

Evidence of the Albo-Cenomanian Unconformity Using Chemical Elements Case Study of Sediments from the Eastern Abidjan Margin

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Abstract

Sedimentological and chemostratigraphical studies using accessory elements on 322 samples of cuttings from oil wells located in the submerged sedimentary basin (offshore) of Côte d'Ivoire. This basin covered the chronostratigraphic interval from the Upper Albian to the top of the Maastrichtian. The aim of this study was to determine the major accident, the Albo-Cenomanian unconformity, using chemical elements. To achieve this goal, we had to count the accessory elements glauconite, pyrite and carbonaceous debris, and identify all the chemical elements present in each cuttings sample. The results clearly indicate that: the sediments are essentially composed of carbonaceous debris and pyrite, with a high potassium content for sediments dating from the Abian period; and glauconite, carbonaceous debris, pyrite, and a sharp decrease in potassium content for sediments dating from the Cenomanian to the Maastrichtian period. Threshold values for ratios of source-indicating chemical elements (Zr, Ti, Y, Th) and paleoenvironmental elements (K, Rb, Mg, Al,) highlighted the MS1 and MS2 mega-sequences in the study area. The difference observed in the threshold values of these ratios can be explained by changes in sedimentary dynamics. The depositional environment varies from an inner continental shelf with strong littoral influence (Upper Albian) to an increasing subsidence outer continental shelf (Cenomanian-K/Pg boundary).

Keywords

Sedimentological, Chemostratigraphical, Margin, Abidjan, Côte d'Ivoire

1. Introduction

In Côte d'Ivoire, geologists [1] have carried out a great deal of research on the Ivorian sedimentary basin, with a view to gaining a better understanding of this secondary-tertiary age basin in the context of oil prospecting. In terms of scientific research, the studies carried out by [2] have defined the lithostratigraphy, palynostratigraphy and chemostratigraphy, as well as the environmental conditions under which the sediments of the eastern Côte d'Ivoire offshore basin were deposited. Work [3] reviewed the geology of the western Ivorian onshore basin. The work of [4] and [5] provides indications of the Quaternary sedimentary environments. More recent sedimentological and micropaleontological studies have subdivided the Tertiary and Cretaceous into foraminiferal biozones. They also provided further details on deposition environments [6]-[12]. All these works date from 1987 to 2021. Of all these works, only [12] addressed the stratigraphy from the Albian to the Maastrichtian based on chemical elements. Chemical elements, which are the infinitesimal unit in sediment composition, are good indicators that, in association with accessory elements and stratigraphic fossils, can help to better reconstruct paleoenvironments and stratigraphy. The aim of the present work is to contribute to the determination of a major accident, the Albo-Cenomanian unconformity, on the basis of chemical elements. To this end, the study is based on cuttings from four offshore boreholes, all located to the east of the Abidjan margin.

2. Presentation of the Study Area

In the context of this work, the wells studied are located in the Abidjan margin (**Figure 1**). These wells are LEO-2X; LEO-3X; LEO-4X and LEO-5X.

3. Materials and Methods

The analysis of accessory elements consists of identifying and counting accessory elements present in Sediments, using a binocular magnifying glass. The elements concerned are glauconite, pyrite and carbonaceous debris. Thanks to their specific characteristics, these elements provide information on the different depositional environments. The various data obtained are processed in Microsoft Excel



Figure 1. Presentation of the study area.

software to plot the variation curve of accessory elements as a function of the depth of each well, in order to interpret the abundance zones (Table 1). Chemostratigraphic analysis involves taking 7 g of sample per dimension, washing them with dichloro-methane (DCM), drying them (left in the open air or under a fume hood) and then grinding them in an agate mortar or with a vibratory ball mill. The pellets are then made from 4 g of sample powder mixed with 1 g of CEREOX-type binder powder. This mixture is compressed under a pressure of up to 15 tonnes to form 33-mm diameter pellets, which will be used for a complete XRF analysis to determine the various concentrations of trace, major and minor elements within the limits detectable by XRF. The XRF analysis is carried out after checking the stability of the device based on the analysis of the standard (GSR-5 (Geochemical standard reference sample rock)) (Table 2). The prepared pellets are then deposited one after the other in a precise order to avoid any error inside the device, using a suction cup to prevent contamination of the sample. We also check for the presence of gas (179 to 182 atm). Dimensions, well name, sample type and respective masses of sample and binder are entered. Each

Table 1. Abundance of accessory elements and deposition environment.

ACCESSORY ELEMENTS	DEPOSIT ENVIRONMENT
Pyrite	Sulfurized anoxic environment
Marine environment	Marine environment
Carbonaceous debris	Environment with continental influences

 Table 2. Repeatability test for the GSR-5 standard weight percent (geochemical standard reference sample rock).

CHEMICAL ELEMENTS	SiO₂ %	Al2O3 %	K₂O %	Ba ppm	Rb₂O ppm	ZrO₂ ppm	ZnO ppm	PbO ppm
CONCENTRATIONS	53.47	17.29	3.54	417.2	213.4	132.4	66.7	9.5
	52.47	16.75	3.53	382.2	214.6	133.7	68.5	10.1
	52.44	16.74	3.53	423.3	214.8	135.5	67.5	9.5
	52.30	16.73	3.54	409.6	215.2	137.5	68.7	10.5
	52.43	16.78	3.53	409.8	215.1	135.4	68.4	10
	52.43	16.74	3.53	405.4	214.8	135.1	68	9.6
	52.41	16.75	3.55	413.7	215.4	133.4	70	10.4
	52.57	16.82	3.54	417.8	214.8	135.9	69.1	10.4
	53.44	17.30	3.53	431.5	214.3	133.2	67.7	10.1
	52.41	16.77	3.54	420.5	215.8	133.9	68.7	9.7
	52.47	16.74	3.56	404	214.7	137.3	68.8	9.7
Min	52.30	16.73	3.53	382.2	213.4	132.4	66.7	9.5
Max	53.47	17.30	3.56	431.5	215.8	137.5	70	10.5

the sample is analyzed in 15 minutes. At the end of the analysis, the proportions of major and trace elements are obtained.

Statistical data processing: CUMPETRO software is used to produce curves for graphically determining enrichment and depletion zones. In this software, the concentration values obtained after XRF analysis are entered. The software plots the various curves and, based on the curves, determines the mega-sequences, sequences and different sediment packages according to the concentrations of their chemical content. Layers with a common history are grouped into mega-sequences, sequences, or packets.

4. Results

4.1. Accessory Elements

Analysis of accessory elements by stratigraphic stage has revealed two main depositional environments (Figure 2). In our four study wells, the sediments were subdivided into two parts according to the results. Part I sediments (2993-2310/LEO-2X); (2498-2362/LEO-3X); (3030-2690/LEO-4X); (3466-3048/LEO-5X), corresponding to Albian sediments, are rich in carbonaceous debris with a low pyrite content. These sediments were therefore deposited in an environment with continental and reductive influences. Part II sediments (2310-869/LEO-2X); (2362-1402/LEO-3X); (2690-1000/LEO-4X); (3048-1661/LEO-5X) range from



G: Glauconite; C D: carbonaceous debris; P: pyrite

Figure 2. Accessory elements in LEO-2X, LEO-3X, LEO-4X and LEO-5X wells from the Albian to the Maastrichtian.

Cenomanian to Maastrichtian, with abundant glauconia. Carbonaceous debris and trace amounts of pyrite are also present. The depositional environment is marine, anoxic and with continental influences.

4.2. Chemostratigraphy

The chemostratigraphic results have enabled us to make the following zonations:

4.2.1. Choice of Keys Ratios and Definition of Threshold Values

The choice of certain elements for the establishment of key ratios is based on their respective mobile and immobile characteristics in the hydrological regime. Al and Fe are relatively less mobile than K, Ca, Na and Mg during chemical weathering [13]. Al is a stable element under conditions of intense hydraulic weathering, while Mg, Ca, Na and K are strongly leached under similar conditions. This therefore tends to enrich aluminum (Al), which is resistant to leaching fluids, in tailings during chemical weathering processes [14]. Thus, the ratio of one of these major elements to Al will be used as a key indicator of chemical weathering and hence hydraulic processes in the depositional environment. The key ratios defined are therefore K/Al, Fe/Al, Mg/Al and Fe/Mg. As kaolinite can be a weathering product of illite due to high hydrolysis intensity, the ratio of these two minerals will help trace hydrolysis conditions. Since gallium (Ga) is commonly enriched in kaolinite and Rb in illite, the Ga/Rb ratio will be used as an indicator of the proportion of kaolinite to illite. All these ratios will help explain the paleoenvironment. Trace elements such as Y, Th, Zr, Hf, Nb are only distributed mechanically due to their refractory nature and very low mobility during weathering and diagenesis processes [13]. They are incorporated into the heavy and/or opaque minerals contained in clastic sediments during weathering and transport and thus reflect the signature of the sediment source [15]. The same applies to Ti, a major element. The ratio of these immobile elements (notably Ti/Y and Th/Al) can therefore be used to track the source of sediments. The threshold values defined for each key ratio at the level of paleoenvironmental indicator elements are therefore for the ratio.

K/Al: 0.146; Ga/Rb: 0.162; Fe/Al: 0.741 and Mg/Al: 0.161. With regard to the ratios of trace elements of sediment origin, the threshold values for the key ratios Ti/Y and Th/Al are 0.064 and 1.043 respectively. Based on these reference values, two mega-sequences can be distinguished, mega-sequence 1 (MS1) and mega-sequence 2 (MS2).

4.2.2. Chemostratigraphic Characterization of Mega-Sequences 1 and 2

MS1 is characterized by Ga/Rb values (0.169) below the reference threshold of 0.4. The K/Al (0.147), Fe/Al (0.73) and Mg/Al (0.16) ratios are above their threshold values of 0.08, 0.43 and 0.09 respectively for these same ratios in wells LEO-2X, LEO-3X, LEO-4X and LEO-5X (**Table 3**).

1) Deposit environment

When K/Al values are below 0.25, this indicates that K is associated with illite,

Mega séquences	Depth (m)	Boreholes		
MS2	2310 - 869			
MS1	2993 - 2310	LEO-2X		
MS2	2362 - 1402			
MS1	2498 - 2362	LEO-3X		
MS2	2690 - 1000			
MS1	3030 - 2690	LEO-4X		
MS2	3048 - 1661			
MS1	3466 - 3048	LEU-5X		

Table 3. The upper limits of MS1 at the various wells are listed in the table below.

and that the original sediments were rich in clays probably dominated by illite. This shows that the strong correlation between Rb and K is due to their binding in this mineral rather than in feldspars or micas. Also, since K values are below 5% in all the wells studied, this would indicate that the sediments in this zone are of diagenetic origin (authigenic feldspars). The K/Al ratio in both wells is greater than 0.14 at MS1, showing that the concentration of K is higher than that of Al (Figure 3). K-bearing minerals (illite) are abundant in the mainly Al-bearing clay sediments of the MS1 mega-sequence. This illite richness in MS1 demonstrates the proximity of the depositional environment to the sediment source. Indeed, the proximity of the depositional environment results in sediment drainage over a short distance, and therefore a short residence time of the sediment in the water. This prevents K leaching from the carrier mineral, illite. In MS1, the low Ga content relative to Rb indicates that the Ga concentration is lower than that of Rb. In other words, the proportion of kaolinite is lower than that of illite in this mega-sequence. All these observations show that the sediments have not undergone intense alteration and that the depositional environment is proximal. Furthermore, the high values of Fe/Al and Mg/Al ratios, respectively in excess of 0.741 and 0.161, attest to the proximal nature of the depositional environment. Indeed, these observations show that MS1 is more enriched in Fe and Mg contained in minerals of terrestrial origin. This high concentration of these elements is probably due to the richness of the chlorite and vermiculite. Fe-bearing mineral phases could be pyrite and/or iron oxides and hydroxides (hematite, goethite, limonite, magnetite). A slight presence of dolomite would also have contributed to the Mg concentration in MS1. The profile of the Mn/Al ratio also shows a break in its evolution at the boundary between MS1 and MS2. This ratio shows high values in MS1, a sign of the significant detrital fluxes due to the proximity of the depositional environment. Mn also has a detrital origin in this part of the sedimentary basin and can be concentrated in a variety of clay minerals. In contrast to MS1, MS2 is characterized by high Ga/Rb values (>0.169) and low K/Al values (<0.147). This observation reflects the high proportion of kaolinite to illite in MS2. This illite depletion is indicated by the decrease in the K/Al ratio and the kaolinite richness by the increases in the Ga/Rb ratio relative to their respective threshold values. This drop in the proportion of illite in MS2 can be explained by the leaching of K into the sediments due to the presence of water in the depositional environment. A transgression would be the reason for the presence of water in the depositional environment. Indeed, along





Z : Zonation ; S S : Stratigraphic stage

Figure 3. Chemostratigraphic profile of the depositional environments of wells LEO-2X, LEO-3X, LEO-4X and LEO-5X.

stay in water would have favored the drainage of sediments over a long distance before reaching the depositional environment, and the leaching of labile elements such as K and Rb. This would explain the drop in the K/Al ratio in MS2, reflecting a fall in illite concentration. This assertion is confirmed by the richness of kaolinite in the depositional medium (MS2), since this mineral forms under conditions of intense drainage. This situation would have favored intense chemical alteration of K-bearing minerals such as illite, micas, chlorite and feldspars. Also, the low Fe/Al and Mg/Al ratios in MS2 reinforce the idea of transgression. This is because, with the arrival of marine waters, terrigenous inputs declined along with Fe and Mg-bearing detrital minerals, to the benefit of kaolinite enrichment due to the leaching of mobile elements. All these data suggest that MS2 was deposited in a distal environment.

2) Source of sediments

The threshold values for Ti/Y and Th/Al ratios indicate the same limits between MS1 and MS2 defined by those of the depositional environment indicator element ratios (**Figure 4**). Ti/Y values are below 0.017 in MS1, meaning that the sediment source in this mega-sequence is poorer in Ti-bearing minerals than in phosphates, the yttrium-bearing minerals. The richness of the Y-bearing mineral phase in this megasequence is confirmed by the high values of the Th/Al ratio above 1.588, since these two elements (Th and Y) have a high correlation coefficient. This high concentration of Th and Y could be explained by the presence of apatite and/or monazite, or even xenotime. The sediment source of the MS1 mega-sequence deposits would therefore be richer in phosphates and have a low concentration of titanium-bearing minerals. The richness of illite, iron and magnesium in MS1 suggests some contribution from mafic volcanic rocks in the source zone, which is clearly in the Ivorian crystalline basement. In contrast to MS1, MS2 is characterized by Ti/Y values greater than 0.017, a sign of richness



Figure 4. Chemostratigraphic profile of sediment sources from wells LEO-2X, LEO-3X, and LEO-5X.

in Ti relative to Y. This decrease in Y content in this mega-sequence is consistent with Th/Al values below 1.588. These changes indicate a shift in the source of the sediments. The marine transgression, identified as responsible for the changes in the depositional environment between MS1 and MS2, would clearly be the cause

of the change in sedimentary zone. Indeed, with the marine arrivals, the depositional environment was flooded and probably distanced from the sediment source. New sedimentary provinces will therefore bring the detritus into the depositional environment (**Figure 5**). Also, hydrodynamics caused by wave forces and the arrival of marine waters will control sediment transport and deposition in the depositional environment. It would then be a source richer in titanium oxides, which could be rutile, sphene or anatase. In addition, the new sediment source is poorer in Th- and Y-bearing phosphates, which could be apatite, monazite or xenotime.

5. Discussion

In this study, from a chemostratigraphic point of view, the inversion of the evolution curves of the ratios of key chemical elements was one of the first criteria



Z : Zonation ; S S : Stratigraphic stage

Figure 5. Chemostratigraphic profile of the bioproductivity of wells LEO-2X and LEO-3X.

for identifying the sedimentary sequences and their respective limits. Associated with this criterion is the evolution of the ratios K/Al; Mg/Al; Ti/Al; Rb/Al; Ti/K; SO/Al; Y/Al; Ti/Nb; Ti/Th; Th/Al; Fe/Al, whose rise in values, in the direction of sedimentation, followed by a sudden drop in these values corroborates the transition from one sequence to another. Naturally, this is also reflected in a fall in the average of these ratios in the same direction. SiO_2 content in fine-grained rocks is controlled by silicate minerals, particularly, quartz, which is the main constituent of most clays [16]. [17] reports that the presence of quartz in sediments indicates that the shoreline is relatively close. This confirms the use of Si/Al and K/Al ratios as a criterion for identifying sedimentary sequences, in this study. The work of [18] confirms the methodological approach of this present study., according to these authors, increases in silicoclastic minerals associated with elements such as Si, Ti, Al, Fe, and K (residing mainly in quartz, clay minerals and accessories silicates) and ratios of elements such as Si/Al (quartz), Ti/Al (ilmenite, titanite, anatase, rutile, brookite) and Zr/Al (zircon), are indicative of elevated silicoclastic fluxes during regressive periods and low sea levels. Decreases in these ratios are typically associated with periods of sea-level rise [18]. The megasequence 1 (MS1) sediments from our wells are characterized by very high potassium content relative to aluminum. Al₂O₃ is a relatively stable element in environments with intense chemical weathering, whereas MgO, CaO, Na₂O and K₂O are easily leached in similar parameters [13], so [19] uses Al_2O_3 on a ratio basis as an indicator of the degree of chemical weathering. In some studies, feldspars are used to differentiate provenance, but only in conjunction with heavy mineral data, and where the effects of chemical and physical attack are minimal [13]. The sediments of this megasequence, which predominantly correspond to Albian stratigraphic stages, would therefore have been deposited in a proximal environment. These results corroborate those of [7], who argue that in this interval, the sediments were deposited in an internal platform-type environment with continental influence. The sediments of megasquence 2 (MS2) correspond to the upper stratigraphic stages, *i.e.* from the Cenomanian to the Maastrichtian. The Ceno-Turo interval of the wells is characterized by a relative drop in potassium content, indicating the alteration of K-rich sediments, and hence their dissolution. This marks the transition from a proximal to a frankly marine environment, corroborating the work of [7], who argues that the Turonian interval saw a decline in the planktonic population and the appearance of benthic forms with elongated tests, reflecting a decrease in oxygen levels. Also, during sedimentation of the Balhoul Formation at the Cenomanian-Turonian transition, redox conditions were highlighted by [20] on the basis of V/Al and U/Al ratios. High levels of Mo (average 6.8 ppm) and V (average 90 ppm) are observed at the surface of sediments deposited during the ZOM [21]. For [20], the higher relative values of V/Al; Mo/Al, U/Al, Cu/Al, Ni/Al ratios in Tunisian black shale samples militate in favor of their strongly reducing character. U abundance always correlates well

with organic carbon content in [22] and with organic carbon in non-sulfide anoxic facies [22] [23]. The high P/Al and Ba/Al contents observed by [16] in Tunisian black shales suggest for this author a deposit in a high-productivity context. In this study, we also found an increase in dinocyst, indicating the presence of a marine environment. Moreover, according to [24] and [25], the appearance of keeled forms indicates a relatively deep environment. All these data suggest a depositional environment of medium to outer platform type. The Lower Senonian interval is characterized by a progressive increase in potassium content. There is thus a slow enrichment in detrital minerals, which would indicate an approaching coastline. These results corroborate those of [26], who argue that in this interval, the predominance of spores and pollen grains and the scarcity of peridinioid cysts reflect an environment relatively closer to the coastal domain. In the upper interval, there is an alternation of potassium richness and poverty, as well as a low proportion of glauconia and detrital minerals, which would be characterized by an intermediate depositional environment. These results are in line with those of [26] who indicate that peridinioid cysts are abundant in the upper part (Campanian-Lower Maastrichtian), which reflects open sea conditions due to the abundance of algal phytoplankton. It is therefore an environment where sea salinity is generally normal. We conclude that in the various boreholes, depositional environments vary from the inner platform under predominant continental influence during the Albian to the middle to outer platform during the Turonian, then open sea conditions from the Upper Senonian to the Maastrichtian.

6. Conclusions

The results of this study applied to sediments located to the east of the Abidjan margin lead to the following conclusions:

From a sedimentological point of view, the sediments were deposited in an environment with continental and reductive influences for those dating from the Albian, and in a marine, anoxic and continental-influenced depositional environment for those from the upper stage, *i.e.* from the Cenomanian to the Maastrichtian.

As for the Chemostratigraphy data, threshold values for ratios of chemical elements indicative of source (Zr, Ti, Y, Th) and paleoenvironment (K, Rb, Mg, Al,) enabled us to highlight the MS1 and MS2 mega-sequences in the study area. The difference observed in the threshold values of these ratios can be explained by changes in sedimentary dynamics. They revealed stratigraphic landmarks of large unconformable surfaces in the Ivorian sedimentary basin. The threshold values of the K/Al, Fe/Al, Mg/Al, Th/Al and Ti/Al ratios were used to identify the Albo-Cenomanian unconformity caused by the major Cenomanian transgression. This transgression is observed in the ratios of a change in depositional environment and sediment source between the MS1 mega-sequence (proximal environment) and the MS2 (distal environment).

Perspectives

The results obtained from sedimentological and geochemical studies of sediments to the east of the Abidjan margin have enabled us to define important stratigraphic landmarks. In the Ivorian sedimentary basin, it is therefore worth considering:

- XRD analyses to identify the various mineralogical associations present;
- studies to apply the conclusions of this study to the west of the Abidjan margin, and finally to the entire sedimentary basin for correlation.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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