Geochemical Classification and Maturity of the Coastal Plain Sediments, South West, Nigeria.

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Abstract Major oxide geochemical analysis was carried out on the coastal plain sediments in the Dahomey Basin, to determine their classification and maturity conditions. The clastic sediments are considered as sodic and non-calcareous continental sands with various classification schemes that categorized the sediments as lithic, arenites, arkose, subarkose, quartzarenite, greywacke and Fe-rich sands. This suggests that the sediments are from multiple sources. The Fe₂O₃, MgO, FeO, K₂O, TiO₂, and CaO oxides have low contents that suggest a chemical destruction under oxidizing conditions during weathering. SiO_2 correlates positively with Na, K, Ca and Mg oxides and negatively with AI, Fe and Ti oxides, suggesting that most of the silica is not appropriated in quartz. TiO₂ correlates positively with Al₂O₃ an expression of their association with clay minerals, while Fe₂O₃ correlates negatively with AI_2O_3 showing non association with AI_2O_3 . The high Al₂O₃/TiO₂ ratio indicates felsic source rock. The plot of SiO₂ versus Al₂O₃+ K₂O+ Na₂O shows that majority of the sediments formed under semi-arid/arid conditions tending towards increasing chemical maturity, an implication that the sediments are from multiple sources. The SiO₂/Al₂O₃ index is moderate to high, showing that some of the samples are mature while some are immature suggestive also of a mixed source. The average Na₂O/K₂O ratio for the studied samples indicates that some of the samples are mature while others are chemically immature.

Keywords: Classification, multiple sources, chemical maturity.

I INTRODUCTION

Clastic sediments are loose, solid particles that originate from the weathering and erosion of preexisting rocks. Siliciclastic sedimentary facies are very important parts of sedimentary basin analysis. The textural features of these siliciclastic facies are due to weathering, processes like erosion. natural transportation and deposition. The compositions of clastic sediments are affected by several factors, such as hydraulic sizing, tectonic environment, diagenesis, weathering and transportation processes [1, 2, 3]. The Dahomey basin is an extensive sedimentary basin extending almost from South-Ghana to Nigeria (precisely the Benin hinge-line). The Dahomey basin

(Fig.1) is a marginal pull-apart basin [4] or Margin sag basin which was initiated during the early Cretaceous separation of African and South American lithospheric plates. A number of authors have identified and described the eight lithostratigraphic units in the Dahomey basin [5,6,7,8,9]. In most parts of the basin, the stratigraphy is dominated by sand and shale alternations with minor proportion of limestone [8].

This study was carried out in different localities in the coastal plain sediments of Lagos State, Southwestern Nigeria lying between longitudes 3° 04' and 3° 35' East and latitudes 6° 22'and 6° 41' North. They extend from the western end of Agbara to Ajah locality (Fig. 2). This present study is aimed at the classification of the coastal sediments and its maturity conditions based on major oxides geochemical data.

STRATIGRAPHY OF DAHOMEY BASIN

Previous work on the Cretaceous stratigraphy of the Dahomey basin in Fig 3 recognized three formations belonging to the Abeokuta; the Ise Formation (which is Neocomian to Albian in age consists essentially of continental sands, grits and siltstones. This is directly overlying the South western Precambrian Basement Complex), the Afowo Formation (which overlay Ise Formation consists of coarse to medium-grained sandstones with variable interbeds of shales, siltstones and clay. The sediments of this formation were deposited in a transitional to marginal marine environment during Turonian to Maastritchtian age) and the Araromi Formation (which consists basically of sand, overlain by dark-grey shales and interbedded limestone and marls, and occasional lignite bands. The formation conformably overlies the Afowo Formation) [7]. The Abeokuta was conformably overlaid by Imo group which comprises shale, limestone and marls. The Akinbo Formation overlies Ewekoro Formation and it consists of shale, glauconitic rock and gritty sand to pure grey and with little clay. Limestone lenses from Ewekoro formation grades literally into the Akinbo shale towards the base. Oshoshun Formation overlies the Imo group which is a sequence of mostly pale greenish-grey. It also consists of claystone underlain argillaceous limestone of phosphatic by and glauconitic materials in the lower part of the formation and were deposited during Eocene [8]. The sedimentation of the Oshoshun Formation was

followed by a regression phase which deposited the sandstone unit of Ilaro Formation [10]. The sequence represents mainly coarse sandy estuarine deltaic and continental beds which show rapid lateral facies change. The coastal plain sands are the youngest sedimentary unit in the eastern Dahomey basin. It conceivably, unconformably overlay the Ilaro Formation but lack convincing evidence [4]. It consists of soft, poorly sorted clayey sand and pebbly sands deposited during Oligocene to Recent.

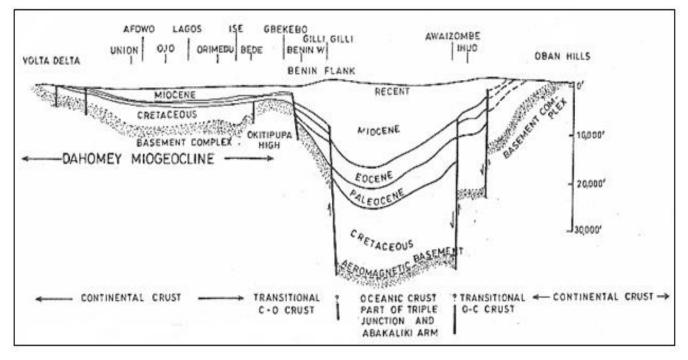
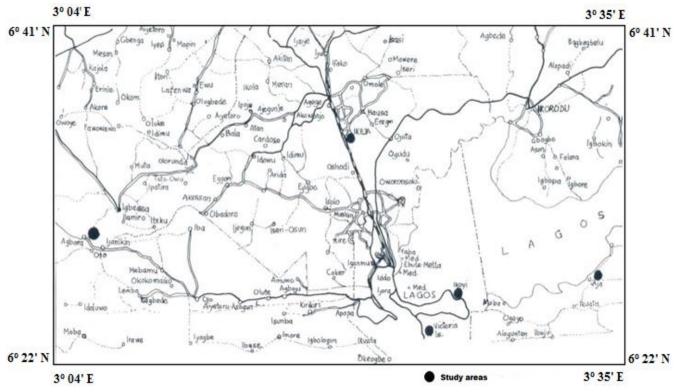


Figure 1: East-West geological section showing the Dahomey Basin and Upper part of the Niger Delta [9]





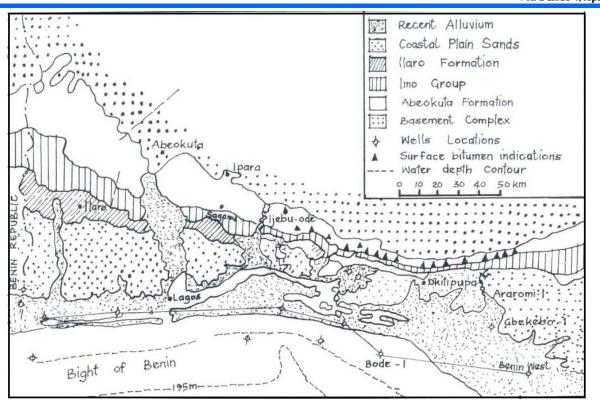


Fig. 3: Geological Map of The Eastern Dahomey Basin [8].

II MATERIAL AND METHODS

There was no outcrop within this study area, therefore samples were collected from five borehole at 3.0 meters interval. Boreholes investigated are located at Agbara, Victoria Island, Ikoyi, Ikeja and Ajah. Three hundred and twenty four subsurface samples (324) were collected while an average of 30 samples, based on the sub-units established was selected for laboratory analysis. Precaution was taken during the sample collection to avoid contamination. The Atomic Absorption Spectrophotometer (AAS UNICAM 969 MODEL) was used for the geochemical analysis. Dilute hydrochloric acid was used on the sample for possible gas presence. Hand lens and binocular microscope were also used for mineralogical identification codes.

Geochemical Analysis

Thirty samples were selected for geochemical analysis. The samples were air-dried, crushed using a jaw crusher, and pulverized with the ball milling machine. 10 grams of each sample was weighed and put in a clean digestion bottle. With the aid of a calibrated plastic syringe, 15mls of 40% Hydrochloric acid was added with the help of an automatic pipette, and 10mls of Hydrofluoric acid was also added. In the process of mixing the two acids, the bottle was tightly closed in order to avoid the escape of silicon=fluoride [SiF4] gas. The digestion bottle was later put on a water bath and warmed up to 70 degree centigrade for about two hours and allowed to cool down to 25-30 degree centigrade. A 100 mls saturated boric acid was added to the solution and the bottle was closed tightened. The bottle was put on a water bath up to

70oc until the milky solution became clear. Distilled water was added to it after cooling to make a solution of 250 mls; part of distilled sample was put in a sample container which was then analyzed with a dilution factor of 25. Major elemental oxides such as SiO2, Al2O3, K2O, Na2O, CaO, MgO, FeO, Fe2O3 and TiO2 were obtained using Atomic Absorption Spectrophotometer [UNICAM 969 model] with a precision of +0.5.

Mineralogical Analysis

A selective staining technique was utilized to separate quartz, feldspar and rock fragments. The lighter mineral fraction of 2mg were collected and placed in a lead and bath in warm concentrated Hydrochloric acid [HCI] for a minute. After washing, the sample was immersed in one percentage aqueous solution of malachite green for five minutes rinsed and dried. The sample was again mounted on a slide with Canada balsam, and studied under the microscope. Quartz remains unchanged in colour while feldspars stain yellowish and rock fragment stain brown. The relative proportion of different detritus minerals were determined by point counting and results recorded in percentage.

III RESULTS AND DISCUSSION

Table 1 shows the major oxides compositions of the coastal plain sediments. The samples are dominated by SiO₂, which ranges from 73.6 to 85% (average = 81.14%). Al₂O₃ ranges from 4.70 to 12.9% (average = 8.19%). This value may be attributed to composition of lithic fragments while the low concentrations of Fe₂O₃ (average = 1.462%) MgO (average = 0.22%); FeO (average = 0.58%); K₂O

(average = 1.05%), TiO₂ (average = 0.01%) and CaO (average = 0.02%) may be ascribed to chemical destruction under oxidizing conditions during weathering and diagenesis. Lack of MnO is probably due to dissimilatory manganese reduction by microbes or source-area composition.

Chemical alteration of rocks during weathering led to the depletion of alkalis and alkaline earth elements and preferential enrichment of Al_2O_3 [11]. Fig 4 presents the plot of SiO₂ against other major oxides. SiO₂ correlates positively with Na, K, and Mg oxides

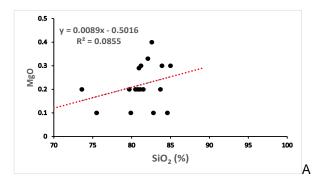
(Figs 4. a,b,c) in an upward trend and negatively with Al, Fe and Ti oxides. (Fig 4.d, e, f), in a downward trend showing that most of the silica is not appropriated in quartz. Fig 5 shows a plot of Fe₂O₃ and TiO₂ against Al₂O₃. TiO₂ correlates positively with Al₂O₃ (Fig. 5) suggesting their association with Clay minerals, while Fe₂O₃ correlates negatively with Al₂O₃ which suggests non association with Al₂O₃. The ratio of K₂O/Na₂O with a ranges of 0.05to 0.58 (average = 0.20), indicates that Na-plagioclases are more than K-bearing minerals. The high Al₂O₃/TiO₂ ratio of 69 - 478 (average = 222) shows a felsic source rock.

Table 1: Major oxides component	s (Wt %) of the Coastal Plain sediments an	d their weathering indices
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Oxides (%)		AGB/ 54-60		AGB/ 144- 156	KJA/ 33-51		KJA/ 117- 123	KJA/ 132- 141	VI/8- 21	VI/33- 64	VI/60- 90	IKY/5 4-66	IKY/6 6-87	IKY/1 50- 207	AJ/42 -54		AJ/14 4-180
SiO ₂	82.09	80.95	73.6	80.5	81.2	81.5	79.7	82.6	83.7	85	81.1	84.6	82.8	80.8	75.5	79.9	83.9
AI_2O_3	4.78	8.09	8.8	8.2	9.4	7.9	6.7	6.1	6.7	8.1	9.5	6.5	7.4	9.5	11.8	12.9	6.9
Fe_2O_3	2.03	2.92	2.8	1.2	0.9	1.1	0.6	1.5	1.3	1.7	1.1	1.3	1.1	0.9	1.8	1.1	1.4
FeO	0.92	0.35	0.6	0.4	0.5	0.3	0.4	0.6	0.8	0.5	1	0.6	0.5	0.4	0.8	0.5	0.7
MgO	0.33	0.29	0.2	0.2	0.3	0.2	0.2	0.4	0.2	0.3	0.2	0.1	0.1	0.2	0.1	0.1	0.3
K2O	0.52	0.38	1.1	1.2	2.5	2.4	1.9	2.3	0.7	0.6	0.35	0.7	1.3	0.3	0.3	0.3	1
CaO	0	1.21	1.4	0.2	0	0.7	1	0.5	4	0.07	0	1.2	1.6	0	0	0	0.1
Na ₂ O	6.45	5.2	4.6	6.8	5.9	8.8	3.3	4.7	8	6	6.4	3.6	4.7	5.3	5.7	4.7	4.1
TIO2	0.01	0	0	0	0	0	0	0	0	0	0		0	0	0.1	0	0.1
TOTAL	97.23	100	97.7	100	100	99.3	96.6	99.7	100	99.7	100	98.4	99.5	97.5	96	98.6	98.5
SIO ₂ /AL ₂ O ₃	17.17	10.01	8.36	9.82	8.64	10.32	11.90	13.54	12.49	10.49	8.54	13.02	11.19	8.51	6.40	6.19	12.16
K ₂ O/AL ₂ O ₃	0.11	0.05	0.13	0.15	0.27	0.30	0.28	0.38	0.10	0.07	0.04	0.11	0.18	0.03	0.03	0.02	0.14
CaO/MgO	0.00	4.17	7.00	1.00	0.00	3.50	5.00	1.25	20.00	0.23	0.00	12.00	16.00	0.00	0.00	0.00	0.33
K ₂ O/Na ₂ O	0.08	0.07	0.24	0.18	0.42	0.27	0.58	0.49	0.09	0.10	0.05	0.19	0.28	0.06	0.05	0.06	0.24
Na ₂ O/K ₂ O	12.40	13.68	4.18	5.67	2.36	3.67	1.74	2.04	11.43	10.00	18.29	5.14	3.62	17.67	19.00	15.67	4.10
Log(K ₂ O/Na ₂ O)	-1.09	-1.14	-0.62	-0.75	-0.37	-0.56	-0.24	-0.31	-1.06	-1.00	-1.26	-0.71	-0.56	-1.25	-1.28	-1.19	-0.61
Log ((Fe ₂ O ₃ +MgO)/ (Na ₂ O+K ₂ O))	-0.47	-0.24	-0.28	-0.76	-0.85	-0.94	-0.81	-0.57	-0.76	-0.52	-0.72	-0.49	-0.70	-0.71	-0.50	-0.62	-0.48
Fe ₂ O ₃ /K ₂ O	3.90	7.68	2.55	1.00	0.36	0.46	0.32	0.65	1.86	2.83	3.14	1.86	0.85	3.00	6.00	3.67	1.40

IV GEOCHEMICAL CLASSIFICATION

The classification schemes used in this study are adopted from the geochemical classification diagrams of several authors [12,13,14,15,16]. The ternary diagram proposed by Blatt et al. (1972) [13] shows that the studied samples are sodic sandstones (Fig. 6A).This ternary diagram omitted sandstones with less than 5% of Al_2O_3 , consequently, quartz arenite is missing.



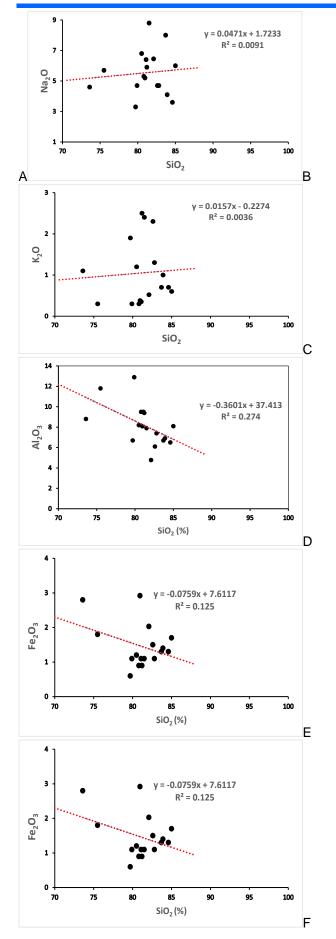


Figure 4: Cross-plots of major oxides against SiO_2 showing the correlations.

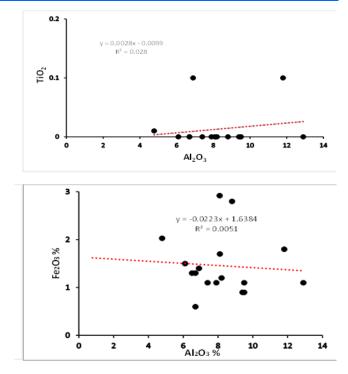


Fig. 5: Cross-plot of Fe and Ti oxides against Al₂O₃

Based on the work by Lindsey, (1999)[16] and data from Pettijohn, (1963, 1975),[17,18], the ternary diagram in Fig 6A shows that the average lithic arenites plotted in the ferromagnesian potassic sandstones field, while the average greywacke plotted in the sodic sandstone field. The average arkoses appeared in the potassic sandstones field (Fig 6B). Folk (1974) classified the coastal plain sediments as quartz arenite. Figure 7 was constructed based on the [12] scheme and the result shows that majority of the sandstones plotted in the litharenite zone while few plotted in the greywacke zone.

According to [17], the lithic arenites are a diverse and poorly defined class. In addition to abundant rock fragments of widely varying composition, many lithic arenites contain clay matrix with different compositions which can contain higher levels of Fe and Mg. Also, many rock fragments of lithic sandstones are composed of materials that vary greatly in composition. Based on compositional fields for major classes of sandstones as proposed by Lindsey, (1999) the studied sediments plotted in the graywacke field (Fig. 8). The result in fig 7 agrees with that in Fig 8.

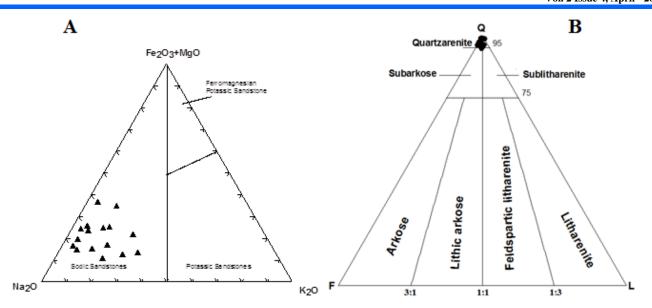


Fig. 6: (A).Ternary diagram of Na₂O-K₂O-(Fe₂O₃+MgO) of the coastal plain sediments, from [13]. (B) QFL plot [14] of the coastal plain sediments

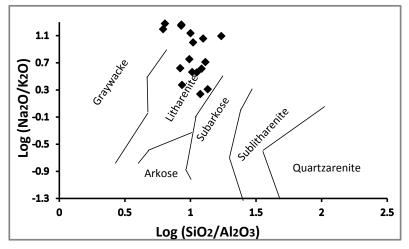


Fig. 7: Chemical classification of the Coastal Plain sediments based on Pettijohn scheme (1972)

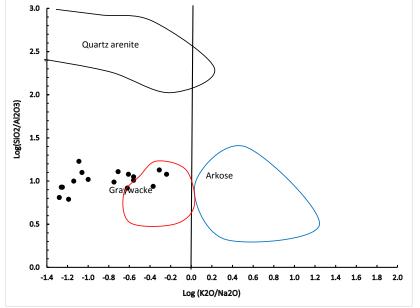


Fig. 8: Compositional fields for major classes of sandstones (data from [17,18] : log (SiO₂/Al₂O₃) versus log (K₂O/Na₂O). The samplesplotted in the graywacke field (Adapted from Lindsey, 1999).[16]

The geochemical classification diagram (Fig. 9) by [15] shows that some samples plotted mainly in the litharenite zone , and some others plotted in the arkose, subarkose and Fe-sand zones. According to Farquhar et al. (2014),[15] the third axis from the scheme (not shown in Fig. 9), classified samples by Ca content by dividing samples into non-calcareous (Ca< 4 %), calcareous (4 % <Ca< 15 %), and carbonate (Ca> 15 %) samples. The coastal plain sediments are classified as non-calcareous. This goes to point out the various sources of the sediments.

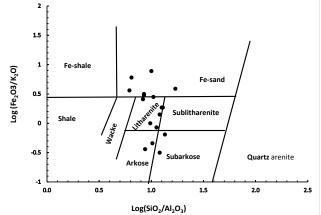


Fig.9. Chemical classification of the Coastal plain sediments based on log (SiO_2/Al_2O_3) vs. log (Fe_2O_3/K_2O)

Maturity

Based on the study of a reference set, [16] proposed the following guidelines for chemical classification of sandstones:

1) quartz arenite: log (SiO₂/Al₂O₃) \geq 1.5

2) graywacke: log (SiO_2/Al2O_3) < 1 and log (K_2O/Na_2O) < 0

3) arkose (includes subarkose): log (SiO_2/Al_2O_3) < 1.5 and log $(K_2O/Na_2O) \geq 0$ and log $((Fe_2O_3+MgO)/(K_2O+Na_2O)) < 0$

4) lithic arenite (subgraywacke, includes protoquartzite): log $(SiO_2/Al_2O_3) < 1.5$ and either log $(K_2O/Na_20) < 0$ or log $((Fe_2O_3+MgO)/(K_2O+Na_2O)) \ge 0$. If log $(K_2O/Na_2O) < 0$, lithic arenite can be confused with graywacke. The coastal plain sediments fall within the requirements of the third condition and thus classified as an arkose (includes subarkose).

The log ratio of SiO₂/Al₂O₃ indicates mineralogical maturity of sediments [12]. It differentiates between quartz-rich high ratio sandstone and clay -rich low ratio shale. The ratio of SiO₂/Al₂O₃ shows moderate to high values indicating that all the samples have low degree of clay. The higher the SiO₂ content the lower the degree of clay. Potter (1978) [19] states that maturity of sandstones is reflected by the SiO₂/Al₂O₃ index. High ratios indicate mineralogical maturity (quartzose, rounded) sediments while low ratios represent chemically immature sediments . For the coastal plain sediments, the SiO₂/Al₂O₃ ratio ranges

between 6.19 and 17.17 with an average of 10.51, thus falling within the moderate to high. This shows that some of the sampled sediments are mature while some are immature suggestive of mixed sources. The Na_2O/K_2O and Fe_2O_3/K_2O ratios can also be used in determining chemical maturity and mineral s stability respectively [20,15]. The average Na₂O/K₂O ratio for the studied sediments is 8.86 with range of values of between 1.74 and 19. These range values present some of the sediments as mature while some are chemically immature, suggestive of multiple sources. By extrapolation, sediments with a low SiO₂/Al₂O₃ ratio and a higher Fe₂O₃/K₂O ratio are mineralogically less stable and more prone to reactivity during supercritical CO_2 exposure [21].The Al₂O₃/(CaO+MgO+Na₂O+K₂O) ratio can be used to determine the stability of mobile oxides as proposed by [22]. The positive values obtained (0.52 to 2.53), shows that there are stable mobile oxides in the coastal plain sediments. Figure 10 presents the bivriate plot of SiO₂ versus Al₂O₃+ K₂O+ Na₂O [23]. The result indicates that majority of the sediments formed under semi-arid/arid conditions suggesting that the sediments are from multiple sources tending towards increasing chemical maturity.

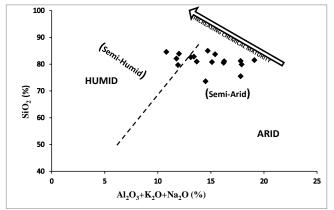


Fig. 10: Chemical maturity of the coastal plain sediment expressed by bivariate plot of SiO₂ versus $AI_2O_3 + K_2O + Na_2O$ (After [25].

An approach towards assessing detrital mineralogy is to use the index of compositional variability (ICV) and ratio of K₂O/Al₂O₃ [24]. The index of compositional variability (ICV) is defined as: (Fe₂O₃+Na₂O+CaO+MgO+TiO₂)/Al₂O₃. More matured sandstone with mostly clay minerals displays lower ICV values that are less than 1.0 and such sandstones are derived from cratonic environment [25]. From the results of the index of compositional variability, most of the sandstones have values greater than 1, indicating that the sandstones are mineralogically immature. Table 2 shows the mineralogical composition of the coastal plain sediments, the quartz, feldspar and lithic (rock) fragments as used to obtain the mineralogical maturity index (MMI).

SAMPLE ID	QUARTZ	FELDSPAR	LITHIC FRAGMENT	MICA	FOSSIL FRAGMENT	MMI
AGB/6-18	94.82	2.86	2.32			18
AGB/30-48	96.48	2.8	1.56			22
AGB/48-54	96.7	1.37	2.43		0.05	25
AGB/54-60	97.5	2.2	2.3			22
AGB/72-84	97.87	1.52	0.61			46
AGB/144-156	96.8	2.03	1.16	0.01		30
KJA/24-30	98.51	1.05	0.04			90
KJA/39-51	97.5	1.92	0.58			39
KJA/51-57	98.56		1.44			68
KJA/66-72	99.85	0.15				666
KJA/84-144	99.72		0.28	0.02		356
KJA/117-123	96.42	2.64	1.92	0.02		21
KJA/126-129	98.59	0.03	1.36		0.01	71
KJA/132-141	99.22	0.92	0.13			94
KJA/153-159	97.84	0.52	0.56		1	91
VI/27-33	97.75	2.55	1.5		0.2	24
VI/60-63	84.8	2.05	1.5		1.1	24
VI/96-105	95.38	2.8	1.82		0.01	21
VI/180-198	96.1	3.64	0.21	0.01	0.25	25
VI/198-210	95.1	2.45	0.25		1.2	35
IKY/3-6	92.32	2.02	0.57	1.29	3.82	36
IKY/36-66	69.18	2.07	0.25		1.5	30
IKY/66-87	98.22	1.2	0.38			62
IKY/102-114	97.5	1.42	0.38	0.01		54
IKY/144-150	96.13	2.38	0.86			30
IKY/150-198	97.57	1.8	0.63		0.01	40
IKY/207-222	97.83	1.74	0.43			45
AJ/0-15	96.09	2.63	0.77	0.5	0.01	28
AJ/21-30	93.1	2.7	0.75		1.02	27
AJ/90-102	95.75	2.5	1.7			23
AJ/144-168	95.56	2.55	0.94		0.25	27
AJ/222-225	97.98	1.5	0.52			49
MEAN	95.71	1.93	0.97	0.27	0.75	70

Table 2: Modal composition of the coastal plain s ediments.

The mineral maturity is calculated by using the mineralogical maturity index (MMI) proposed by [26] and evaluated as ; $\frac{Proportion of Qtz}{Proportion of Fsp+Proportion of R.F}$ (1) The MMI values in Table 2 are greater than

19 suggesting the sediments to be super mature in line with the values in Table 3 but these are at variance with other maturity parameters already discussed.

Table 3: Maturity scale of sandstones: Limiting % of Q and (F + RF) MI and maturity stage [26,27] .

Q =≥ 95% (F + RF) = 50%	MI = ≥ 19 supper mature		
Q =95-90% (F + RF) = 5-10%	MI = 19 - 9.0 sub mature		
Q = 90-75% (F + RF) =10- 25%	MI =9.0-3.0 sub mature		
Q =75-50% (F + RF) = 25- 50%	MI =3.0-1.0 immature		
Q = < 50%	MI ≤ 1		
(F + RF) > 50%	Extremely immature		

V. CONCLUSION

The coastal plain sediments are sodic and noncalcareous continental sands. Various classification schemes classified the sediments as lithic arenites, arkose, subarkose, quartz arenite, greywacke as well as Fe-rich sands suggesting that the sediments are from multiple sources. Majority of the sediments formed under semi-arid/arid conditions tending towards increasing chemical maturity suggesting that the sediments are from multiple sources. The SiO₂/Al₂O₃ index is moderate to high, showing that some of the samples are mature while others are immature suggestive also of a mixed source. The average Na₂O/K₂O ratio for the studied sediments also show that some of the sediments are mature while some others are chemically immature implying a multiple source. The mobile oxides in the coastal plain sediments are said to be stable. The index of compositional variability values indicate that the sediments are mineralogically immature. However, the mineralogical maturity index as well as the maturity scale and stage show that the sediments are super mature, suggesting variability from the other maturity parameters.

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