

Clay Fraction in Mayo Kebbi (West-Chad): Physicochemical and Mineralogical Properties

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Abstract The samples used in this study were collected in the Mayo Kebbi region (western Chad). From a geological point of view, the Mayo Kebbi is a region with great potential. A lot of work has been done in this part of Chad. The aim of this study is to determine the proportions and types of minerals present in the $<2\mu$ m fraction of the study area, their physico-chemio-mineralogical properties, their origin and the paleoenvironmental conditions that prevailed during their formation. Mineralogical analyses carried out on bulk rock and the positive hydrochloric acid test revealed that the fresh rocks of the two profiles studied are limestones. X-ray diffractometric analysis combined with ethylene glycol treatments and heating performed on the $<2\mu$ m fraction of the collected materials, reveal the presence of smectitic type clay. The results obtained from these analyses reveal that smectite is the major mineral in these materials, with contents varying between 63 and 98%. It is associated with very low proportions of kaolinite (1 to 30%), illite (1 to 2%), and chlorite (1 to 5%). Quartz is the only non-clay accessory mineral identified. Geochemistry of these samples revealed that they consist primarily of SiO₂ (1.3-78.67 wt. %), CaO (50.81-0.3 wt. %), Al₂O₃ (18.25-0.37 wt. %), and Fe₂O₃ (0.09-6.52 wt. %). The pH is slightly alkaline for these materials. The CEC (Cation Exchange Capacity) and exchangeable bases oscillate between 9.23-13.95 and 6.4-10.53 meq/100 respectively. The saturation indice is between 6 and 24 and the residual moisture values between 1.94 and 10.99%. These mineralogical and physico-chemical properties of these clay-rich Mayo Kebbi's materials indicate that they can be used in many conventional clay applications. Furthermore, the findings of the geochemistry, the mineralogy of the bulk and $<2\mu$ m fractions, added to the consideration of some geological parameters suggest that the smectites of the Mayo Kebbi's area, in Western Chad, have a dual origin. One part of these smectites is formed during partial hydrolysis and erosion of the formations located on the slopes near the mayo. The second part is formed in situ. Moreover, the results also suggested that the smectites in the study area were formed in an area with low topography and in which the dominant alteration is bisiallitization.

Keywords: smectite, mineralogy, physicochemical properties, sudano-sahelian area, Mayo Kebbi west, Chad

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1. Introduction

Clay minerals constitute the most abundant part of the earth's crust (90% by mass; [1]). There is no one definition of the term clay. Indeed, the word "clay" includes two connotations, one related to grain size and the other to mineralogy. Ref [2] define clay as a mineral that dominates the fine fraction less than 2 microns in rocks and soils. The International Association for the Study of Clays (AIPEA) and the Clay Mineral Society refer to clay as any natural material composed of very fine particles (< 2 μ m), which becomes plastic with appropriate water content and hardens by drying or fritting [3,4,5,6]. Clays are likely to form in 3 ways: by inheritance,

by transformation, or by neoformation [7,8,9,10]. Inheritance consists in the contribution of phyllite elements formed elsewhere on the continent and transported either by water or by wind. The clays formed according to this model undergo only slight modifications of structure and composition during transport. In the second model, the clay minerals undergo rearrangements in their silicate networks without complete destruction of their previous organization. But they undergo during transport transformations which can be important, and which make pass from a mineralogical type to another, either by degradation or by aggradation [11,12]. These phenomena can take place in situ or during transport. In the case of neoformation, in contrast to previous models, clay minerals undergo a complete reorganization of their crystalline structure and are

formed by precipitation of ions in solution $(Si^{4+}, Al^{3+}, K^+; [12])$.

Clay minerals are classified into three major families, according to the International Association for the Study of Clays (AIPEA), namely: phyllosilicates, fibrous, and interstratified minerals. The phyllosilicates are clays which present phylliform structures. They are the most widespread and the most studied. This family is subdivided into three large groups [13], which are: (a) the 1:1 clay, to which belongs the group of kaolinites. Their basal distance is between 7.1 and 7.4 Å; (b) the 2:1 clay, this group includes micaceous clays, such as illites (constant thickness of 10Å) and vermiculites (variable thickness from 10 to 14Å), micas (biotite, muscovite), but also swelling clays among which smectites (montmorillonite, beidelite, saponite); and (c) 2:1:1 clay, it is about clays with low capacity of exchange such as chlorites. The thickness of the sheets is 14Å. As for fibrous minerals, they are subdivided into two subfamilies, including: palygorskites (also known as attapulgites) and sepiolites. The last family of clay minerals are minerals in which there are alternating layers of different nature (chlorite/vermiculite; illite/smectite/chlorite).

The study of the formation of clay minerals allows to obtain some information on the alteration and the climatic conditions, the type of source rock as well as an evaluation of the origin and the abundance of detritism [9,12,14]. The nature of the clays formed depends on several factors, including: the nature of the source rock, the topography, the climate [10,12].

Clay minerals are very necessary minerals, and their use goes back to many decades. Despite the years, they continue to be used as much or more. Clays are used in many fields. For example, they are used in the oil industry as a barrier to hydrocarbons or as a drilling mud [15]. In the agronomic field, they are used because they retain mineral substances essential to plant nutrition, thus influencing soil reserves [8]. In addition, some clay minerals are used to promote the retention in the soil of potentially polluting molecules such as pesticides and limit their dispersion in the natural environment. They also actively participate in the stabilization of soil organic matter [16]. Clay is the primary material used in the ceramic industry. It is in this sense used in the manufacture of bricks, tiles, porcelain, pottery, and tiles. Their use in cosmetology and pharmaceuticals is very old [15]. The smectites are for example exploited for the manufacture of many creams for dermatological care, powders, ointments, or shampoos. In the pharmaceutical field, they are used in pharmaceutical formulations or in the treatment of gastric ulcers [15].

In terms of mineral resources, Mayo Kebbi is one of the richest regions in Chad. The main mineral resources exploited are gold, uranium, oil, and limestone (major deposit sites identified in Louga and Baoaré). According to the July 2007 feasibility report for the establishment of the Baoaré cement plant, produced by the CAMCE (China CAMC Engineering Co), clay deposits are found in the localities of Baoaré and Margalao, with estimated reserves of 1 and 9 million tons respectively [17].

According to Ref [17], the study area is one of the most important limestone sites in Chad. In fact, most of the studies that have taken place there have focused on characterizing limestone as a raw material for the cement industry. Very few have characterized the $< 2 \mu m$ fraction of materials present in this area or conducted studies on clays in this region. The present study will therefore aim to determine the proportions and types of clay minerals present in the study area, their physico-chemio-mineralogical properties, their origin, and the conditions that prevailed during their formation.

2. Geological Setting

The sampling area is located in the Western Mayo Kebbi Region.

Formed during the Pan-African orogeny between 800 and 570 Ma, the Mayo-Kebbi massif in southwestern Chad is located between the Congo Craton to the south, the West African Craton to the west, and the Sahara metacraton to the east. Four major lithotectonic ensembles (Figure 1) are distinguished in the Precambrian basement of West Mayo Kebbi [18,19,20,21,22]. These are, from the oldest to the most recent: 1- the metavolcanosedimentary series of Goueygoudoum and Zalbi, 2- the mafic and intermediate complex, 3- the magmatic ensemble of the Mayo Kebbi batholith, and finally 4- the post-tectonic intrusions. These complexes are buried under sedimentary phanerozoic cover formations [22].

The greenstone belts include the Zalbi and Goueygoudoum metavolcanosedimentary series as well as the intermediate mafic complex. The constituent rocks of these greenstone belts are affected by greenschist-type metamorphism [22]. Ref [23] estimated the age of the Zalbi series to be approximately 777 \pm 5 Ma. This series comprises several petrographic types, including: metagabbros, metabasalts, metabasites, leucogneiss, chloritoschists, talcschists and serpentinites [23]. Structurally, it is characterized by the development of an N-S to NNE-SSW trending foliation bearing an E-W stretching lineation with extensions greater than 50° to the west [20]. This series extends into Cameroon in the Poli Group [24]. The Goueygoudoum series outcrops north of the town of Pala and is separated from the Zalbi volcano-sedimentary series by the Pala batholith [22]. Unlike the Zalbi series, outcrops of this series are rare, due to extensive Phanerozoic sedimentary cover [18,23]. Petrographically, the Goueygoudoum series consists of epi-metamorphic rocks of sedimentary, volcano-sedimentary, and volcanic origin. Located east of the Zalbi metavolcano-sedimentary series as an amphibolo-gneissic complex [25], the mafic and intermediate complex consists of metagabbros, metagabbros-diorites, and metadiorites. It also appears as enclaves in the Pala batholith.

The Pala batholith includes the Gauthiot Falls, Léré, and Figuil magmatic complexes. The Gauthiot Falls magmatic complex outcrops in the central part of the Mayo Kebbi and is dominated by a mylonitic-structured quartz metadiorite containing metagabbro septa. Then, the second complex corresponds to the central part of the Pala batholith and is mainly dominated by tonalites (biotite and hornblende). Finally, the Figuil magmatic complex is dominated by syntectonic tonalitic to trondhjemitic orthogneisses, separated from the Mafic and Intermediate Complex by the Figuil Shear Zone [22].



Figure 1. Geological map of Mayo-Kebbi in southwestern Chad [22]

The post-tectonic intrusions have a composition of granodiorite, granite, charnockite. They cut across all the previous lithotectonic sets and magmatic complexes. They represent the last magmatic manifestations associated with the Pan-African orogeny at the scale of the Mayo Kebbi massif and constitute the extension of the Poli series in Cameroon [22]. These are: G1 granitoids of the first generation, composed of quartzite gabbros with pyroxene or amphibole, quartzite diorites, granodiorites and tonalites; G2 granitoids, G3 granitoids (quartz leucocratic diorites, granitoids, and biotite tonalites), G4 granitoids (biotite and amphibole porphyritic granodiorites and granites), and G5 granitoids (pink Zalbie granite; [22]).

Among the sedimentary cover formations are the Léré and Lamé series. The Léré series consists of Lower Cretaceous formations, namely: conglomerates, arkosic sandstones alternating with Estéria shales [23]. The Lamé series is made up of formations of marine and continental origin from the Upper Cretaceous (Albian-Cenomanian; [26]). These are conglomerates, sandstones, arkoses, clays and lenses with lumachelles of lagoon origin. The limestones that outcrop between Baoaré and Louga, near the Cameroon border, have yielded mollusks (gastropods). Louga, the study area, belongs to the Lamé series.

3. Sampling and Analytical Techniques

The sampling area is located in southwestern Chad, following the geographical coordinates $9^{\circ}10'00''$ North latitude and $14^{\circ}22'60''$ East longitude.

Twelve (12) samples (8 for the first outcrop and 4 for the second) were collected in the Mayo Kebbi area, near the Cameroon-Chad border, from two outcrops located about 1 km apart. The first outcrop A1 is located at N09°08'43.4" and E14°24'39.8", at the bottom of a slope, at 346 m altitude on the bank of a mayo. From this outcrop, eight samples were collected, namely Rs1, L1, L2, L3, L4, L5, L6, and L7 at depths of 4, 3, 2.5, 2, 1.3, and 0.2m respectively. The second outcrop A2, 140 cm high, is located at N9°09'10.5" and E14°25'02.0", at an altitude of 357 m. Samples on this outcrop L8, L9, Rs2, and L10 were collected at the following depths: 1.3, 07, 04, and 01m.

The conditioning, crushing, and pulverization of the samples were done at the Laboratory of Alterology and Engineering Geology of the University of Yaoundé 1 (Cameroon). The attribution and determination of the colors of the different levels or samples was done using the Munsell code. The mineralogical composition on fine and total fraction was determined by X-ray diffraction (XRD) at the Geosciences Laboratory of the University of Lille (France). The disoriented aggregates were carried out according to the protocol of Ref [27] in order to avoid as much as possible, the orientation of crystallites. The <2 µm fraction was taken from the suspension following Stokes' law. A few cm² of sample were put in distilled water, then decarbonated with hydrochloric acid under magnetic stirring. The acidity of the solution confirms the total decarbonation. The deflocculation of the clayey material and the elimination of the excess of acid are carried out by successive rinses with distilled water between each stage of settling of the clayey material. After mechanical homogenization and a settling time of 50mn calculated according to Stokes law, the surface part (1 cm) of the solution enriched in fraction $<2 \ \mu m$ is taken with a syringe. The pipetted solution is then centrifuged (3500 rpm for 45 min). The recovered clay material is spread in a single direction on a grooved slide to orient the minerals. Qualitative and semi-quantitative measurements of the clay fraction were performed using a Brucker D4 Endaevor DRX diffractometer with copper anticathode. The goniometers are controlled by microcomputer using PC-APD and DIFFRAC Commander software for optimum 2 θ angles between 3° and 32°. The raw data are processed under MacDiff 4.2.5. These oriented aggregates were subsequently subjected to three additional successive treatments, including: air drying, glycolation, and heating to 500°C for 4 hours to identify and differentiate clay mineral types. Measurements are performed on a normal, heated, and glycolated sample. The examination of the 3 diffractograms with the Macdiff software allows a qualitative and semi-quantitative study of the clay minerals present on the thin slide. The method's error is estimated at 5% on the estimation of the percentage of each clay in the sample.

The principle of saturation with ethylene glycol consists in maintaining the preparations under vacuum overnight in a glass evaporator containing ethylene glycol. The replacement of the water occupying the interfoliar spaces by the ethylene glycol molecules of relatively larger size leads to the widening of the interfoliar spaces and consequently increases the reticular space corresponding to the basal reflection of the hydrostable clay minerals. Thus, that of smectite at 14Å in natural conditions, increases to 17 Å after this treatment [12-28].

The heating, carried out in a mold oven, ensures a homogeneous and precise temperature. It provokes either the departure of the OH of structure, or that of the water molecules which occupy the interfoliar space of the hydrostable clay minerals. After firing at 520°C for

1h30mn, the reticular distance of smectites will decrease in an irreversible way from 14 to 10Å. This same treatment also has the effect of disorganizing the crystal lattice of kaolinite. It will no longer show any reflection at 7Å. Chlorite, which has remained stable, can be distinguished from kaolinite by its rays at 7Å and 14Å [28].

Chemical analyses were performed by emission spectrometry (Sudbury, Canada). The 12 samples were crushed in a tungsten mill to obtain a fine powder. An aliquot was heated to 1050° C in a furnace to determine the loss on ignition (LOI) and to oxidize all iron. The cooked product, approximately (1.2g) was mixed with an appropriate amount of Li₂B₄O₇ (6.0g) melted for 5 minutes in a Pt crucible and dissolved in nitric acid. Major elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Analytical uncertainties were estimated at 1-5% for most samples.

The ammonium acetate method made to determine cation exchange capacity values.

4. Results

4.1. Lithological Descriptions

The present study was conducted on two outcrops, located in an area near the Chad-Cameroon border, and the description of the two outcrops is presented in the following lines. Twelve (12) samples were collected. The bedrock in this area is easily exposed.

The first outcrop has a depth of 430m. This outcrop is divided into 07 levels (Figure 2), which are from the base to the top: the first level (430- 300 cm) corresponds to that of the fresh rock which is a carbonated rock (it reacted by effervescence to hydrochloric acid). This rock is overlain by loose formations: from 300 to 250 cm, a very pale brown sandy-silt level; from 250 to 200 cm, a light brown sandy-silt level; from 200 to 130 cm, a light yellow sandyclayey-silt level; a light grey sandy-silt level of 70 cm thick (130 to 100 cm); a light brown sandy-silt level of 50 cm thick (100-50 cm). The passage to the upper level is progressive; and light brownish-gray sandy-clayey-silt level of 20 cm thick. This level is characterized by strong biological activity. It is covered by a layer of thin organic matter, consisting of yellowish or brownish leaves and friable twigs. Corresponding to the different levels, eight (08) samples, namely Rs1, L1, L2, L3, L4, L5, L6, and L7, were taken from this outcrop at respective depths of 4, 3, 2.5, 2, 1.3, 1, and 0.2 m.

About 1km from the previous outcrop, the second outcrop is located on a hillside at a height of 357m. It is differentiated in 4 levels; which are from the base to the top: (1) a pale yellow silty-clay level, 70 cm thick (140-70 cm) followed by (2) a light brown silty level, 30 cm thick (70-40 cm); from 40 to 10 cm is a carbonate rock, the fresh rock of this second outcrop. It is a medium-grained rock, whitish to beige in color. This outcrop ends with a light brown sandy-clay-silt level. This level is marked by root development and strong biological activity (presence of termites and earthworms). Four samples were taken from this outcrop, namely: L8, L9, Rs2, and L10 at respective depths of 1.3, 0.7, 0.4, and 0.1 m.



Figure 2. Morphology of profiles of the Mayo Kebbi's samples: A- limestone (fresh rock); B- very pale-brown sandy-silt layer; C- light brown sandy-silt layer; D- light yellow sandy-clayey-silt layer; E- light gray sandy-silt layer; F- light brown sandy-silt layer; G-light brownish-gray sandy-clayey-silt layer; H- light brown silty layer; I- pale yellow clayey silt layer; J- olive-brown sandy-clayey-silt layer



Figure 3. General view of the Mayo Kebbi's samples. (A) Geological outcrop (Profile 1); (B) Partial view of the geological outcrop (profile 2); (C) whitish sample with sandy texture; (D, E) geological outcrop showing fresh rock; (F) geological outcrop showing brick red's sample; (G) light yellow sandy-clayey-silt layer; (H) geological outcrop showing the olive brown sample's texture; (I) geological outcrop showing the texture of L4

4.2. Mineralogical Composition

The qualitative and semi-quantitative mineralogical compositions of the different samples analyzed in this work are summarized in Table 1, Table 2, and Figure 3. The mineralogical results on bulk rock obtained on samples Rs1 and Rs2 showed that these two samples are composed almost exclusively of calcite (Table 1). Furthermore, these results show that all the samples analyzed, except L12, are composed almost exclusively of smectite, with contents varying from 91 to 98%. It is in all these samples,

associated with very low proportions of illite and kaolinite. The illite content does not exceed 3% and the kaolinite content goes up to 8% (L9). The healthy rocks, Rs1 and Rs2, have the same mineralogical composition of the clay fraction. They are both almost totally composed of smectite, associated with illite and kaolinite. Of the two, the sound rock (Rs2) of the second profile has the highest content of kaolinite (8%). Of the 12 samples, sample L10 is different. It contains just 63% smectite (the lowest of all), 2% illite, 30% Kaolinite. It also contains chlorite (5%) and quartz as accessory minerals (Figure 4).

Table 1. Bulk rock mineralogical	compositions of Rs1 and	Rs2 samples from Mayo	kebbi
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Samples	Quartz	Calcite	Smectite	Muscovite	Kaolinite	Vermiculite
Rs1		++++				
Rs2	+	++++				

Table 2. Semi-quantitative mineralogical compositions of the <2µm fraction of different samples from Mayo kebbi

Samples	Smectite	Kaolinite	Illite	Chlorite	Accessory mineral
First profile					
R1	98%	1%	1%	-	
L1	96%	2%	2%	-	
L2	98%	1%	1%	-	
L3	96%	2%	2%	-	
L4	96%	1%	3%	-	
L5	97%	1%	2%	-	
L6	97%	1%	2%	-	
L7	96%	2%	2%	-	
Second profile					
R2	98%	1%	1%	-	
L8	91%	8%	1%	-	
L9	95%	4%	1%	-	
L10	63%	30%	2%	5%	Quartz



Figure 4. XRD patterns of the oriented $< 2\mu$ m fraction of Mayo Kebbi's samples after untreated, heated at 500°C, and glycolated treatments on (A) first profile (Rs1 to L7) and (B) second profile (Rs2 to L10)

		First Profile								Second Profile			
Major element	L.D	Rs1	L1	L2	L3	L4	L5	L6	L7	L8	L9	Rs2	L10
SiO ₂	0.04	1.30	66.36	69.36	67.30	78.67	52.29	70.85	73.48	50.86	51.70	3.04	87.69
CaO	0.01	50.81	4.08	2.13	1.72	1.10	1.82	1.49	1.01	12.50	0.773	51.80	0.284
Al ₂ O ₃	0.02	0.37	13.52	13.13	14.45	10.34	18.25	13.63	12.47	12.31	16.08	0.71	4.89
Fe ₂ O ₃	0.01	0.09	1.35	2.74	2.56	0.63	6.52	1.18	1.85	3.65	4.20	0.12	1.49
MnO	0.00	0.02	0.02	0.04	0.03	0.07	0.12	0.02	0.03	0.057	0.046	0.028	0.032
MgO	0.01	0.16	0.90	0.93	1.16	0.74	2.54	1.01	0.77	0.86	1.48	0.16	0.20
Na ₂ O	0.02	0.03	1.00	2.28	1.42	1.73	0.47	2.40	1.09	0.06	0.06	0.03	0.12
K ₂ O	0.01	0.04	1.61	1.78	1.66	1.70	2.19	1.65	1.73	1.25	1.77	0.09	0.85
TiO ₂	0.01	0.01	0.18	0.71	0.33	0.09	0.74	0.15	0.25	0.50	0.51	0.01	0.17
P_2O_5	0.002	0.02	0.05	0.36	0.14	0.15	0.11	0.04	0.02	0.122	0.214	0.023	0.018
LOI	0.05	46.28	9.80	5.20	7.90	3.89	13.96	5.86	6.64	17.28	15.46	43.28	3.50
Total		99.13	98.86	98.66	98.67	99.12	99.01	98.28	99.33	99.45	99.25	99.29	99.24
L.O.I: Loss On Ignition; L.D: Detection limit													

Table 4. Physical properties of Mayo Kebbi's samples

Physical properties												
	Denth	pH			Pasidual		I	Exchang	CEC	S/T		
Samples	(cm)	pH water	$\begin{array}{c c} pH \\ water \end{array} pH kcl \Delta pH \end{array}$		moisture	Ca ²⁺	Mg^{2+}	\mathbf{K}^{+}	Na^+	S (meq/100g)	(meq/100g)	(%)
First Profile												
L6	0-20	7.60	5.93	1.67	4.49	0.75	0.23	0.51	0.01	1.49	10.51	14.00
L5	50-100	8.13	5.90	2.23	10.99	1.96	0.42	0.51	0.03	2.92	15.15	19.00
L4	100-130	7.72	6.27	1.45	3.41	0.59	0.28	0.21	0.01	1.09	9.72	11.00
L3	130-200	8.18	6.32	1.86	7.18	1.21	0.33	0.27	0.09	1.90	12.06	16.00
L2	200-250	8.25	6.28	1.97	5.48	0.85	0.26	0.16	0.07	1.33	9.23	14.00
L1	250-300	8.00	5.80	2.20	6.84	1.53	0.10	0.13	0.02	1.79	13.95	13.00
	Second Profile											
L10	0-10	7.66	6.24	1.42	1.94	0.33	0.12	0.11	0.01	0.56	9.42	6.00
L9	40-70	7.94	6.40	1.54	8.22	2.37	0.27	0.42	0.01	3.07	12.80	24.00
L8	70-130	7.84	6.30	1.54	5.93	2.07	0.24	0.44	0.01	2.76	11.71	24.00

4.3. Chemical Composition

Table 3 shows the chemical composition of the major elements in the 12 samples from the Mayo kebbi West area. SiO₂, Al₂O₃, and Fe₂O₃ are the most important oxides while K₂O, Na₂O, MgO, TiO₂, and MnO are present but in small quantities. Cao contents are very important in the source rocks of both profiles where they are respectively 50.81 wt. % for Rs1 and 51.80 wt. % for Rs2. They are very low in the upper levels. SiO2 values range from 78.67 to 52.29 wt. % in the overlying levels of the first profile and from 87.69 to 50.86 wt. % in the second profile. Al₂O₃ contents range from 0.37 to 18.25 wt. % in the overlying levels of both profiles. Fe₂O₃ contents are less than 7 wt. % in both profiles. Na₂O (0.03 to 2.40 wt. %) and K₂O (0.04 to 2.19 wt. %) contents may be related to the presence of minor amounts of Na/K feldspars.

4.4. Physical Properties

The physical properties of the Kebbi mayo area (CEC, pH, S/T, ...) are reported in Table 4. The ammonium acetate method revealed CEC values between 9.23 and 13.95 meq/100g for the first profile and 9.42 to 12.80 meq/100g for the second. These values are lower in contrast to the CEC values of Sabga clays in Cameroon (38-46 meq/100g; [29] Moreover, these values are also largely lower than the CEC values characteristic of those

of pure montmorillonite [29]. CEC is used as a measure of soil fertility by showing the nutrient holding capacity of a given soil. The richer a soil is in clay and organic matter, the greater its CEC. CEC is strongly related to the C/N ratio and the pH of the soil. The pH values vary from 7.60 to 8.25 for both profiles, indicating a slightly alkaline character and confirming the presence of carbonates. The sum of exchangeable bases oscillates respectively between 9.23-13.95 and 6.4-10.53meq/100g. The saturation rate is between 6 and 24. Finally, the residual moisture values vary between 1.94 and 10.99%.

5. Discussion

5.1. Genesis of the Mayo Kebbi's Smectite, Formation Conditions

The mineralogical composition of the $< 2\mu$ m fraction of the samples from the western area of the Mayo Kebbi, as presented in the preceding paragraphs, is made up of: smectite, kaolinite, illite, chlorite and quartz. The presence of the mayo is an important factor in determining the origin of the smectites in this area. Based on geochemical data, it can be seen that: (1) all the fresh rock samples of the two profiles (Rs1 and Rs2) have CaO contents above 50 wt. % and (2) all other samples, except the two previous ones, have a CaO content between 0 and 12 wt. %. This observation shows the considerable discrepancy between the CaO contents of the fresh rocks and the overlying formations and may indicate different sources for the smectites present in the sound rocks and the formations above. Given their position, Ref [30] indicated that these formations are loose formations. This therefore implies that there would have been transport of these via the mayo. This would also be equivalent to saying, like [31] that these overlying formations would come from the erosion of materials located on the slope of the mayo. Mineralogy of the < 2 μ m fraction revealed high smectite contents (63-98%) in these formations. Thus, from the above, the smectites in this part of the Mayo Kebbi would be derived from partial hydrolysis of the formations located on the slope near the mayo.

However, observations are also made on the fresh rock mineralogy and on the $< 2\mu m$ fraction mineralogy of the different samples. The results indicated that the total rock mineralogy of samples Rs1 and Rs2 indicated that they are almost exclusively calcite. The results obtained by mineralogy of the fine fraction of the other samples, L1 to L10, provided the same composition (98% smectite, 1% kaolinite, and 1% illite). The carbonate rocks, from which the fresh rock samples were taken, were identified as limestones base on their mineralogical composition and thanks to the positive hydrochloric acid test. These limestones (Rs1 and Rs2) yield almost exclusively smectites (98%) in the $< 2\mu m$ fraction. According to Ref [10,12] the nature of the clays formed depends on several factors, including: the nature of the source rock, topography, climate. Regarding the source rock, Ref [10] indicates that the alteration of an acid rock (granite for example) gives rather Kaolinite and that of a basic rock (basalt for example) gives rather smectites. In fact, based on the work of Ref [10], it can be argued that the smectites in this part of the Mayo Kebbi come from the partial hydrolysis of the limestone on which the sediments transported by the mayo were deposited. In other words, the smectites in this part of the Mayo Kebbi were formed in situ. Similar to the work of Ref [10], the smectites in this part of Chad are thought to come from basic rocks. However, it should also be considered that other studies such as those of Ref [30] also suggest that they would also form from acidic rocks (granitoids).

In addition to these observations, there are also other geological parameters, including: (1) the fact that the study area is part of the Lamé series and (2) according to Ref [17], it is one of the most important limestone sites in Chad. As a result of all the above arguments, one could argue that the smectites of this sector of the Mayo Kebbi have a double origin. They would result either (1) from a partial hydrolysis of the formations located on the slopes near the mayo, which would have undergone a short transport; or (2) would have formed in situ.

5.2. Paléo-environnemental Significance of the Study Area Smectites (Mayo Kebbi)

The study of the formation of clay minerals provides indications of weathering and climatic conditions, the type of possible source rock, and an evaluation of the origin and abundance of detritism [9,12,14]. According to Ref [9], regions formed by few landforms that experience a lot of precipitation, but little erosion are affected by mainly chemical alteration, which favors the formation of neoformed clay minerals such as kaolinite and smectite. On the other hand, regions composed of significant landforms result in cold annual temperatures and little precipitation, thus causing significant mechanical weathering. The latter conditions prevent intense chemical weathering and thus favor the formation of chlorite and interbedded minerals. Kaolinite forms mainly under tropical to subtropical climatic conditions where precipitation and chemical alteration are intense. Smectite is derived from the chemical alteration of volcanic rocks. It indicates semiarid climatic conditions with a marked seasonality alternating wet and dry periods. Micas come from the mechanical alteration of igneous and metamorphic rocks and allow to evaluate the importance of detritus. Chlorite comes from the mechanical alteration of ferromagnesian silicates under arid conditions with a cold climate. The interbedded clays indicate a semi-arid climate with contrasting seasons [9]. Thus, the nature of the clays formed depends on several factors, including: the nature of the parent rock, the topography, the climate [10,12]. Concerning the mother rock, Ref [10] indicates that the alteration of an acid rock (granite for example) gives rather Kaolinite and that of a basic rock (basalt for example) gives rather smectites. For the topography, Ref [32] suggests that the topography controls the drainage. To this effect, on a slope where drainage and leaching are good, the formation of type 1:1 clays is favored. On the other hand, the clays of type 2:1 form preferentially in confined environments (basin). As for the climate, it conditions the more or less abundant presence of water and the temperature. Consequently, the clay minerals resulting from the alteration are distributed according to a latitudinal zonal arrangement, superimposed on that of the great types of climates [9,33].

Diffractometric analysis revealed a predominance of smectite in the fine fraction of our samples. These are type 2:1 clay minerals [9,16,34,35,36]. According to Ref [32], smectites form from basic source rocks in environments with low hydrolysis and low topography. For this last parameter, Ref [14], indicates that it could be preferentially a basin or a valley. It should also be noted that smectites do not form only from basic rocks. Authors such as [37] have indicated that they can also form from acidic rocks, granites for example. Thus, from the results obtained (predominance of smectite), the following hypotheses are put forward on the paleoenvironmental reconstruction of the study area: (1) the climate of the study area would be tropical semi-arid type with a marked seasonality alternating wet and dry periods; (2) the topography would be low, probably a valley or a basin; the two hypotheses mentioned above, combined with this predominance of smectite have led to say that (3) the dominant type of hydrolysis is bisiallitization.

6. Conclusion

The study area is situated in the western part of the Mayo Kebbi region, a few kilometers from the Chad-Cameroon boundary. Results obtained from total rock diffractometric analysis revealed that calcite is the dominant mineral in both fresh rock samples. In contrast,

those obtained from the diffractometric analysis of the <2µm fraction revealed that smectite is the major mineral in these materials, with contents ranging from 63 to 98%. It is associated with kaolinite, illite, and chlorite. Quartz was identified as the only accessory mineral. From geochemical point of view/geochemically, these materials are mainly composed of SiO₂, Al₂O₃, and Fe₂O₃. CaO is in the majority in the fresh rocks. The latter, due to the positive hydrochloric acid test and their mineralogical composition, were identified as limestone. In addition, these materials also revealed CEC values significantly lower than those of pure montmorillonite and a slightly alkaline pH. Due to their mineralogical and physicochemical characteristics, these clay-rich Mayo Kebbi materials can be used in many classical applications of clay materials, such as heavy mineral retention, waste disposal, cosmetics, catalysts, and agriculture.

The mineralogical and geochemical results obtained suggest that the smectites of the Mayo Kebbi zone have a double origin. One part of these smectites comes from the erosion and partial hydrolysis of the formations located on the slope of the mayo. The second part is formed in situ. The results obtained have also allowed us to suggest that in the sampling area, the climate is semi-arid tropical, that the topography is low, and that the dominant type of hydrolysis is bisiallitization.

It would be interesting for a better optimization of this study to proceed to the determination of the dominant type of smectite in the fine fraction of these materials. In order to enrich the database of clayey materials of Chad, the prospecting of clays in other localities of the South and the Southwest should also be considered.

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