CLAY MINERALS IN RECENT SEDIMENTS OF THE NIGER DELTA

by

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ABSTRACT

RECENT sediments of the Niger delta contain the detrital clay minerals kaolinite, montmorillonite and a small amount of illite. The montmorillonite content increases with water depth and distance from the shore, and the results of laboratory experiments on natural Niger delta clay support the assumption that this is due to differential flocculation and sedimentation.

The easterly Guinea Current, transporting montmorillonite-rich floccules in suspension, may cause an increase in the montmorillonite content of the clays in the eastern part of the delta.

Mineralized faecal pellets are present in most marine sediment samples. Chamosite occurs authigenically in coastal water shallower than 35 fathoms, as brown and darkgreen pellets. Green pellets, composed of highly expandable, montmorillonite-type glauconite, are particularly common around the 100 fathom isobath. Both chamosite and glauconite have a high magnesium content, which seems to be usual during their early stages of formation.

The formation of chamosite and glauconite is governed by redox potential and the availability of iron. If no reduction takes place, the pellets remain grey and their composition is similar to that of the clay matrix. Grey pellets are less restricted to a particular depth than are the chamosite and glauconite pellets, but distinct maxima occur around the 250 fathom isobath.

INTRODUCTION

IN 1959, in connection with a study on delta formation, a number of Recent samples from the subaerial and submarine part of the Niger delta were collected during the Recent Sediment Survey jointly organized by Shell Internationale Research Maatschappij N.V. and the British Petroleum Company Limited.

Sedimentological aspects have been dealt with by Allen (1964). In the present contribution the detrital clay minerals and the authigenic clay minerals present in the sediments are described.

The author wishes to thank the management of Shell Research N.V. and of British Petroleum Company Limited for permission to publish this paper. He also expresses his gratitude to Dr. J. P. van der Sluis for his friendly co-operation and valuable suggestions and discussions.

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X-RAY METHODS

Most of the X-ray diffraction analyses were performed with Philips diffractometers with proportional counters and discriminators, using nickel-filtered copper radiation at 36 kV and 20 mA.

Some analyses of authigenic minerals were performed using a cylindrical camera or a focusing camera of the quadruple Guinier-de Wolff-II type using iron-filtered cobalt radiation. Additional data were obtained from microscopic examination of thin sections, differential thermal analysis, X-ray fluorescence analysis, spectrochemical analysis and from electron micrographs.



FIG. 1. Typical X-ray diffraction patterns of two marine clays from the Niger delta.

Comparative Semi-quantitative Mineralogical Analysis

Oriented slides for X-ray diffraction analysis were prepared from the < 2-micron fraction of each detrital sample. No chemical pre-treatment was applied. To obtain a measure of the relative proportions of the constituents in a given fraction, the peak areas (integrated intensities) of the basal reflections characteristic of these minerals were measured on the diffraction patterns. The peak area, i.e. the area bounded by the part of the trace forming the peak and a hand-drawn, slightly curved base line separating the peaks from the background on which they are superimposed, serves as a measure of the amount of the specific minerals present. For purposes of comparison the use of peak-area percentages was adequate. Figure 1, which shows two

diffraction patterns, one obtained from a sample deposited in shallow water near the shore and the other from a sample derived from a much deeper part of the delta, about 60 miles from the shore, also shows how the peak-area percentage is obtained. The total area bounded by the three peaks is measured and the ratio of the area within one of the peaks to the total area gives the peak-area percentage.

The main constituents of the detrital Niger delta clays are kaolinite, montmorillonite and illite. Illite (plus mica) is almost always present in minor quantities and its peak-area percentage fluctuates within fairly narrow limits, leaving montmorillonite and kaolinite as the significantly varying components of the clay fraction. Of these, the peak-area percentage of montmorillonite has been chosen to express variations and trends of the clay composition.

RESULTS AND DISCUSSION

Detrital Clay Minerals

Two hundred and thirty-four samples from the Recent subaerial and submarine parts of the Niger delta have been analyzed to determine their clay-mineral content. Kaolinite, montmorillonite and illite, in this order, are the main constituents. Electron micrographs showed the presence of halloysite, its concentration being less than 0.1% of the < 2-micron fraction.

Figure 2 shows the location of the sample stations and the montmorillonite peak-area percentages of the X-ray patterns obtained from the < 2-micron fraction. Most of the samples from the bottom of the main stream of the Niger, which transports the greater part of the mud from the continent into the sea (Nedeco, 1959, pp. 454–504), were found to have montmorillonite peak-area percentages of more than 30 (sometimes up to 60). The variation may be due partly to differential settling resulting from differences in particle size and current action and partly to variation in the quantity of montmorillonite supplied by different local sources.

In the sea, near the shore, the peak-area percentage value usually drops below 30 and only at greater depths and distances from the shore does it increase to about 50. This indicates that near shore montmorillonite does not settle in proportion to its concentration in suspension. The peak-area percentage contour lines of the map show a zonal distribution that is more or less parallel to the coast. This particular distribution is considered to be the result of differential settling. It appears that the sediments with a low montmorillonite content are generally sandy, and those with a high montmorillonite content are clayey.

Flocculation and sedimentation experiments were performed in the laboratory on natural Recent sediment samples to determine whether the conclusion drawn by Whitehouse et al. (1960), i.e. that kaolinite and illite

flocculate and settle faster than montmorillonite when they come into contact with salt water, also applied to Niger delta clay.

Our experiments were as follows. A fresh-water suspension was made of Niger delta clay (1.5 g/l). The samples consisted of a mixture of kaolinite, montmorillonite and illite. The suspension was carefully placed on top of a 180-cm high column of water of ocean-water chlorinity, standing in a glass tube about 10 cm in diameter. The clay flocculated and sank to the bottom within a few hours. A simple device at the bottom allowed the removal of sediment samples at various levels. After the samples had been washed, oriented slides were prepared for X-ray diffraction analysis.



FIG. 3. X-ray diffraction patterns, showing the basal reflections of (a) the bottom clay after flocculation and sedimentation in sea water, and (b) the top clay layer.

As expected, we found a slight enrichment of kaolinite in the lowest part of the sediment and a slight enrichment of montmorillonite in the top clay layer of the sediment (see Fig. 3). This can only be explained by assuming that the floccules do not have the same mineralogical composition and settle more slowly the higher their montmorillonite content.

It is suggested that the ions present in salt water reduce the thickness of the postulated double layer surrounding the clay crystallites. The crystallites, no longer hindered in approaching each other closely, may flocculate if clay content and salt concentration are sufficient. According to Whitehouse's











PLATE 1. Photographs of faecal pellets.

1a. Soft faecal pellets, core vSL 358, 90 cm below surface.

Ib and c. Pellets, composed of chamosite, some quartz and a rim of goethite. Niger delta. Thin section. (b) Shallow water. Recent. (c) Elelenwa 2, 7220 ft. Miocene.

1d. Nearly pure chamosite pellets (oöliths) and well-rounded crinoid fragments partly transformed into and surrounded by chamosite and siderite. Thin section. Sample BNK 1280a. Algeria. Carboniferous.

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experiments, kaolinite, illite and montmorillonite each have a different "rate" of floccule formation. As a result of this differential flocculation, floccules consisting mainly of kaolinite and illite will form rapidly and will tend to settle relatively faster than floccules with an increased montmorillonite content, which are formed less rapidly and are smaller. In moving water, these smaller floccules will be transported over greater distances than the larger floccules, resulting in the lateral mineralogical differentiation mentioned above.

From the *vertical* differentiation obtained in our experiments in still water we infer that in the case of the Niger delta the transport of the clay minerals by moving water has brought about a *lateral* differentiation.

Figure 2 further shows two special features:

- (1) An eastward increase in the montmorillonite content, which is thought to be due to the fact that:
 - (a) since, at a distance of 25 miles and more offshore, the clay still in suspension contains more montmorillonite than the clays in suspension nearshore, the Guinea Current (Equatorial Counter Current) will transport mainly such montmorillonite-rich clays in an easterly direction;
 - (b) east of Calabar, there are widespread volcanic rocks that may yield montmorillonite-rich clays after weathering in the humid tropics and these, once transported into the sea, may increase the montmorillonite content in the eastern part of the area investigated. It has not yet been possible to check this hypothesis.
- (2) The less marked parallel-to-coast zonation in the eastern part of the area investigated is possibly due to tidal action, which is at a maximum near the Cross River estuary and causes movement of large water masses across this region. As a result, some mixing of the bottom sediments is likely.

Up to now no convincing examples have been published of areas having, in their Recent sediments, a clay-mineral distribution that could be explained satisfactorily by differential flocculation and sedimentation (Millot, 1964, p. 218).

Griffin (1962) and Pinsak and Murray (1960) have related the differences in clay-mineral distribution in the Gulf of Mexico to the supply by different sources. There is no regular increase of the montmorillonite content with increasing depth and distance from the shore. Some small-scale changes in clay composition between the rivers and their adjacent salt-water environments were noted by Griffin (see also his Plate I). These small-scale changes, mainly involving an increase in the kaolinite content in relation to montmorillonite, may possibly be attributed to differential flocculation and sedimentation.

Van Andel and Postma (1954), discussing the composition of the clay fraction in Recent sediments of the Gulf of Paria, divide the Gulf area into two parts: (1) the delta platform with illite predominant and some kaolinite and montmorillonite, and (2) the other parts of the Gulf with illite still

predominant, the same amount of kaolinite and somewhat more montmorillonite with respect to the delta platform clay. Of the four possible reasons suggested for this difference, the authors consider differential flocculation and sedimentation to be the most probable.

Finally, Millot (1964, p. 218) states that, in spite of the fact that he considers the feature of differential sedimentation as proven, no area has yet been found where its effects are clearly visible.

Why does the clay-mineral distribution pattern in the Niger delta provide such a clear example of the effects of differential flocculation and sedimentation? The reasons would seem to be mainly physico-geographical, viz.:

(1) Source areas and current patterns.—The clays deposited in the Niger delta are derived mainly from one direction, the north, the drainage area of the Niger. Qualitatively, these clays are of uniform composition throughout and even quantitatively do not show wide differences. The Gulf of Mexico, on the other hand, is surrounded by a variety of sources, each delivering clay of a different composition; this is also true of the Gulf of Paria, though to a lesser extent. Moreover, sea-current patterns in both gulfs are probably more complex than in the Niger delta area and, in the case of the Gulf of Mexico, they are also, partly, seasonal.

(2) The climate.—Clays from tropical areas tend to be less variable and complex in composition than clays from areas of more temperate climate. In the Niger delta, kaolinite and montmorillonite (two extremes as regards flocculation and sedimentation behaviour) are the main components of the clay fraction. Into the Gulf of Mexico, on the other hand, the Mississippi brings a predominantly montmorillonitic clay with appreciable amounts of illite, mixed-layer minerals, chlorite and vermiculite. Consequently, the X-ray patterns are much less suited to semi-quantitative analysis than are those of Niger delta clays.

The above-mentioned factors combined may have made the Niger delta more favourable for a study of the effects of differential flocculation and sedimentation than areas such as the Gulf of Mexico, where variations in the clay composition due to differences in source area and differential settling are difficult to unravel and where the clay composition is less suitable for tracing minor variations.

Authigenic Clay Minerals

In addition to the detrital clay minerals kaolinite, montmorillonite and illite, we have found in the Niger delta sediments authigenic forms of chamosite and an immature form of glauconite occurring mainly in faecal pellets and only incidentally associated with remnants of Ostracoda, Foraminifera, etc.

Faecal pellets are present in nearly all the marine sediment samples taken off the Nigerian coast, in concentrations ranging from less than 1% to almost 100% of the sediment. They occur in a variety of colors and degrees of induration, from grey and soft to dark green or dark brown and hard. The distribu-

tion of these various types is not random, but follows well-defined, characteristic patterns (Fig. 4) that are also seen on maps showing the distribution of sediments and fauna. It suggests close correlation between faecal pellet type and depositional environment.

The distribution pattern of the green pellets, for instance, coincides remarkably with the areas that, on the basis of various sedimentological and faunal criteria, have been distinguished as areas where deposition of clay is slow or hardly occurs at all. The deepest occurrences are at about 120 fathoms. These pellets are either pale green and earthy, or dark green and glossy. The earthy pellets, occurring mainly in the northwestern zone, constitute 5 to 10% of the sediment and the others, occurring mainly in the eastern zone, constitute up to 25% of the sediment.

The brown and brownish-green pellets are found within the 35 fathom isobath. The occurrence of brown pellets in abnormally deep water (68 fathoms) in the eastern part of the area investigated (see Fig. 4) is explained by contamination of older, shallow-water sediment, which outcrops at that location. This conclusion is based on the presence of typically shallow-water Ostracoda.

The grey pellets occur in many of the clayey sediments without special regard to depth. Among the pellets of this color, there is a very friable kind that, at depths exceeding about 100 fathoms, is so abundant that it constitutes almost the whole of the bottom sediment (Plate 1a). This abundance indicates strong burrowing activity and a moderate rate of clay deposition. In the sediments in shallower water, grey pellets are less abundant and, where present, usually occur in burrows in homogeneous clays.

In order to gain a more precise understanding of how the pellets differ from one another, a large number selected from 68 bottom-sediment samples were subjected to X-ray diffraction analysis so as to determine their mineral composition. The results are presented in Fig. 4.

Glauconite pellets.—The mineral glauconite, as defined by Gruner (1935) and by Hendricks and Ross (1941), is absent; nevertheless, the green pellets from samples taken between the 70 and 120 fathom isobaths do contain an iron-rich, expandable clay mineral (containing from 2 to 4% potassium) that differs markedly from the clay matrix (see Table 1). According to Hower (1961) such a composition is favorable for diagenetic conversion to the mineral glauconite; loss of water and expansion properties, further uptake of potassium and upgrading of the lattice are required.

Following Burst's (1958) classification, the immature glauconite of the Niger delta belongs to his group III, which is representative of minerals with extremely disordered, expandable, low-potassium, montmorillonite-type structures. Comparing the X-ray diagram and expansion properties of the most expandable specimens of Niger delta glauconite with those of the glauconites from Burst's group III or with the "early-stage glauconite" described by Ehlmann *et al.* (1963), Hulings (1961), Pratt (1961) and Manghnani and Hower (1964), the Niger delta glauconite certainly is in an early

	Glauconite pellets* (with quartz impurity)	Clay matrix < 2 micron* (with quartz impurity)	
SiO,	48%	43.5%	
Al_2O_3	13.5	24	
Fe ₂ O ₃	19†	10.6†	
FeO	n.d.	n.d.	
MgO	3.2	2.0	
CaO	1.1	0.8	
Na ₂ O	0.3	0.3	
K,Ò	2.91	1.5‡	
TiO,	0.3	0.7	
H_2O+	9	15.0	
H ₂ O	3	1.6	
	100.3	100.0	
Ba	0.010	0.014	
Co	0.005	0.004	
Cr	0.014	0.010	
Cu	0.004	0.029	
Mn	0.052	0.032	
Ni	0.010	0.012	
\mathbf{Sr}	0.015	0.011	
v	0.026	0.012	

TABLE 1.—APPROXIMATE CHEMICAL COMPOSITION OF GLAUCONITE PELLETS AND OF THE CLAY MATRIX

* Average values obtained by spectrochemical analysis of five glauconite samples and four clay samples. The values for the clay samples gave a sum of about 110% and were recast to 100%.

 \dagger Owing to smallness of sample the FeO content could not be determined. All iron reported as Fe₂O₃.

[‡] Determined by X-ray fluorescence analysis.

For details of spectrochemical method see footnote to Table 2.

stage of its development. The percentage of expandable layers in the Niger delta glauconite is even higher than in the other described glauconites, being 70-80% and 55% respectively. Based on chemical and X-ray data (Fig. 5), no significant amount of clay matrix material is present in the pellets; therefore, the greater part of the expandable material will represent the early glauconite.

This type of poorly crystallized material can presumably form quite easily under suitable conditions (Millot, 1964, pp. 380, 392 and 399). In the laboratory at a temperature of 60°C for instance, similar poorly crystallized structures were prepared in only a few months from material amorphous to X-rays. This is shown by the X-ray patterns (Fig. 5) of powdered window-glass, before and after aging for 6 months with magnesium oxide and water.



FIG. 5. Portions of X-ray diffraction patterns of several early-stage glauconites, altered glass and clay matrix.

Chamosite pellets.—Pellets from sea-bottom samples taken at depths of less than about 35 fathoms chiefly consist of structurally disordered chamosite with lesser amounts of goethite. Siderite, pyrite and quartz are occasional minor constituents. These pellets are usually brown in color, but are sometimes also dark green (Plate 1b).

Chamosite is a ferrous-iron-containing mineral; in a marine environment with a pH of about 8, the oxygen content must be low for the formation of chamosite. Most of the iron enters the sea as a ferric clay-mineral constituent (average iron content of the < 2-micron fraction is 6.5% Fe), and as coatings, e.g. on quartz grains. Some of this ferric iron may become mobile and available as ferrous iron for the formation of chamosite, if it is reduced by organic material present in the surface layer of the sediments. The animals living in or close to the sea bottom will consume some iron-containing compounds, together with their food, which leads to the production of iron-containing pellets. The iron content of such grey pellets is unknown. These grey pellets, which have not undergone "glauconitization" or "chamositization", were found to contain about the same amount of iron as the clay matrix, or even less. We think that after the pellet has been produced the iron content increases during the mineralization process. It is noteworthy that in the Niger delta chamosite formation starts mainly from faecal pellets, as does glauconite.

To a depth of 7500 ft in shallow-marine deposits of Miocene age in the Niger delta, chamosite pellets have been found that do not differ from the Recent



FIG. 6. X-ray diffraction patterns of Recent and Palaeozoic chamosite.

ones with respect to their X-ray pattern and thin sections (Plate 1c), so that the conclusion is drawn that no further ordering occurred. Jurassic and older chamosites are often fairly well crystallized (Brindley and Youell, 1953) and may show more or less concentric rings (Plate 1d). The Recent chamosites from the Niger delta are poorly crystalline with a broad 7 Å and a weak 14 Å reflection (Fig. 6) and do not show any texture. If the Recent Niger delta

	Recent* Nigeria (with goethite and quartz impurities)	Miocene* Nigeria (with goethite and quartz impurities)	Jurassic England (recast to 100% by Brindley)	Devonian† Algeria (with siderite and dolomite impurities, corrected for dolomite)
SiO,	52%	46%	23.81%	32%
Al ₂ Ô ₃	8	13	23.12	15.5
Fe ₂ O ₃	20‡	23‡	0.23	34
FeO	n.d.	n.d.	39.45	n.d.
MgO	8.3	4.7	2.72	4.0
CaO	0.5	0.5		
Na ₂ O	0.3	0.4		0.2
K ₂ O	< 0.5	< 0.5		< 0.5
TiO ₂	0.4	0.4		0.3
$H_{2}O +$	11	11		
$H_2O -$	0.4	0.4	10.67	13.5
			. <u> </u>	
	101.4	99.9	100.0	100.0
Ba	0.012	0.014		0.006
Co	0.009	0.009		<0.007
Cr	0.011	0.032		0.024
Cu	0.003	0.008		0.010
Mn	0.225	0.081		0.32
Ni	0.015	< 0.027		< 0.13
\mathbf{Sr}	0.012	0.013		< 0.04
v	0.028	0.023		0.11

 TABLE 2.—Approximate Average Chemical Composition of some

 Chamosites

* Average values obtained by spectrochemical analysis of 2 samples.

† One sample analyzed. Recast to 100%.

 \ddagger Owing to smallness of sample, the FeO content could not be determined. All iron reported as Fe₂O₃.

The spectrochemical analyses were performed with a 3.4 m Jarrell-Ash emission spectrograph. The method used was that described by J. Kroonen and D. Vader: "Line interference in emission-spectrographic analysis. A general emission-spectrographic method including sensitivities of analytical lines and interfering lines". Elsevier Publishing Company, Amsterdam, 1963.

All samples were heated to about 700°C, before weighing and spectrochemical analysis.

chamosites are considered as the precursors of some of the older forms, the transformation to better crystallization must require higher temperatures and pressures than those prevailing at the depth at which these Miocene chamosites are found; longer periods of time may also be necessary.

It is difficult to trace the diagenetic history of chamosite. Since chamosite does not contain interlayer water and is not expandable as montmorillonitictype glauconite is in its early stages, there is no analogy with the easily determinable difference between expandable and not-expandable glauconites. The possibility exists that chemical analysis will permit distinction to be made between intermediate stages in the diagenetic development of chamosites. Table 2 shows the average chemical composition of some Recent, Miocene, Jurassic and Devonian chamosites. Owing to the presence of quartz and goethite impurities, the aluminum and magnesium contents are to be considered as minima, but their ratio is not affected by the impurities. Only kaolinite, which may form a few per cent of the mixture although its presence was not detected by X-rays, will affect this ratio.

It can be seen from Table 2 that the Niger delta Recent chamosite has a rather high magnesium content, 2 or 3 times higher than that of the older chamosites. It is not known whether this difference is caused by diagenesis involving a change in the Mg-content, or whether the older samples were originally low in magnesium. The Al_2O_3/MgO ratio is about 1.0 in the Recent chamosite, about 2.8 in the Miocene and 3.9 and 8.5 in the two older chamosites. In any case, it appears that the Recent chamosites, just as the immature forms of glauconite, have a fairly high magnesium content. Once formed, the chamosite pellet may undergo chemical changes and adjustments to subsurface conditions (Schoen, 1964, p. 862).

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