17	0.57
#4	15.6	30.4	3.27	11.3	2	0.34	1.8	0.3	2	0.4	1.4	0.21	1.5	0.25	0.54
#5	10.3	19.9	2.13	7.1	1.2	0.18	1.2	0.2	1.6	0.4	1.2	0.19	1.3	0.21	0.45
#6	57.3	114	13.5	48.9	8.9	1.94	6.9	1.1	5.9	1.1	3.2	0.45	3	0.45	0.73
#7	11	19.4	1.96	6.3	0.9	0.22	0.6	< 0.1	0.4	< 0.1	0.2	< 0.05	0.1	< 0.04	0.86
#8	13.2	27.5	3.11	10.7	1.9	0.34	1.7	0.3	1.8	0.4	1.1	0.19	1.2	0.2	0.57
#9	10.9	22.9	2.54	9.1	1.6	0.21	1.3	0.2	1.2	0.3	0.8	0.12	0.8	0.12	0.43
#10	7.4	14.3	1.61	5.5	1	0.15	0.9	0.1	0.9	0.2	0.6	0.09	0.6	0.1	0.47
#11	5.7	11	1.1	3.3	0.7	0.1	0.4	< 0.1	0.2	< 0.1	< 0.1	< 0.05	0.1	< 0.04	0.53
#12	7.4	12.9	1.52	5.9	1.5	0.37	1.9	0.4	2.3	0.5	1.5	0.23	1.5	0.23	0.67
#13	5.1	10.3	1.15	4	0.7	0.1	0.6	0.1	0.8	0.2	0.5	0.08	0.6	0.11	0.46
#14	18.9	32.5	4.01	14.5	2.6	0.31	2.1	0.3	1.8	0.4	1	0.16	1	0.17	0.39
#15	33.8	68.3	8.13	29.3	5.4	1.1	4.7	0.7	4.4	0.9	2.5	0.37	2.3	0.37	0.65
#16	15.2	30	3.17	10.6	1.9	0.28	1.5	0.3	1.5	0.3	1	0.16	1.1	0.16	0.49
#17	27.3	58.3	6.6	23.2	3.7	0.35	2.5	0.4	2.1	0.5	1.5	0.22	1.4	0.22	0.33
#18	31.3	61.4	6.87	24.4	4.8	0.84	3.5	0.6	3.4	0.7	2	0.27	1.7	0.25	0.59

^c: concentrations determined by using FUS-MS; DL = Detection limit

Table 4: Comparison of elemental composition of the tar sands of Nigeria and Athabasca

This Study	Nigerian tar sands					Athabasca tar sands				
	Adebiyi <i>et al.</i> (2008)	Ipinmoroti and Aiyesammi (2001)	Obiajuwua and Nwachukwu (2000)	Olabanji <i>et al.</i> (1994)	Oluwole <i>et al.</i> (1987)	Tissot and Welte (1984)	Jacob and Filby (1982)			
[in %]										
SiO ₂	49.6383	-	-	14.13	8.81	-	-	-	-	-
Al ₂ O ₃	3.8278	-	-	10.68	-	-	-	-	-	-
Fe ₂ O ₃	1.8822	0.0237	0.0234	4.83	2.15	0.83	0.00542	0.42	-	-
MnO	0.0091	0.0212	-	0.0216	0.01217	0.00386	-	0.00694	-	-
MgO	0.0372	-	-	6.09	-	-	-	-	-	-
CaO	0.06	0.00315	0.0029	0.368	0.155	0.08	0.00211	0.05	-	-
Na ₂ O	0.0221	-	-	0.0174	-	-	-	-	-	-
K ₂ O	0.0889	0.0112	0.0101	0.656	0.15	0.26	0.00155	0.22	-	-
TiO ₂	0.40017	0.055	0.065	0.0545	0.137265	0.2066	-	0.25	-	-
P ₂ O ₅	0.035	-	-	0.233	-	-	-	-	-	-
LOI	3.46	-	-	-	-	-	-	-	-	-
S	-	-	-	6.12	1.32	2.2	-	4.64	-	-
[ppm]										
Sr	13.6111	-	-	200	-	-	-	-	-	-
Zr	289.333	-	-	70	-	-	-	-	-	-
Cr	28.2778	87.1	-	97	206.96	29.7	-	15.1	-	-
Ni	7.5889	23	21	-	41.775	<50	74.2	14.4	-	-
Cu	3.1022	98.1	<0.02	72	11.6	-	-	-	-	-
Pb	7.2161	9.29	-	69	97.35	-	-	-	-	-
Li	-	-	-	762	-	-	-	-	-	-
F	-	-	-	388	-	-	-	-	-	-
Sc	3.7194	-	-	-	-	-	-	-	-	-
Be	1.2144	-	-	-	-	-	-	-	-	-
V	32.9444	35.7	37	-	-	-	198	-	-	-
Ba	30.2222	-	-	-	-	-	-	-	-	-
Zn	31.3889	232	7	119	-	-	-	-	-	-
Ga	6.1656	-	-	23	-	-	-	-	-	-
Ge	0.9922	-	-	17	-	-	-	-	-	-
As	5.0461	60.2	-	-	-	-	-	-	-	-
Rb	3.8333	-	-	118	-	-	-	-	-	-
Nb	6.2217	-	-	-	-	-	-	-	-	-
Mo	2.2	-	-	-	-	-	-	-	-	-
Ag	1.0094	-	-	-	-	-	-	-	-	-
In	0.19	-	-	-	-	-	-	-	-	-
Sn	1.3272	-	-	-	-	-	-	-	-	-
Sb	0.4961	-	-	-	-	-	-	-	-	-
Cs	0.6528	-	-	-	-	-	-	-	-	-
La	19.4278	-	-	-	-	-	-	-	-	-
Ce	38.0944	-	-	-	-	-	-	-	-	-
Pr	4.35	-	-	-	-	-	-	-	-	-
Nd	15.3333	-	-	-	-	-	-	-	-	-
Sm	2.7833	-	-	-	-	-	-	-	-	-
Eu	0.5061	-	-	-	-	-	-	-	-	-
Gd	2.2389	-	-	-	-	-	-	-	-	-
Tb	0.365	-	-	-	-	-	-	-	-	-
Dy	2.1056	-	-	-	-	-	-	-	-	-
Ho	0.4433	-	-	-	-	-	-	-	-	-
Er	1.2717	-	-	-	-	-	-	-	-	-
Tm	0.1954	-	-	-	-	-	-	-	-	-
Yb	1.2556	-	-	-	-	-	-	-	-	-
Lu	0.1971	-	-	-	-	-	-	-	-	-
Hf	6.6389	-	-	-	-	-	-	-	-	-
Y	14.1611	-	-	-	-	-	-	-	-	-
Co	3.6661	-	-	-	-	-	-	-	-	-
Ta	0.7328	-	-	-	-	-	-	-	-	-
W	1.0467	-	-	-	-	-	-	-	-	-
Tl	0.0967	-	-	-	-	-	-	-	-	-
Bi	0.039	-	-	-	-	-	-	-	-	-
Th	5.3278	-	-	-	-	-	-	-	-	-
U	3.1111	-	-	-	-	-	-	-	-	-

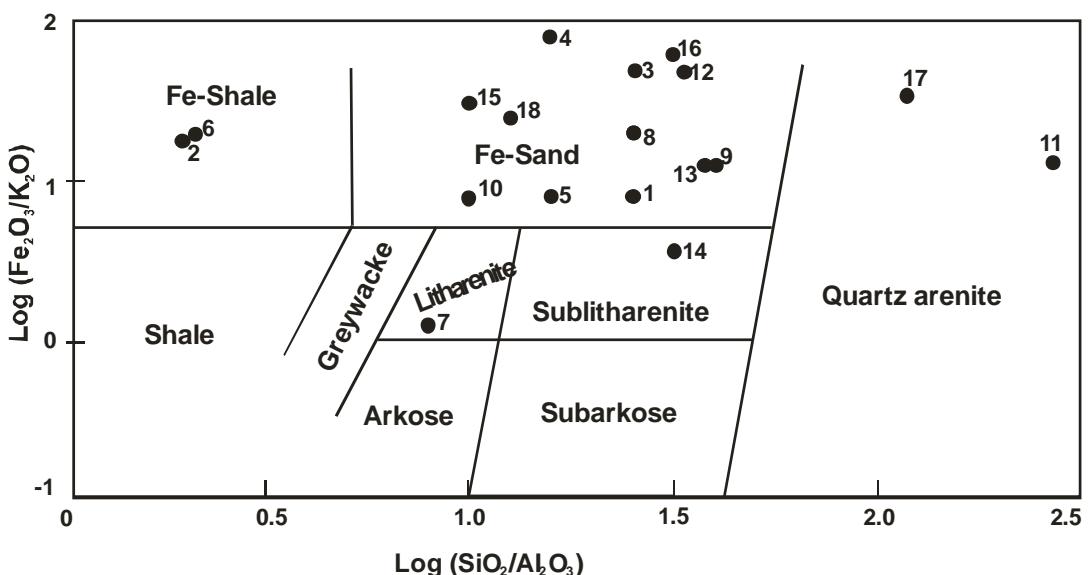


Fig. 2: Geochemical classification of the studied bituminous sediment samples (fields after Herron, 1988)

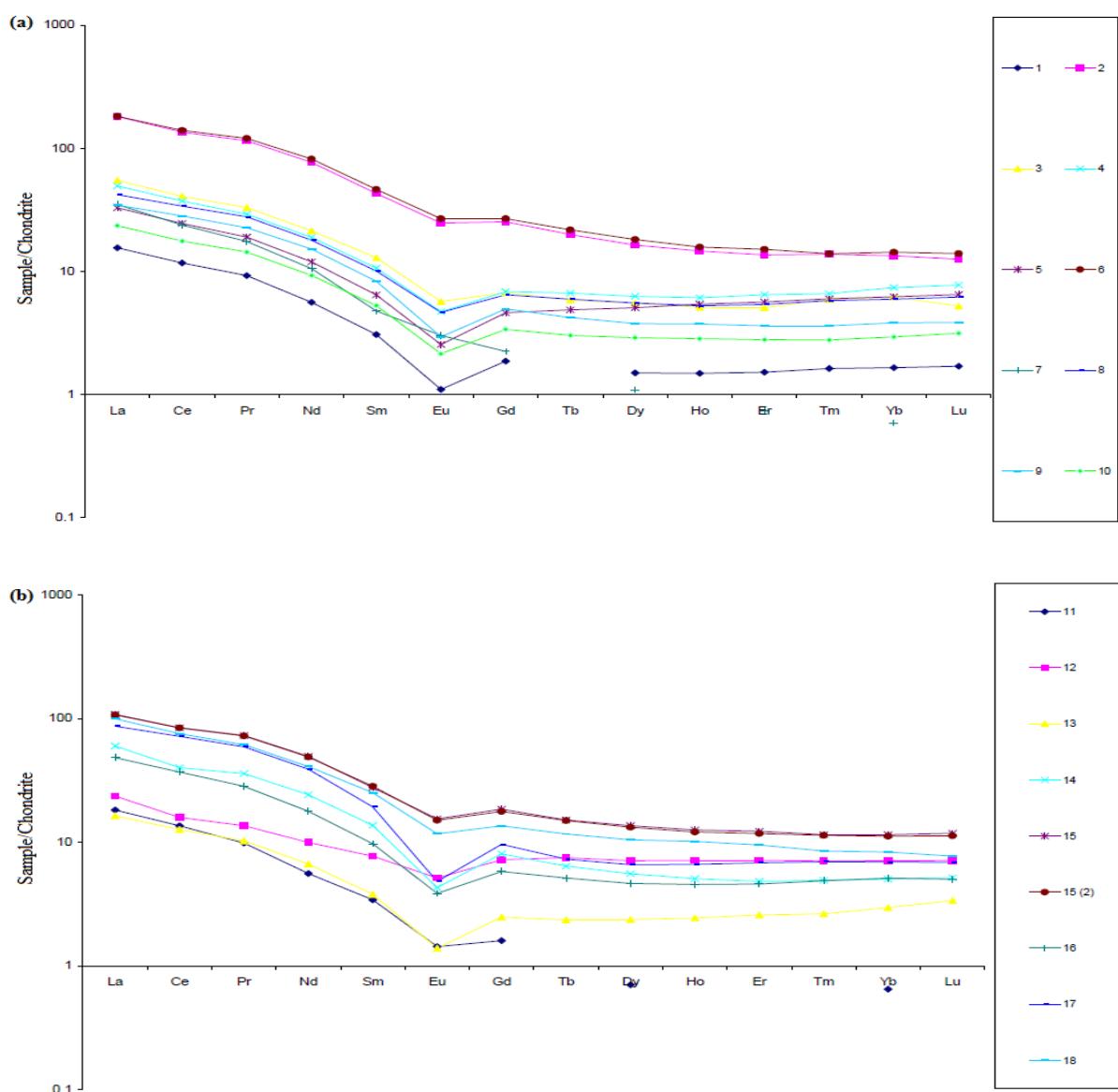


Fig. 3a & b: Chondrite-normalized rare earth element patterns of bituminous sediment samples from Dahomey Basin. Normalizing values are from Taylor and McLennan, 1985

Statistical treatment

The chemical analysis results obtained were subjected to statistical analysis using IBM® SPSS® Statistics version 20 to characterize the geochemistry of major, trace and rare earth elements (REEs) (Table 5). The descriptive statistics of major, trace, REEs and LOI of the ash bituminous sediment samples is listed in Table 5.

Table 5: Descriptive statistics of major, trace, rare earth elements and LOI of the ash bituminous sediment samples

Element (N = 18)	Min.	Max.	Mean	SD
[%]				
SiO₂	1.69	89.21	49.6383	27.29220
Al₂O₃	.22	18.87	3.8278	5.40709
Fe₂O₃	.06	6.81	1.8822	2.00913
MnO	.00	.02	.0091	.00536
MgO	.01	.12	.0372	.03025
CaO	.02	.16	.0600	.04044
Na₂O	.01	.04	.0221	.00903
K₂O	.03	.36	.0889	.09542
TiO₂	.039	.933	.40017	.296146
P₂O₅	.01	.11	.0350	.02526
LOI	.00	22.53	3.4600	6.48013
[ppm]				
Sc	.99	15.00	3.7194	4.26948
Be	.99	3.00	1.2144	.64960
V	11.00	86.00	32.9444	25.85587
Ba	6.00	102.00	30.2222	25.88789
Zn	29.00	50.00	31.3889	6.77486
Ga	.99	24.00	6.1656	6.97351
Ge	.99	1.00	.9922	.00428
As	4.99	6.00	5.0461	.23806
Rb	1.90	16.00	3.8333	4.29500
Nb	.99	18.00	6.2217	4.80940
Mo	1.90	4.00	2.2000	.70377
Ag	.49	2.70	1.0094	.65366
In	.19	.19	.1900	.00000
Sn	.99	3.00	1.3272	.76979
Sb	.49	.60	.4961	.02593
Cs	.49	2.00	.6528	.47225
La	4.90	57.30	19.4278	16.19785
Ce	9.50	114.00	38.0944	32.10797
Pr	1.03	13.50	4.3500	3.82268
Nd	3.30	48.90	15.3333	13.84779
Sm	.60	8.90	2.7833	2.50323
Eu	.08	1.94	.5061	.55728
Gd	.40	6.90	2.2389	1.94910
Tb	.09	1.10	.3650	.30256
Dy	.20	5.90	2.1056	1.63760
Ho	.09	1.10	.4433	.30277
Er	.09	3.20	1.2717	.89112
Tm	.05	.45	.1954	.12353
Yb	.10	3.00	1.2556	.82620
Lu	.04	.45	.1971	.11980
Hf	.80	15.80	6.6389	4.21986
Sr	3.00	40.00	13.6111	10.28499
Y	1.90	28.00	14.1611	8.06205
Zr	34.00	666.00	289.3333	190.66941
Cr	1.90	140.00	28.2778	39.06459
Co	.99	15.00	3.6661	4.18719
Ni	1.90	30.00	7.5889	11.15110
Cu	.99	20.00	3.1022	6.14747
Ta	.09	1.50	.7328	.47234
W	.99	2.00	1.0467	.23793
Tl	.09	.20	.0967	.02590
Pb	4.99	18.00	7.2161	4.05550
Bi	.039	.039	.03900	.000000
Th	.70	13.40	5.3278	3.83725
U	.20	13.20	3.1111	4.05243

Min. = Minimum; Max. = Maximum; SD = Standard Deviation

The majority of major, trace and rare earth elements show strong positive correlation with each other, suggesting a common source for the studied tar sand samples. Alumina (Al_2O_3) correlates well with TiO_2 , K_2O , MgO , MnO , Fe_2O_3 ,

Sc , Be , V , Ba , Sr , Y , Cr , Co , Ni , Cu , Zn , Ga , Ge , Rb , Nb , Mo , In , Sn , Cs , Ta , W , Pb , Bi , Th , U , La , Ce , Pr , Nd , Sm , Eu , Gd , Tb , Dy , Ho , Er , Tm , Yb and Lu , which implies a terrigenous origin. The fairly good negative correlation of SiO_2 with CaO ($r = -0.57$) indicates the presence of carbonate phase in the studied bituminous sediment samples.

Table 6: Varimax rotated component loadings of 55 major, trace and rare earth elements and LOI on five significant components explaining 93.83% of the total variance

Elements	F 1	F 2	F 3	F 4	F 5
SiO_2	-.016	-.237	.097	-.880	.090
Al_2O_3	.594	.794	.054	.063	.061
Fe_2O_3	.523	.723	.396	.019	.088
MnO	.448	.660	.451	.120	-.135
MgO	.456	.815	.205	.236	-.057
CaO	-.257	.089	.137	.812	-.117
Na_2O	.033	.513	.191	.504	.483
K_2O	.421	.871	-.074	.101	-.034
TiO_2	.828	.302	.404	.016	-.142
P_2O_5	.131	.356	.831	.098	-.015
LOI	.538	.818	-.029	.132	.062
Sc	.664	.715	.171	.069	.020
Be	.434	.891	-.021	.073	.025
V	.515	.566	.587	.166	-.039
Ba	.560	.799	.004	-.049	-.033
Sr	.590	.720	.232	.061	.136
Y	.881	.170	.062	-.296	.109
Zr	.433	-.464	.665	-.144	-.300
Cr	.307	.395	.792	.028	.307
Co	.718	.655	-.003	.097	-.001
Ni	.431	.892	-.021	.073	.025
Cu	.431	.892	-.021	.073	.025
Zn	.426	.895	.013	.074	.028
Ga	.659	.731	.122	.041	.087
Ge	.832	.358	-.037	.088	-.071
As	-.173	-.001	.953	.022	.065
Rb	.413	.896	-.008	.103	.013
Nb	.663	.644	.328	.071	-.107
Mo	.351	.862	.338	.079	.047
Ag	.280	-.408	.783	-.025	-.219
Sn	.333	.684	-.079	.219	.008
Sb	-.173	-.001	.953	.022	.065
Cs	.427	.895	-.020	.075	.026
La	.786	.586	.070	-.057	-.157
Ce	.798	.562	.074	-.049	-.176
Pr	.799	.567	.058	-.045	-.162
Nd	.804	.565	.053	-.042	-.146
Sm	.815	.560	.044	-.044	-.100
Eu	.766	.631	.033	.030	.029
Gd	.832	.546	.049	-.017	.012
Tb	.832	.537	.057	-.057	.077
Dy	.873	.463	.091	.002	.099
Ho	.908	.394	.078	-.019	.096
Er	.894	.396	.149	-.008	.120
Tm	.877	.420	.151	-.035	.136
Yb	.861	.416	.197	-.004	.152
Lu	.861	.392	.223	-.020	.153
Hf	.425	-.444	.703	-.109	-.280
Ta	.589	.277	.602	.008	-.185
W	.237	.675	.005	.058	.034
Tl	.012	-.071	-.117	-.210	.931
Pb	.631	.745	.128	.061	-.015
Th	.791	.416	.207	-.061	-.265
U	.504	.704	.064	-.056	.469
Eigen values	19.918	19.878	6.614	2.153	2.108
% of Variance	36.885	36.810	12.249	3.986	3.903
Cumulative %	36.885	73.695	85.944	89.930	93.833

F = Factor

Factor analysis was employed in order to assess inter-element relationships and also to ascertain the main geochemical/sedimentological processes that controlled the distribution of the elements. The varimax rotated factor matrix is presented in Table 6. A 5-factor statistical model was

adopted, which accounts for 93.8% of the total variance. Factor 1 (36.9% of the variance) provides strong positive loadings for Al₂O₃, Fe₂O₃, TiO₂, LOI, Sc, V, Ba, Sr, Y, Co, Ga, Ge, Nb, REEs Ta, Pb, Th, and U. Factor 2 (with high loadings of Al₂O₃, Fe₂O₃, MnO, MgO, Na₂O, K₂O, LOI, Sc, Be, V, Ba, Sr, Co, Ni, Cu, Zn, Ga, Rb, Nb, Mo, Sn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, W, Pb and U) accounts for 36.8% of the total variance. Factor 3 which explains 12.3% of the total variance groups the elements P₂O₅, V, Zr, Cr, As, Ag, Sb, Hf and Ta. Factor 4 (with positive loadings of CaO and Na₂O, and a negative loading for SiO₂) accounts for 3.99% of the total variance while Factor 5 (with high loading of Ti) accounts for 3.9% of the total variance. The loadings in Factors 1 and 2 are indicative of elements associated mainly with aluminosilicate minerals. The loadings in Factor 3 reflected elements associated with a mixture of lithophile, siderophile and chalcophile elements. Also the positive loadings of V in Factors 1, 2 and 3, suggests dual sources contributing to the presence of V. The grouping of elements in Factors 4 and 5 are indicative of elements showing affinity mainly for silicate and sulphide phases, respectively (Table 6).

Conclusions

The studied samples display high values in SiO₂, Al₂O₃ and Fe₂O₃. Silica (SiO₂) is the most abundant oxide in all the samples analyzed. Zircon (Zr) is the most abundant trace element followed by V, Zn, Ba and Cr. Also the strong positive correlation of the great majority of elements (major, trace and REE) with each other suggest a common source of origin for the studied tar sand samples. Furthermore, plots of log (Fe₂O₃/K₂O) versus log (SiO₂/Al₂O₃) classified the studied samples as Fe-shale (#2 and #6), Fe-sand (#1, #3, #4, #5, #8, #9, #10, #12, #13, #15, #16 and #18), litharenite (#7), sublitharenite (#14) and quartz arenite (#11 and #17), indicating a different diagenetic history for the tar sand samples.

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