Lithological, Chemical and Mineralogical Revision of Ypresian Attapulgite Formations of Allou Kagne (Thiès, Western Senegal)

Arfang Lamine Soumaré[1], Mouhamadou Bachir Diouf[2], Mamadou Fall[3]

Laboratory of Sedimentology and Biostratigraphy, Department of Geology, Faculty of Science and Technology, University Cheikh Anta Diop of Dakar, Senegal

Abstract: ***The chemical characterisation of Allou Kagne attapulgite ore according to the $CaCO_3$ content, allowed to highlight three main facies: attapulgites, calcareous attapulgites and marls. This lithological diversity would be the result of processes of leaching, hydrolysis and decarbonation more or less controlled by the structural context of the site. Mineralogical X-ray diffraction (XRD) and chemical X-ray fluorescence (XRF) analyses were carried out on hundreds of drillings distributed at the foot of Thiès cliff (western Senegal). The results show that Allou Kagne attapulgite ore is a combination of several phyllosillicates (palygorskite, smectite and sepiolite) whereas they were formerly considered as hormites associated with quartz, opal and past gypsum.***

Keywords: Allou Kagne,lithostratigraphy,phyllosillicates, attapulgite, mineralogy.

1. Introduction

Previous studies carried out in the region of Thiès show that the lower Eocene presents bottom to top_attapulgites, marls and limestones intercalated by marly benches. These facies, particularly well expressed at the foot of Thiès cliff, have been recently assembled in a single lithostratigraphic unit called the Formation of Thiès [1]. The attapulgites correspond to the horizon of Tiemassas described by [2] and renamed Tiemassas member of the Formation of Thiès [1]. The appearance of an ostracod fauna and *Globorotaliarex* Martin [3] allowed to date the lower Eocene. The study area is located between the horst of Ndiass and the Thiès cliff, which was the site of a tectonic event involving a NNE-SSW fault-system.

As part of this work, we studied five hundred (500) cores drillings in the Allou Kagne area. Mineralogical and chemical analyses were carried out in the attapulgite series of the foot of Thiès cliff in Allou Kagne (Thiés, Senegal), with the aim of refining the lithological, chemical and mineralogical characteristics of Tiémassas member. This latter has been sometimes described as papyraceous clays, foliated marls and sometimes as foliated clays.

2. Material and methods

The attapulgite deposit of Allou Kagne is located at the foot of the Thiès cliff, which is a soft cuesta situated in the West of Thiès city (Fig. 1). The cartographic data of the study area come from the database of GCWD (Geographic and Cartographic Work Direction) of Senegal updated in July 2017.

The ALS Minerals Laboratory of Johannesburg (South Africa) carried out the X-ray fluorescence (XRF) analysis, used to determine the chemical composition of the major elements oxides. In addition, the total rock analyses were made depending on the colour of the attapulgites.

Concerning the X-ray diffractometry (XRD), it was performed in the Tolsa Group laboratory in Madrid, by means of a SIEMENS D8 ADVANCE device.

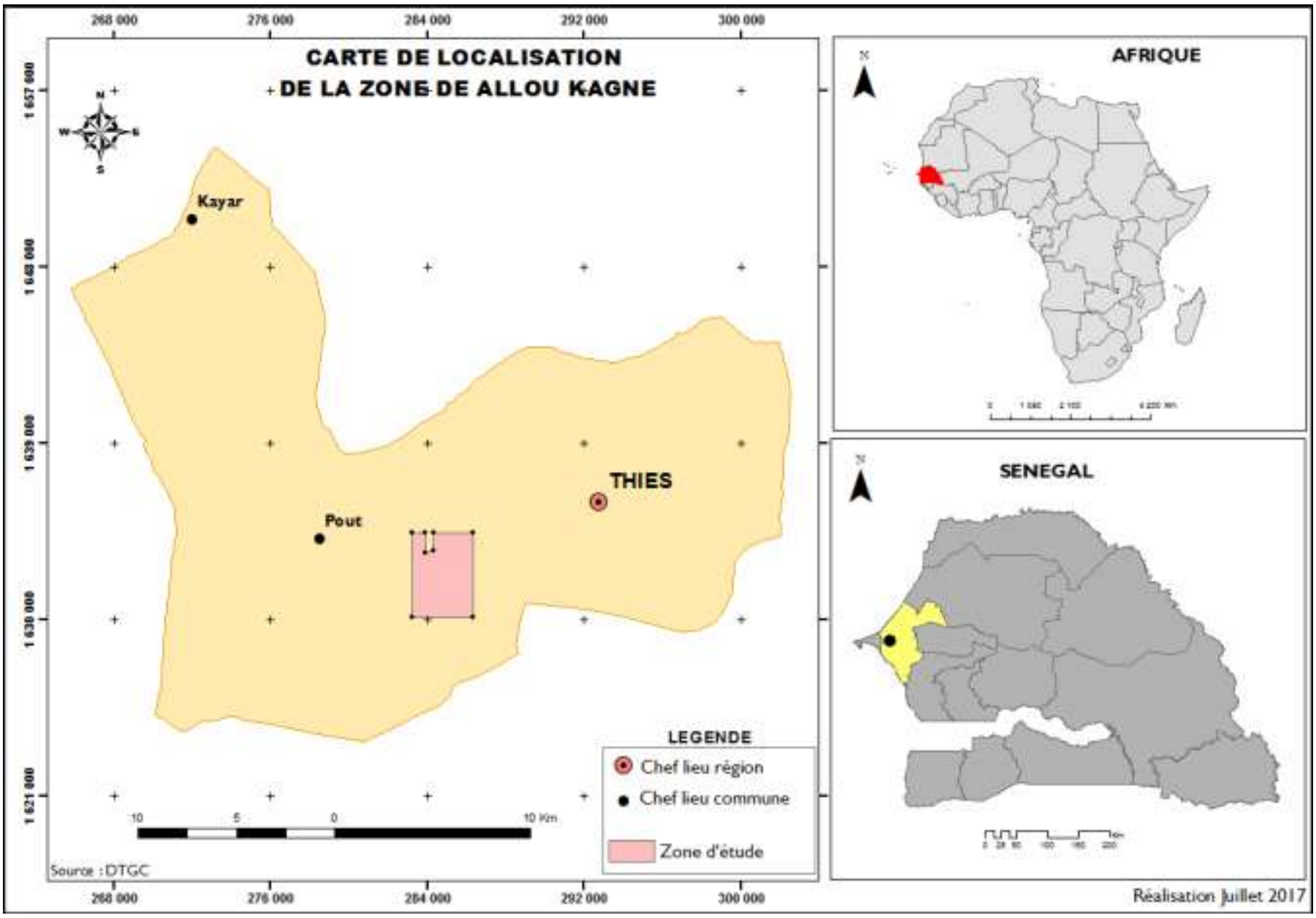


Figure 1: Location map of the study area (Geographic and Cartographic Work Direction of Senegal)

3. Lithological and chemical study of Allou Kagne attapulgites

In the study area, the attapulgites deposits, resting on the karstic limestone of the Palaeocene, form a geological key bed in the lower Eocene (Ypresian). Locally, the series is covered with a black grey clayey soil to lateritic fines gravels. For a good lithological characterisation of the various facies identified, we used the table of terminology of sedimentary rocks from calcareous to clayey pole, (Table 1).

Table 1: Terminology of sedimentary rocks from calcareous to clayey pole[4].

Limestone content (%)	100-95	95-65	65-35	35-5	5-0
Rocks	Limestone	Clayey limestone	Marl	Calcareous clay	Clay (attapulgite)

3.1. Allou Kagne attapulgites

In the West of the study area, the attapulgites with low calcium carbonate (Fig. 3) show monotonous aspect with flint intercalations in the form of lenticular benches or nodules. The attapulgites are finely bedded and strongly jointed, giving the appearance of crushed rock. They are in the form of a single horizon with a low $CaCO_3$ content (between 0 and 5 %) and present also flint nodules. We have also noted the presence of the gritty-phosphatic level. The associated fauna is identical to that found throughout the study area and includes internal moulds of lamellibranchs, sea-urchin tests and fish teeth.

3.2. The marly attapulgites and the marls of Allou Kagne

In the East of the study area, the calcareous clays and the marls (Fig. 2) are recognized by their rigidity and whiteness. This series has a thickness over 20 m at Allou Kagne. It is interbedded by 10 cm thick fossiliferous gritty-phosphatic calcareous level, at an average depth of 15 meters. The $CaCO_3$ content permits to distinguish two horizons: an upper horizon, with $CaCO_3$ contents between 5 and 35 % represented by calcareous clays and a very carbonated lower horizon with $CaCO_3$contents ranging from 35 to 45 % representing the marls. The base of the series is intercalated by frequent levels of flint of some centimetres in thickness. However, the summit of these calcareous clays is intersected by a second ochre gritty-phosphatic level of a few centimetres. These gritty-phosphatic levels contain various fossils (fish teeth, lamellibranch valves, sea-urchin tests) which are allochthonous deposits probably reworked from the limestones of the Palaeocene that outcrop on the eastern flank of the Horst of Ndiass. These different facies (attapulgite, calcareous clay and marl) can have an ochre colour, which distinguishes them from others. The latter is doubtless due to the presence of iron oxides in the ore. These facies would therefore result from a syn-sedimentary oxidation and would probably reflect a shallow depositional environment. This suggests that the calcareous clays and the underlying white marls would be deposited in a deeper environment. In this upper unit, the fossiliferous gritty-phosphatic level is ochre and associated with lateritic fine gravels. The fauna associated with this level includes fish teeth, small lamellibranch shells, and spicules of sea-urchins. This gritty-phosphatic level, encountered both in the East and in the West of the study area, allows to follow the evolution of the sedimentation conditions. Concerning the phosphatic occurrences, they constitute lithological key beds and seem to announce the establishment of the geodynamic conditions of the phosphatogenesis during the middle Eocene.

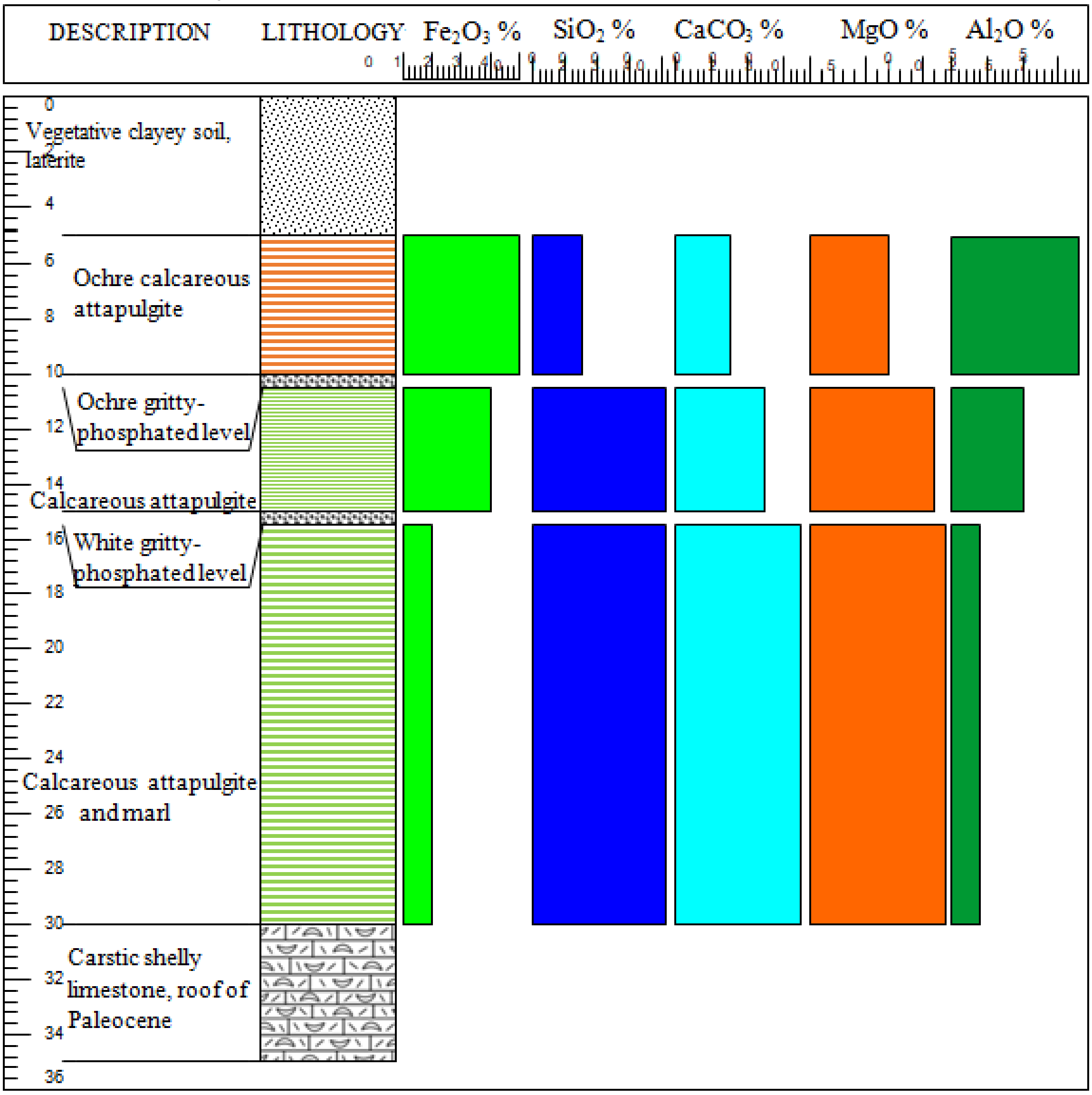


Figure 2: Lithostratigraphic and chemical characterisation of attapulgites of the eastern sector of the study area

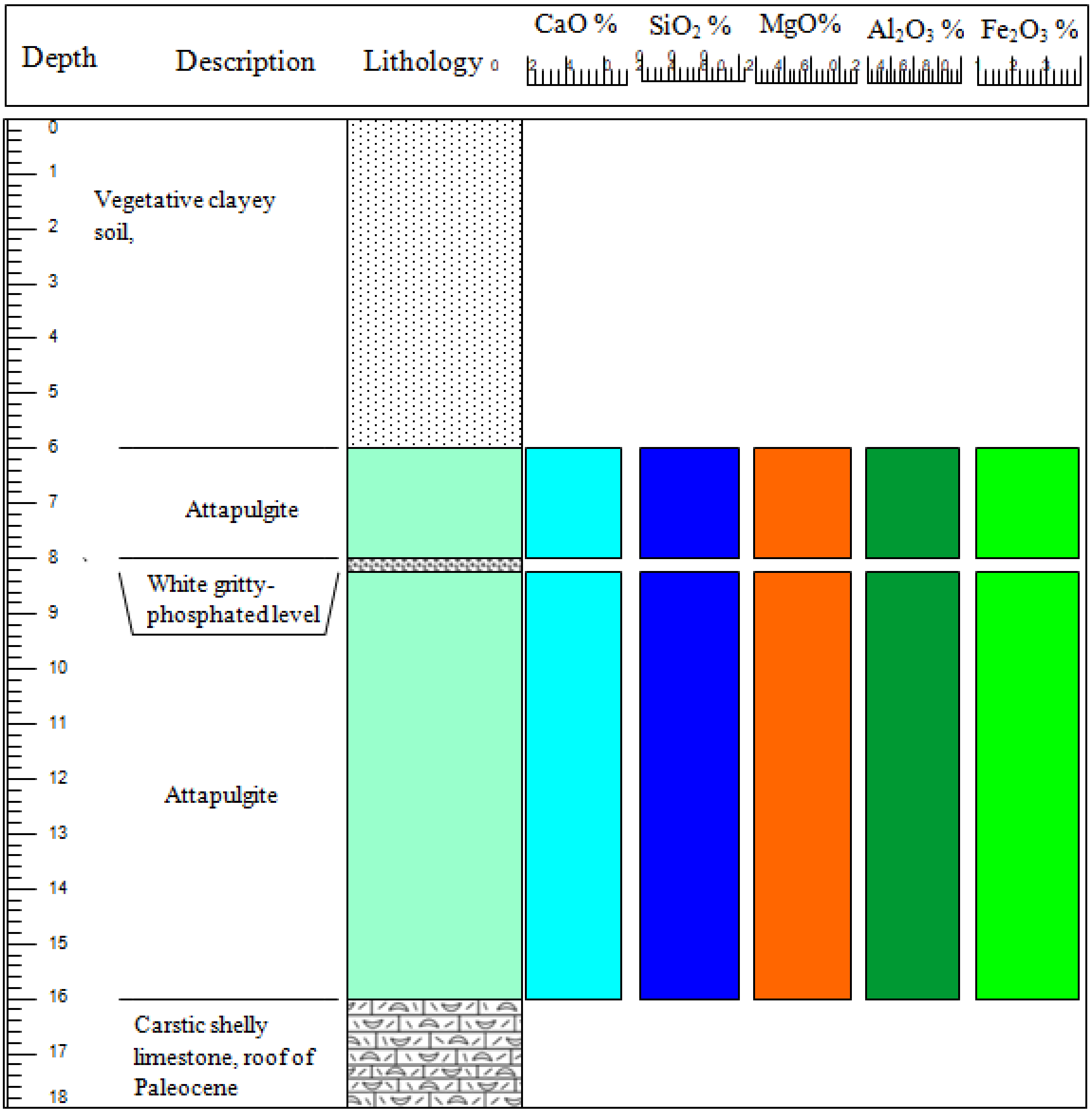


Figure 3: Lithostratigraphic and chemical characterization of attapulgites of the western sector of the study area

4. Chemical characterisation of Allou Kagne attapulgites

4.1. Spatial distribution of calcium carbonate contents in Allou Kagne attapulgites

The distribution map of calcium carbonates shows a lateral variation of the carbonate contents (Fig. 4).

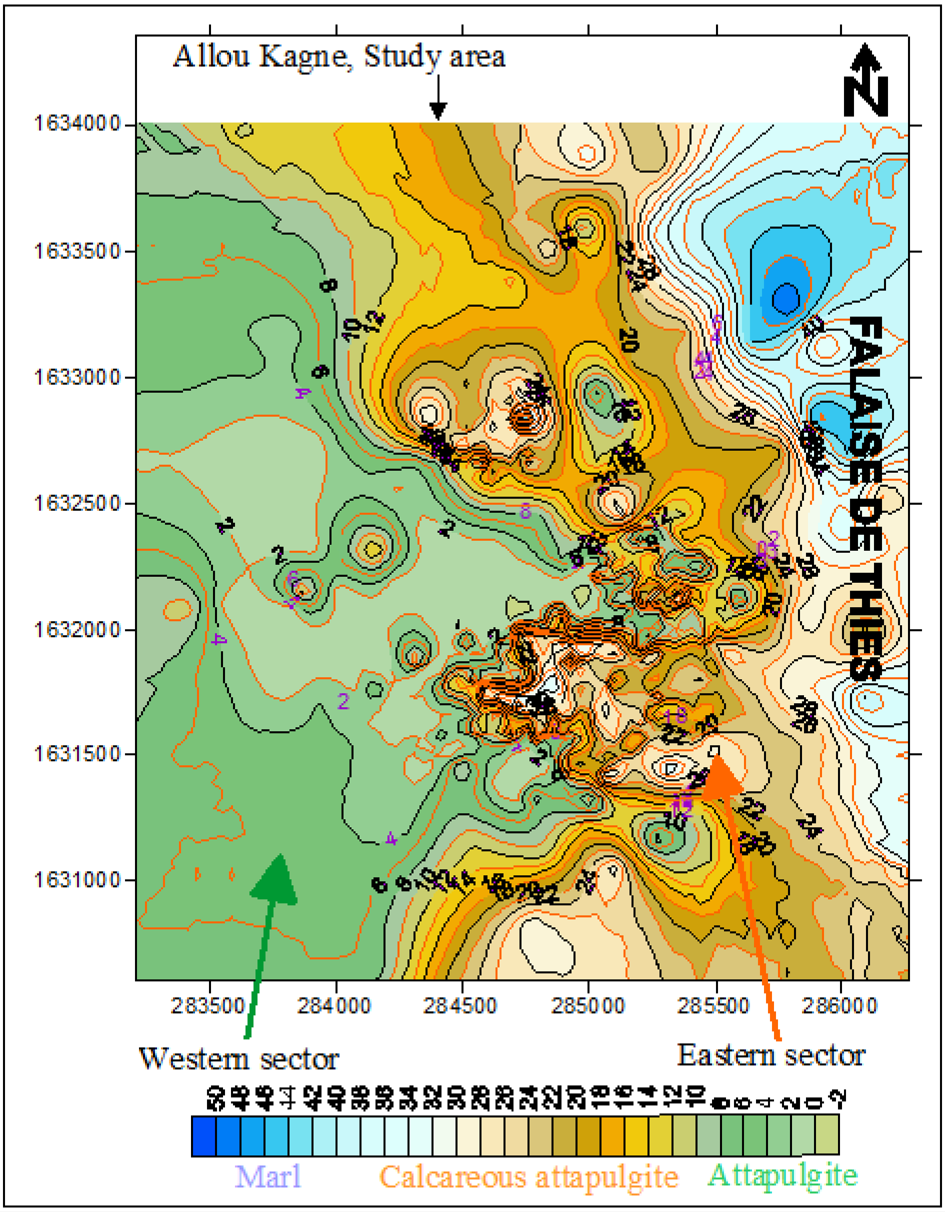


Figure 4: Lithological variation based on the $CaCO_3$ content

The isovalues show a low concentration of $CaCO_3$ (ranging from 0 to 5 %) in the West zone, but which increases towards the East, zone of the attapulgites formation.

As for the centre zone, the $CaCO_3$ contents range from 5 to 30%, with a carbonate enrichment gradient showing two bands from West to East: a first band characterised by 5 % < $CaCO_3 \leq 10$ %); a second one with 10 % < $CaCO_3 \leq 30$ %, corresponding to the formation zone of the calcareous attapulgites. Finally, a last band in the East with $CaCO_3$ content over 30 %, representing the marl sector. Consequently, the lateral variation of the $CaCO_3$content has allowed to highlight three lithological facies present in Allou Kagne (attapulgites, calcareous attapulgites and marls).

4.2. Oxide composition of attapulgites (XRF)

Four (04) samples were analysed by X-ray fluorescence (Table 2).

Table 2: Major elements chemical composition of the attapulgite samples of Allou Kagne

Samples	Al_2O_3 %	CaO %	MgO %	SiO_2 %	Fe_2O_3 %
Attapulgite (western sector)	7.77	1.59	6.09	62.59	4.14
Ochre attapulgite (eastern sector)	8.95	5.38	7.22	52.24	4.35
Calcareous attapulgite (eastern sector)	5.13	11.85	11.40	41.35	2.69
Marl (eastern sector)	2.31	17.20	11.85	40.75	1.40

In the eastern sector, the attapulgite series is characterised by a high concentration of CaO (17 %) and of MgO (11.85 %), contrary to those of the western sector: CaO (1.59 %) and MgO (6.09 %). The ochre attapulgite is rich in Fe_2O_3 and Al_2O_3 compared to calcareous attapulgites and marls. These differences in the composition of the oxides seem to reflect different conditions of sedimentation and/or evolution. Compared to two attapulgites of references (Table 3), those of Allou Kagne are very heterogeneous.

Table 3: Quantitative chemical analysis of the attapulgites of the study area and of two attapulgites of references

Oxides	Attapulgite %	Marl %	Ochre attapulgite %	Attapulgite of Attapulgus, GA, USA[a] %	Attapulgite of Torrejon (Espagne)[b] %
Al_2O_3	7.77	2.31	8.95	9	10
CaO	1.59	17.20	5.38	2	NR
MgO	6.09	11.84	7.22	10	12
SiO_2	62.59	40.75	52.24	54	52
Fe_2O_3	4.14	1.40	4.35	3	5

NR: not reported
[a][5]
[b][6]

The slightly carbonated attapulgites of Allou Kagne are more siliceous than those of USA and Spain. Different hypotheses have been made on the origin of the silica in the ore. It is generally considered that the biogenic silica disseminated in the sediment (spicules of sponges of shallow environments, tests of radiolaria of pelagic environments, ...) dissolves and precipitates in the form of opal.

The attapulgites are formed by precipitation of ions in solution (Si, Al, Mg, Fe, ...) in a confined and basic environment [7]. These chemical elements may react between them and the minerals formed are stable in the physico-chemical conditions in which they originate.

4.3. Processes involved in the decarbonation of the attapulgite series

The decarbonation leads to the solubilization of limestones and dolomites generally under the action of CO_2 dissolved in water. The results of chemical analyses show the progressive passage from slightly carbonated attapulgites of lower stratigraphic levels to calcareous attapulgites of upper levels and at the end to the marls of the foot of the Thiès cliff. The chemical characterisation of this series based on the $CaCO_3$ content has also allowed to highlight an increase of the carbonate contents *per descensum* **(Fig. 2)**.

The attapulgite series of Allou Kagne formed in a calm and shallow marine environment, unfavorable to the life. A biostasis regime reigning on the continent causes a syngenetic process of enrichment of the sedimentation environment in calcium and silica. This would explain the correlation between the carbonation and the progressive silicification of attapulgites. The lateral circulation of the water within the landscapes would be favoured by the structural context characterised by several generations of faults, some oriented NS, others oriented NE-SW to WE [8] - [9]. Finally, the landform of Allou Kagne area is determined by third generations faults of variable directions (NS, EW, ...). Thus, in the western sector located lower than the east sector, the attapulgite series are subjected to more intense leaching, hydrolysis and decarbonation phases.

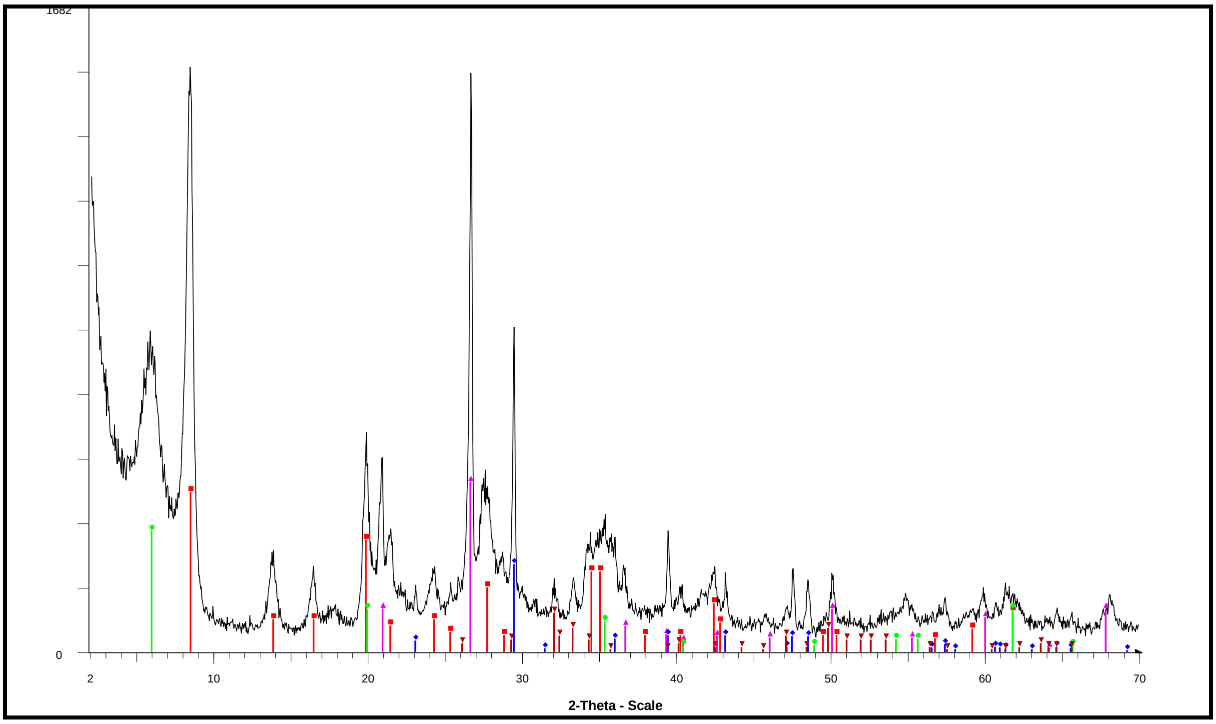
5. Mineralogy of Allou Kagne attapulgites

The results of the examination of different diffractograms of gross samples, from the eastern sector of the study area, analysed by X-ray diffraction (XRD) are mentioned in Table 4.

The ochre attapulgites are characterised by the presence of two phyllosilicates (palygorskite and smectite) (Fig. 7) and low contents of calcite, dolomite and silica (quartz and opal) (Figs. 5, 6 and 7).

Table 4: Semi-quantitative estimation by X-ray diffractometry on disoriented powder of samples of the eastern sector of Allou Kagne

Samples	COMPOSITION %								
	Phyllosilicates				Quartz	Opal	Calcite	Dolomite	Fluorapatite
		Attapulgite (palygorskite)	Sepiolite	Smectite					
Ochre attapulgite	90	58	0	42	5	1	4	0	0
Calcareous attapulgite	48	70	28	2	1	13	9	29	0



Smectite-Attapulgite-Calcite-Quartz-Opal.

Figure 5: Diffractogram of the ochre attapulgite sample

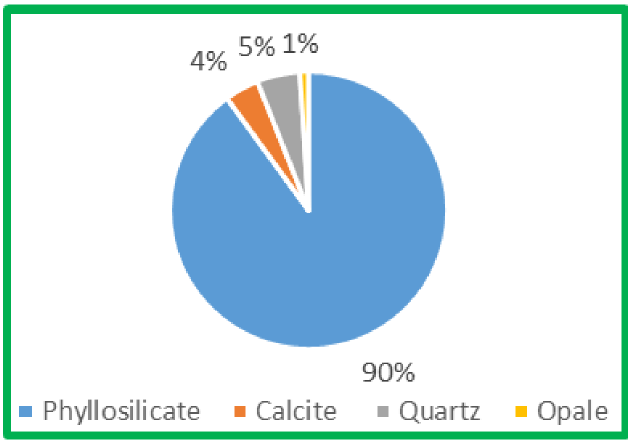


Figure 6: Mineralogical composition of the ochre attapulgite sample

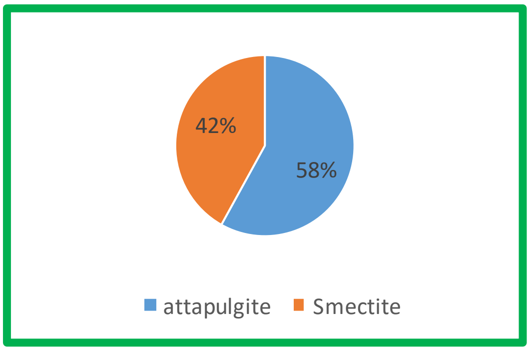
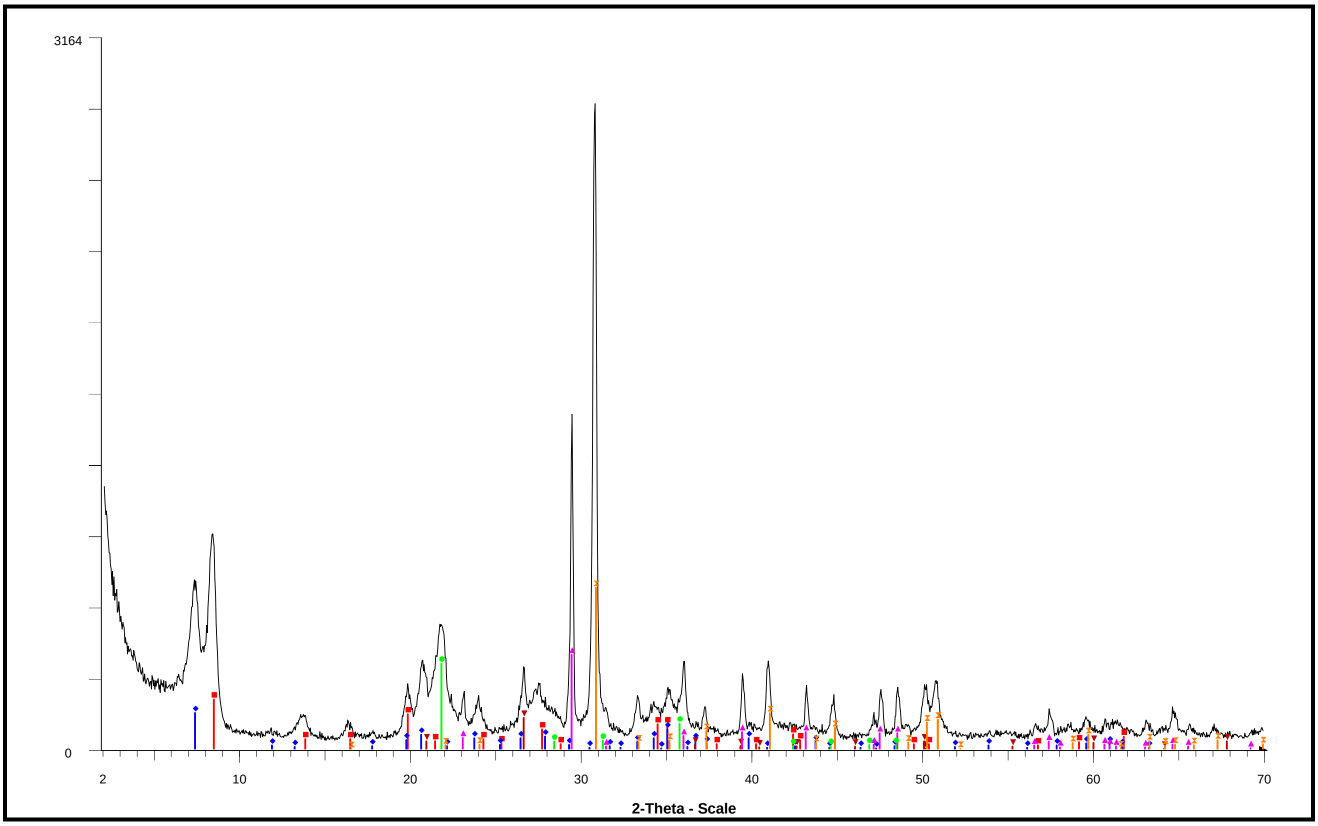


Figure 7: Importance of phyllosilicates in the ochre attapulgite sample

The clayey fraction of the calcareous attapulgite is composed of three phyllosilicates (palygorskite, sepiolite, smectite) (Fig. 8). This ore is enriched in carbonates (calcite 9 % and dolomite 29 %), (Fig. 9). These latter are responsible for the high $CaCO_3$ content (between 5 and 35 %) in the attapulgite series.

Paper ID: ART20179594 DOI: 10.21275/ART20179594



Sepiolite-Attapulgite-Calcite-Quartz- Opal-Dolomite.

Figure 8: Diffractogram of the calcareous attapulgite sample

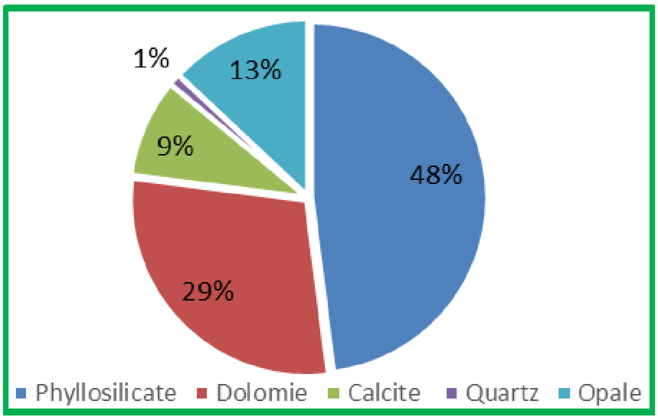


Figure 9: Mineralogical composition of the calcareous attapulgite sample

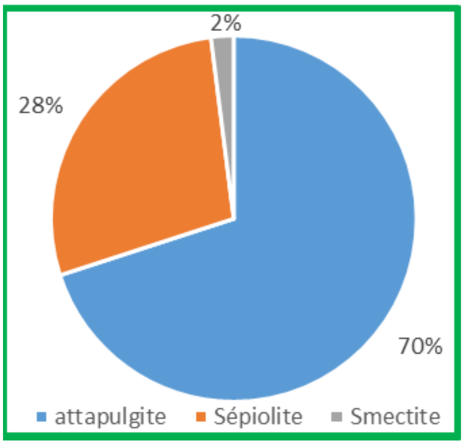
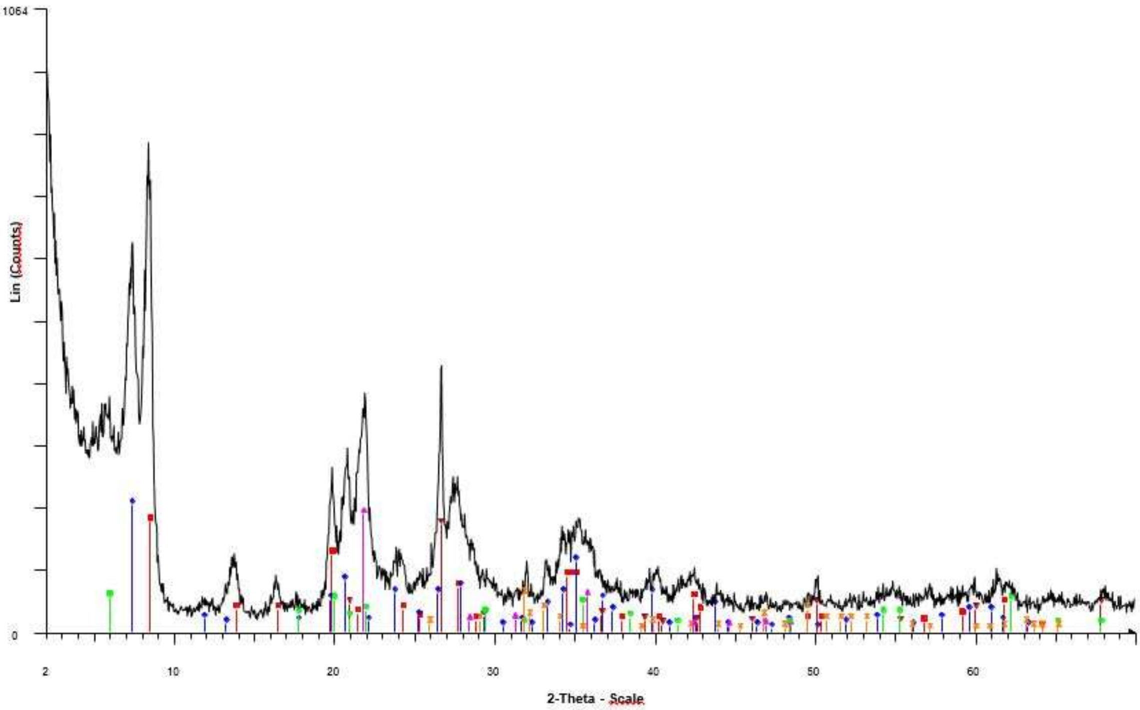


Figure 10: Importance of phyllosilicates in the calcareous attapulgite sample

In the eastern sector, the sedimentation begins with a level of marl with a small clayey fraction (48 %) (Figs. 9 and 10) consisted of sepiolite, palygorskite and a low percentage of smectite. Above the bed key, the ochre calcareous attapulgite, rich in iron oxides, is characterised by the absence of the sepiolite and an increase of the smectite content. So, the sedimentary environment would be shallow and open.

In the western sector, the result of the examination of the five (05) samples is mentioned in Table 5. The attapulgites, which were formerly considered as hormites (palygorskite and sepiolite) by [10], are characterised by the presence of the three phyllosilicates: palygorskite, sepiolite and smectite. A study of [11] on the sedimentary series of the Ouarzazate basin (southern Morocco) shows that the palygorskite of carbonated bars represents 50 to 75 % of the clayey fraction. In this upper unit, this mineral is always associated with sepiolite and sometimes with smectite. The phyllosilicates (palygorskite, sepiolite, smectite) form in badly drained and rather alkaline soils [7], [12]. As in this morrocan basin, in Allou Kagnethe palygorskite is also associated with smectite and sepiolite, especially in this sector (Fig. 11 and 12). Many researchers have studied these basic or alkaline conditions which are favourable to the neoformation of phylosilicate: high pH (9 - 11), high Si and Mg activity, and low Al activity [13]. The neoformation of attapulgites in calcimorphic soils or pedologic calcareous crusts [14] and in the basic series [15] - [16] has been widely studied.

The results of chemical and mineralogical analyses confirmed all, the presence of the chemical elements used in the mineralogical composition of phyllosilicates (palygorskite, smectite and sepiolite), of minerals of chemical precipitation (calcite, dolomite, quartz and opal).



Smectite-Sepiolite-Attapulgite-Quartz-Opal

Figure 11: Diffractogram of the attapulgite sample

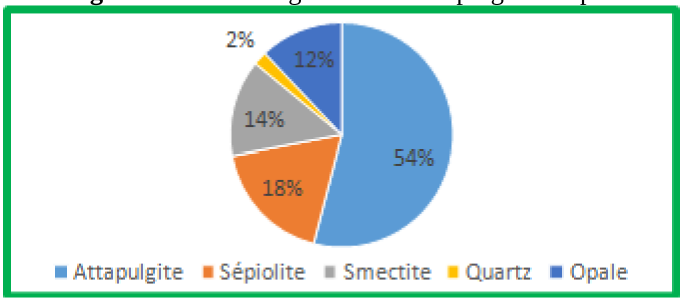


Figure 12: Mineralogical composition of the attapulgite sample

Table 5: Semi-quantitative estimation by X-ray diffractometry on disoriented powder of attapulgite samples of Allou Kagne attapulgite ore

SAMPLES	COMPOSITION %							
	Phyllosilicates	Palygorskite	Sepiolite	Smectite	Quartz	Calcite	Dolomite	Opal
Attapulgite 2	86	54	18	14	2	0	0	12
Attapulgite 4	85	50	15	20	4	0	0	12
Attapulgite 6	82	48	14	20	3	0	0	15
Attapulgite 8	77	35	23	18	3	0	0	20
Attapulgite 10	79	31	29	20	3	0	0	18

6. Model of formation of Allou Kagne attapulgites

Considering the lithostratigraphic, chemical and mineralogical arguments, a formation model of attapulgites of Allou Kagne can be proposed. In this sense, several works (Elouard 1966 *in* [17]; [18] and [9]) have mentioned the context of the deposit of attapulgites in western Senegal. Very early, Capedecomme and Kublicki *in* [17] showed in 1954 that the characteristic mineral of the base of the phosphated formations of western Senegal is an aluminous and ferriferous palygorskite. The presence of glauconite indicates a marine environment, type continental shelf, and reducing sedimentation conditions. During the Palaeocene, the western zone of the Senegalese sedimentary basin is characterized by the presence of an irregular topographic bottom, with a gentle slope dipping towards the South-West. This pit was located in the East of the horst of Ndiass [9]).

The lower Eocene of the western zone of the Senegalese sedimentary basin begins with an increasingly clayey deposit which characterized by the predominance of attapulgites. This indicates a calm sedimentation environment, away from the shore [12], protected from pelagic influences by a shoal located on the West of the horst of NDiass in the Dakar region [18]. It is a series dominated by attapulgite clay, rich in glauconite, flint and phosphate at its base. At its summit, it is more marly and intercalated by clayey limestones. In Allou Kagne, this sedimentation begins with a level of marl and calcareous attapulgite with a low phyllosilicates contents. The sedimentation continues with the deposit ochre attapulgites, rich in smectite reflecting an oxidizing and shallow environment. In hot climate with alternance of wet and dry seasons, leaching and confinement alternating, smectite formed and silica remains in place. This clayey sedimentation is interbedded by gritty-phosphatic beds keys, witnesses of the reworking of the carbonated facies rich in fossils, which adjoin the horst of NDiass. The tectonic activities after the sedimentation of this series would be the cause of its decarbonation and enrichment in phyllosilicates (palygorskite, sepiolite and smectite). Therefore, the stratigraphically lower West zone is more rich in attapulgite. These sedimentation conditions will persist in the basin until the phosphate precipitation in the presence of Ca and Mg salts, between the middle Eocene and the Oligocene. The deposits of phosphated clays and clayey sand mark the uplift of Thiès plateau, which forms a shoal favour able to the phosphated sedimentation [18].

7. Conclusion

The chemical characterisation based on $CaCO_3$ content shows an increase per descensum of carbonate contents which decrease laterally from East to West. It also allowed to highllight three main lithological facies in Allou Kagne: attapulgites, calcareous attapulgites and marls.

As for mineralogical analyses, they show that the clayey fraction consists of three phyllosilicates (palygorskite, sepiolite and smectite). This attapulgite deposit is associated with minerals of chemical precipitation (calcite, dolomite, small amounts of quartz, opal and gypsum). The various tectonic events and the oxidation-reduction phases have an important role in the determination of the current quality of Allou Kagne attapulgites.

References

[1] J. Roger, B. J. Noël, J. P. Barusseau, O. Serrano, P. Nehlig, and C. Duvail, "Notice explicative de la carte géologique du Sénégal à 1/500 000, feuilles nord-ouest, nord-est et sud-ouest. Ministère des Mines, de l'Industrie et des PME, Direction des Mines et de la Géologie, Dakar, 61p.," 2009a.

[2] J. Elouard, "Attapulgites du Sénégal occidental," Labo. Géol. Fac. Sc., Dakar, Rapport Inédit, 1966.

[3] L. Castelain, "Aperçu stratigraphique et micropaléontologique du bassin du Sénégal. Historique de la découverte paléontologique," presented at the Coll. Micropal. Ouest-Africain, Dakar 63, 1965, pp. 135–160.

[4] A. Foucault, J.-F. Raoult, F. Cecca, and B. Platevoet, "Dictionnaire de Géologie." Dunod, p. 416, 2014.

[5] S. R. Patterson and F. M. Surface, "Clays," *In*Lefond J.S.ed., Industrial Minerals and Rocks (Nonmetallcs Other than Fluids) 4th Ed., New York, *American Institute Mining, Metallurgical, and Petrollum. Engineers*, pp. 519–585, 1975.

[6] E. Galán and A. Castillo, "Sepiolite-palygorskite in Spanish tertiary basins: genetical patterns in continental environments," *In* Singer, A. and Galán E.eds., Palygorskite-Sepiolite: Occurrences, Genesis Uses. *Developments in. Sedimentology. Elsevier Amsterdam*, vol. 37, pp. 87–124, 1984.

[7] J. Beauchamp, "Les Argiles," *Université de Picardie Jules Verne*, 2005. [Online]. Available: https://www.u-picardie.fr/beauchamp/mst/argiles.htm. [Accessed: october 24th, 2017].

[8] A. Martin, "Alimentation en eau de Dakar. Etude hydrogéologique du horst de NDiass," Thèse 3e Cycle et Rapport BRGM, Dakar, 1967.

[9] T. Miyouna, E. H. Sow, A. Diop, P. M. Ndiaye, and I. Niang Diop, "Evolution morpho-structurale et bathymétrique de la partie septentrionale du Bassin Sénégalais du Paléocène," *J. Sci.*, vol. 9, no. 1, pp. 1–16, 2009.

[10] E. Garcia-Romero, M. Suarez, J. Santaren, and A. Alvarez, "Crystallochemical characterization of palygorskite and sepiolite from the Allou Kagne deposit Senegal [J].," *Clays Clay Miner.*, vol. 55, no. 6, pp. 606–617, 2007.

[11] L. Daoudi, E. Jourani, and A. Knidiri, "Les argiles fibreuses des formations phosphatées du bassin de Ouarzazat (Maroc) : Caractérisation et Signification génétique.," *Covaphos*, vol. 5, no. III, pp. 30–41, 2009.

[12] M. Diagne, M. Fall, M. B. Diouf, N. P. Dione, and E. H. M. Samb, "Mineralogical Characterisation of the Sedimentary Phosphate Deposit of Tobène (Western Senegal)," *J. Shipp. Ocean Eng.*, vol. 6, no. 4, pp. 226–240, 2016.

[13] C. E. Weaver and K. C. Beck, "Miocene of the S.E. United States: A model for chemical sedimentation in a peri-marine environment," *Sediment Geol*, vol. 17, pp. 1–234, 1977.

[14] A. Singer, "Pedogenic palygorskite in the arid environment," *In Singer, A. and Galán E. eds., Palygorskite-Sepiolite:* Occurrences, Genesis Uses. *Developments in. Sedimentology. Elsevier Amsterdam*, vol. 37, pp. 169–175, 1984.

[15] E. Galán and A. Ferrero, "Palygorskite-Sepiolite Clays of Lebrija, Southern Spain," *Clays Clay Miner.*, vol. 30, no. 3, pp. 191–199, 1982.

[16] R. L. Hay and R. K. Stoessell, "Sepiolite in the Amboseli Basin of Kenya: a new interpretation," *In Singer, A. and Galán E. eds., Palygorskite-Sepiolite:* Occurrences, Genesis Uses. *Developments in. Sedimentology. Elsevier Amsterdam*, vol. 37, pp. 125–136, 1984.

[17] L. Wirth, "Attapulgites du Sénégal Occidental," Faculté des Sciences et Techniques, Université Cheikh Anta Diop de Dakar, Sénégal, 26, 1968.

[18] J. R. Lappartient, "L'Eocène inférieur de la partie septentrionale de la Cuesta de Thiès (Sénégal)," *Annales de la Faculté des Sciences de Marseille*, vol. 43, pp. 249–258, 1970.