

# A COMPARATIVE STUDY OF THE DIAGENETIC ALTERATION OF CLAY MINERALS IN MESOZOIC SHALES FROM PAPUA, NEW GUINEA, AND IN TERTIARY SHALES FROM LOUISIANA, U.S.A.

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(Received 10 March 1969)

**Abstract**—Gradual change from 60% montmorillonite/40% illite randomly interstratified clay minerals at 3500 ft depth to 20% montmorillonite/80% illite at 10,200 ft can be observed in a complete section of Mesozoic shales at Barikewa in New Guinea. The top of a similar complete type Mesozoic section at 10,544 ft in the nearby Omati borehole contains 20–40% montmorillonite in randomly interstratified montmorillonite/illite. From 10,800 ft downward there is only 10–20% expandable material. Consequently depth of burial rather than stratigraphic level controls the proportion of expandable material present. Similar diagenetic alterations occur in the Wilcox Formation, Louisiana, also controlled by burial.

The amount of illite 2M polymorphs in the Papuan samples is usually less than 5 per cent, the illite 10Å peak sharpness ratio is about 1.4. Corresponding values for the Louisiana samples are 43% 2M polymorphs and about 2.0 sharpness ratio. Chemical analysis of the Papuan shales show low MgO and K<sub>2</sub>O values when compared with the Louisiana samples. The latter sediments contain some chlorite, the former hardly any. Differences demonstrate a higher proportion of relatively unweathered material in the American samples.

Increase of chlorite content, increase of magnesium content and decrease of kaolinite content from 12,368 ft down in the Louisiana samples suggests a change in sedimentation pattern.

## INTRODUCTION

THIS study is concerned with the clay mineralogy and chemistry of Jurassic and Cretaceous shales in two 14,000 ft deep boreholes drilled in the Papuan Basin, S.E. New Guinea, as compared with old and new data from Eocene shales from deep wells in the Mississippi Basin, U.S.A. Well locations are shown in Fig. 1 and Fig. 5 respectively. The Papuan shale samples come from fine homogeneous mudstones deposited on the outer continental shelf during Mesozoic time. The Louisiana shale samples come from the Eocene Wilcox Formation and originate from various wells as much as 16,000 ft deep. The material is the same as used in Burst's (1959) classic study on diagenesis.

Initially the author intended to use the American samples as mineralogical reference material and for correlation of sedimentary facies based on bulk rock chemistry only. Because of a possible new interpretation of the X-ray data, the mineralogy of the Wilcox shales is reconsidered in this paper. The Wilcox samples analysed represent an incomplete suite as most samples come from burial depths greater than 10,000 ft. Observed differences between bulk chemistry of the Papuan and Louisi-

ana samples, and also differences in the sharpness of the illite diffraction peaks, and in the proportion of illite polymorphs in both rock suites are the basis for this comparative study on the mineralogy and geochemistry of the shales.

## GEOLOGICAL SETTINGS

Only the general outlines of the geology of the Papuan Basin in S.E. New Guinea are known. (Australasian Petroleum Company, 1961; Osborne, 1966; St. John, 1967). During the Mesozoic the Australian continent is thought to have extended over part of what is now the shallow and narrow sea between New Guinea and Australia. The continent was of subdued relief and a narrow trough separated the shelf from a shallow and possibly emergent swell to the north-east. Jurassic and Cretaceous sediments encountered in the Omati No. 1 and Barikewa No. 1 boreholes were deposited on the outer shelf of the Australian continent (Fig. 1). These sediments are thought to have been derived from the Australian continent to the south. An isopach map of the Mesozoic sediments in Western Papua is given in Fig. 2 and a generalized cross section through the Papuan

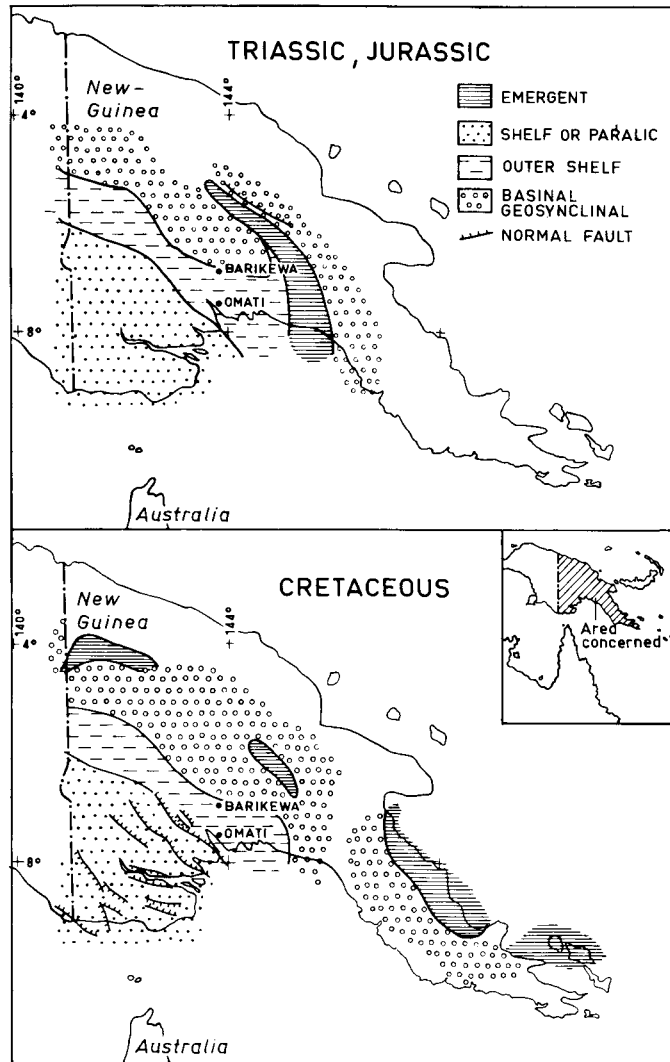


Fig. 1. Triassic, Jurassic and Cretaceous palaeotectonic maps of New Guinea (after St. John, 1967).

delta region and Central foothills in Fig. 3.

Figure 4 represents the sections of the Barikewa No. 1 and Omati No. 1 boreholes, nineteen miles apart in the Central foothills of south-east New Guinea. The Barikewa section consists of 3000 ft of Tertiary argillaceous limestone overlying 10,000 ft of shales of Jurassic and Cretaceous age. The Omati section comprises 10,000 ft of dense Tertiary argillaceous limestones overlying at least 4500 ft of Cretaceous and Jurassic shales. The Mesozoic rocks in both sections consist mainly of fine marine shales, often dark and pyritic,

with rare sandy intercalations and few fossils. Glauconite intercalations occur in the Cretaceous sandstones; the shales can be slightly calcareous. Lithological and palaeontological correlation of the two sections is fair. No nearby outcrops of Mesozoic rocks exist.

No Mesozoic or younger igneous or metamorphic activity has occurred near the deposits. Climatic conditions in the Jurassic are unknown, those in the Cretaceous are thought to have been those of a warm equable climate (Brown *et al.*, 1968).

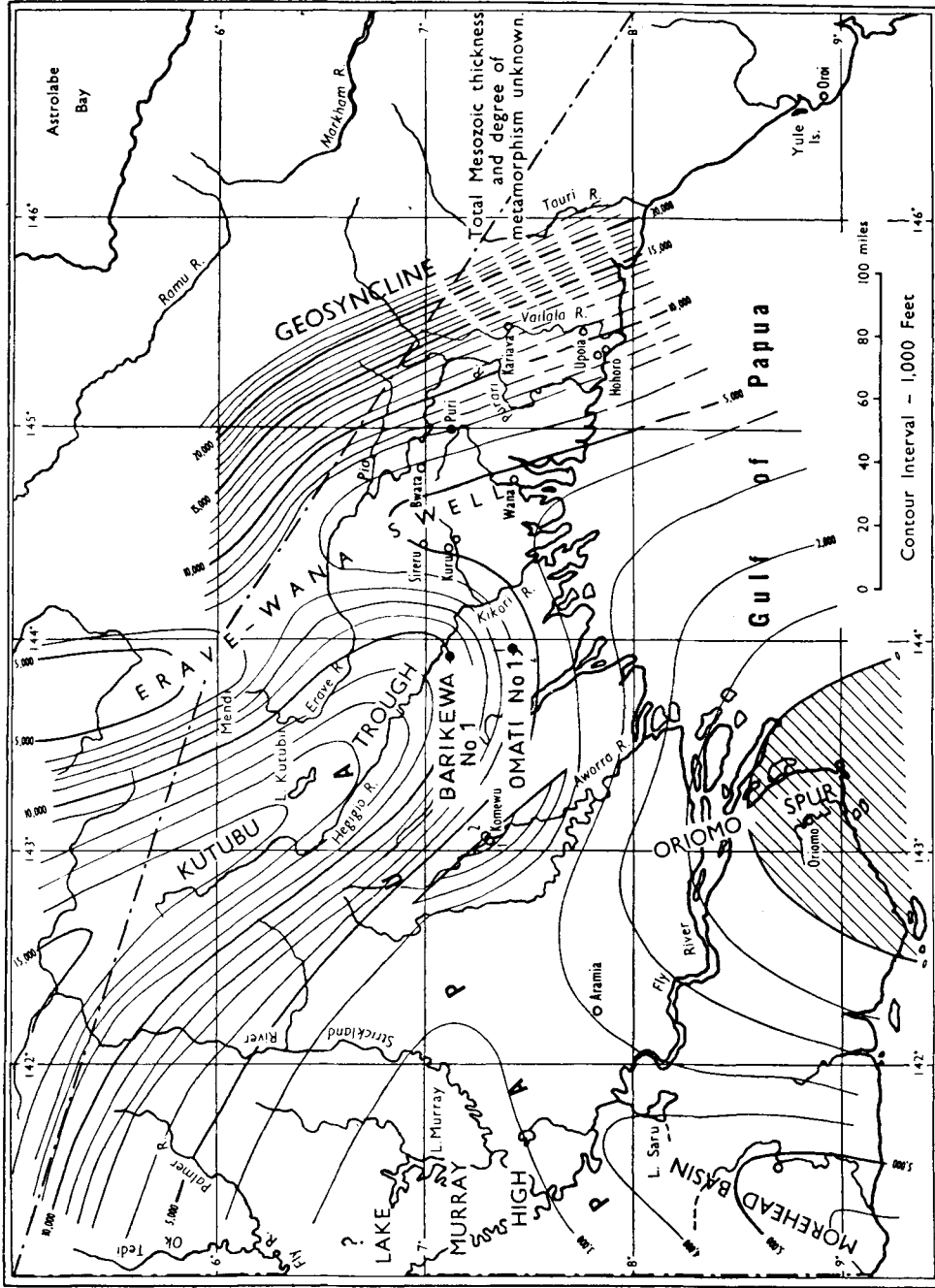


Fig. 2.. Isopach map of Western Papua, showing the thickness of Mesozoic sediments in the Kutubu Trough (after Australasian Petroleum Company Pty., 1961).

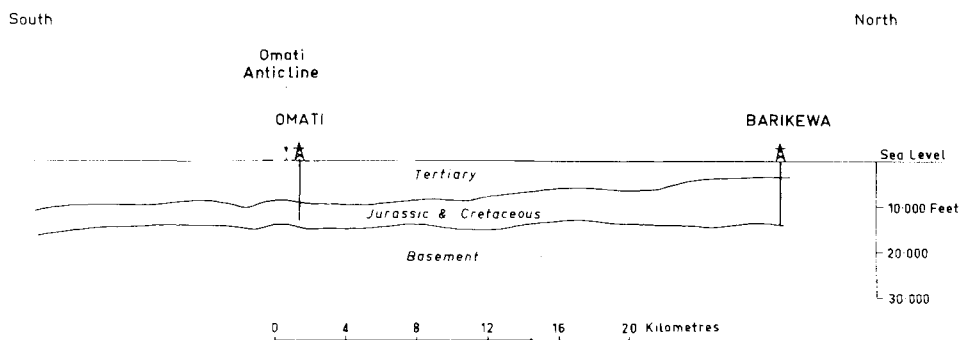


Fig. 3. Generalized section across the delta region and southern Central Foothills, Papua (constructed after A.P.C., 1961).

Structural subsidence is essentially the only tectonic factor that has affected the still sub-horizontal deposits (Fig. 3).

The geology of the alluvial valley of the Lower Mississippi River has been treated by Fisk (1944) and Fisk and MacClelland (1959). The geology of the Eocene Wilcox Formation has been summarised by Burst (1959). The Wilcox exposure trend and structural contours of the subsurface top are shown in Fig. 6. The Wilcox Formation is about 2000 ft thick, and is lithologically composed of interstratified shales, silts, and friable to well-cemented sandstones. Marine beds are common in the exposed section in Alabama; the Wilcox sediments west of the Mississippi embayment are almost exclusively non-marine. In Louisiana, the part of the Wilcox Formation studied in this paper is of mixed deltaic, lagoonal, beach, and marine origin (Burst, 1959).

A north-south cross-section from Vicksburg, Mississippi, to Plaquemines, Louisiana, after Fisk (1944), is given in Fig. 7 and shows a steepening dip of the Wilcox Formation gulfward from central Louisiana. The Silberman well intersects the Wilcox Formation at a depth of about five thousand feet, where it is still gently dipping. The William Edwards and Luma Darbonne wells intersect with a steeply dipping Wilcox Formation at a depth of over 10,000 ft.

Sediments from the present Mississippi River are derived from various sources. The Missouri River contributes mainly montmorillonite of bentonitic origin, whereas the Ohio River contributes much more illite derived from the crystalline rocks in the Appalachian Mountains (Johns and Grim, 1958). In the delta sediments may be mixed with clays carried by ocean currents. Burst (1959) stated that: "The Wilcox sedimentation is judged to have been similar to that in Recent time. It is characterised by a series by a series of deltaic

advances and broad interdeltic bay and lagoon areas usually separated from the open sea by long ridgelike barrier islands". Montmorillonite is a common constituent of Wilcox outcrop material. The higher levels of the Wilcox Formation can contain small amounts of calcite and dolomite.

#### SAMPLE TREATMENT AND ANALYTICAL METHODS

The shale samples were finely ground and subsequently carbonates and soluble salts were removed by a sodium acetate buffer. Organic matter was decomposed by repeated hydrogen peroxide treatment. Free iron oxides were removed by the sodium dithionite-citrate-bicarbonate method. Complete disaggregation was obtained for the Tertiary Louisiana samples. Disaggregation of the Mesozoic Papuan samples remained incomplete. After separation of the remaining rock fragments and sands from the silts and clays by sieving and separation of the coarse silt by decantation the  $< 2 \mu$  fraction was separated by tube centrifugation. Samples were subsequently saturated with  $Mg^{2+}$  and  $K^+$  and excess salt was removed from the samples by washing (centrifugation and decantation) with methanol and acetone. The samples were never allowed to dry during the treatments (see Jackson, 1956). Subsequently standard amounts of clay suspension were transferred to glass slides to form oriented aggregates. In total, 14 samples from Barikewa, 7 from Omati and 18 from Louisiana wells were treated. Sample depths are shown in Table 1.

A series of X-ray diffractograms was obtained from both  $Mg^{2+}$  and  $K^+$  saturated clays after successively drying in air, heating at  $230^{\circ}C$  for 12 hr,  $585^{\circ}C$  for 1 hr and after saturation with ethylene glycol vapour (Brown, 1961). Some diffractograms were obtained for material treated overnight with 1N HCl.

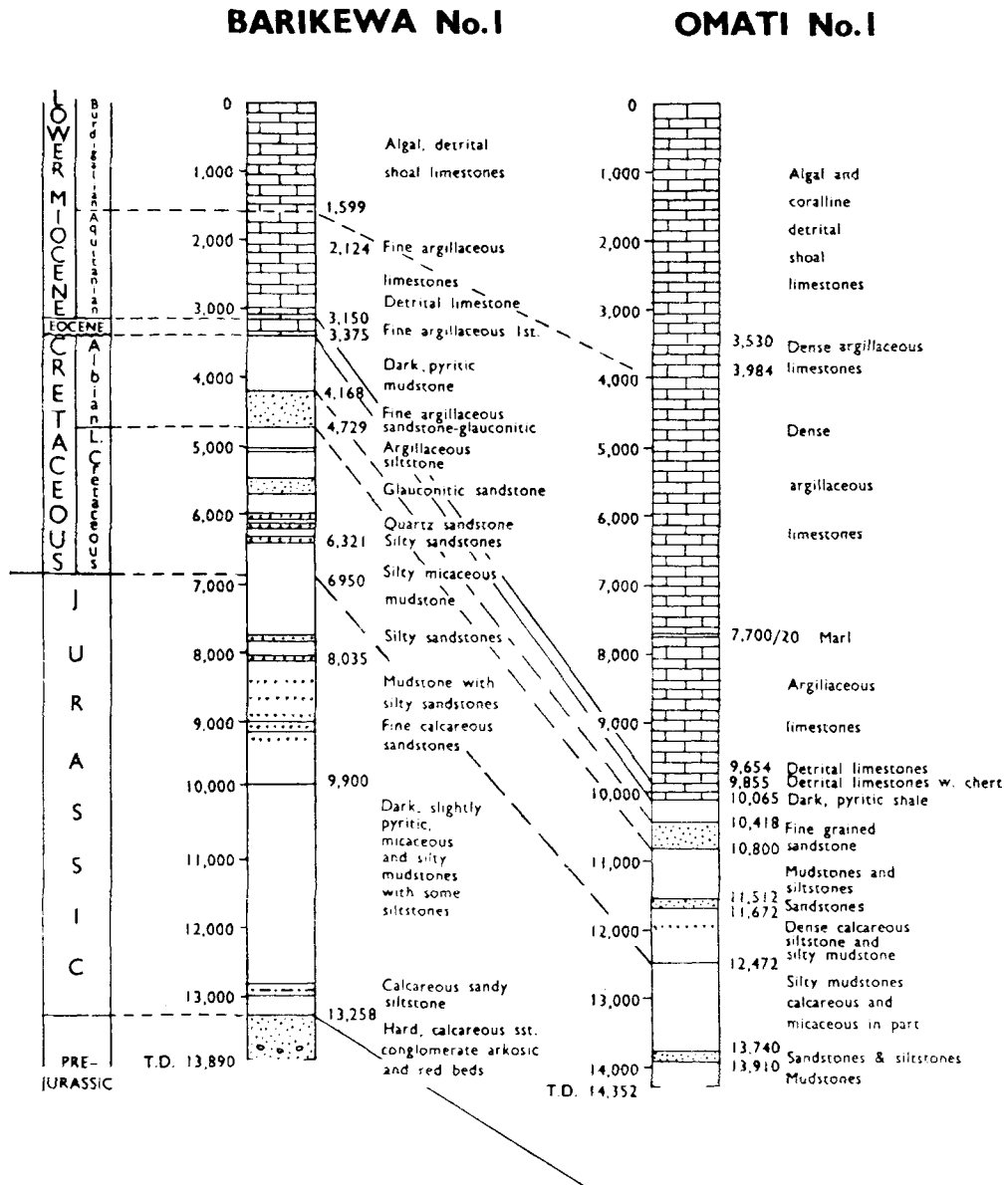


Fig. 4. Columnar sections showing stratigraphic succession of the Barikewa No. 1 and Omati No. 1 boreholes in the Central Foothills, Papua (after A.P.C. 1961).

The X-ray diffraction was carried out on a Philips unit with a PW 1010 generator, a PW 1025 diffractometer, PW 1152 monochromator, using  $\text{CuK}_\alpha$  radiation,  $4^\circ$  scatter slit and Xenon proportional counter. Standard experimental conditions were 40 kV, 20 mA, 1600 V EHT, scanning speed of  $2^\circ 2\theta$  per min, paper speed 20 cm per 15 min, ratemeter setting at 8 with time constant

8 and multiplication factor 1. Scanning occurred over the range from  $2^\circ$ – $44^\circ 2\theta$ .

To enable the determination of the illite polymorphs present, the  $<5 \mu$  fraction was boiled for 30 min in 2N HCl to ensure biotite and chlorite removal. Randomly oriented samples were scanned between  $20^\circ$  and  $32^\circ 2\theta$  for  $\text{CuK}_\alpha$  radiation at a speed of  $\frac{1}{4}^\circ 2\theta/\text{min}$  and the 2M/2M + 1Md poly-

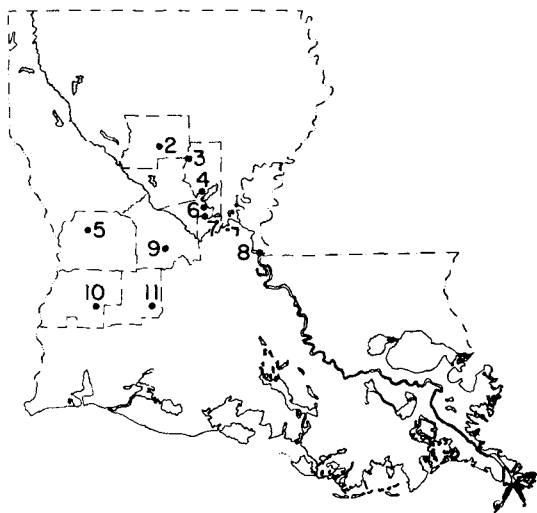


Fig. 5. Location of wells in Louisiana, U.S.A., from which samples have been studied. Numbers 6, 9 and 11 correspond to the locations of the Silberman, William Edwards, and Luma Darbonne wells (after Burst, 1959).

morph ratio was determined by measuring the areas under the  $2.80\text{\AA}$  and the  $2.58\text{\AA}$  peaks (Maxwell and Hower, 1967). The magnesium plus iron content of the illites was determined by measuring  $d(060)$  in the neighbourhood of  $1.5\text{\AA}$  with KBr as standard (Maxwell and Hower, 1967).

The illite sharpness ratio, that is the ratio of  $10\text{\AA}$  peak height/ $10.5\text{\AA}$  peak height, (Weaver, 1961) and the illite crystallinity index (Kubler, 1966) were measured in diffractograms of  $\text{K}^+$  saturated airdried clay fractions. The latter parameter expressed as the width in mm of the  $10\text{\AA}$  peak at half height is dependent on the setting of the diffractometer.

A systematic search for paragonite with (001) at  $9.7\text{\AA}$  was made by repeated measurements of (007), (006) and (010) in the regions  $17^\circ$ – $18.5^\circ$ ,  $26.5^\circ$ – $28.5^\circ$  and  $45^\circ$ – $47.3^\circ 2\theta$   $\text{CuK}\alpha$  at low scanning speed (Harder, 1956).

Twenty total rock samples from the Papuan boreholes and nineteen samples from the Gulf Coast wells were chemically analyzed for the major elements using the method of Shapiro and Brannock (1962). Titanium was determined by

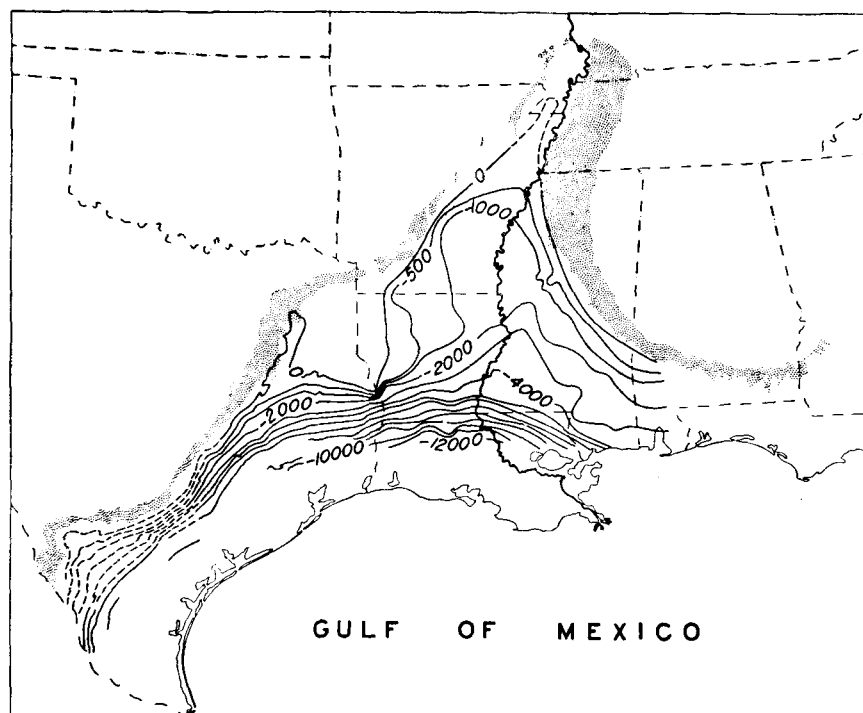


Fig. 6. Exposure trend of the Eocene Wilcox Formation (stippled pattern) and structural subsurface contours on Wilcox top (after Burst, 1959).

## CLAY MINERALS IN MESOZOIC SHALES

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Table 1. Characteristic mineralogical and chemical parameters of illites.  
Jurassic and Cretaceous shales, Central Foothills, Papua

|  | $\frac{2M}{2M+1Md}$ | $d$ (060) | $\frac{Mg+Fe\ total}{O_{10}(OH)_2}$ |                                  | Sharpness ratio<br>K <sup>+</sup> airdried | Crystallinity<br>index in mm;<br>K <sup>+</sup> airdried |
|--|---------------------|-----------|-------------------------------------|----------------------------------|--|--|
| Barikewa   |                     |           |                                     | Barikewa                         |  |  |
| No. 1 borehole<br>depth<br>(ft)                    |                     |           |                                     | No. 1 borehole*<br>depth<br>(ft) |  |  |
| 3500-3505  | 3                   | 1.502     | 0.3                                 | 3500-3505                        | 1.2  | 12   |
| 3730-3735  | 3                   | 1.502     | 0.3                                 | 3730-3735                        | 1.2  | 16   |
| 4746-4750  | 0                   | 1.501     | 0.2                                 | 4770-4775                        | 1.4  | 20   |
| 5918-5923  | 10                  | 1.500     | 0.1                                 | 5918-5923                        | 1.4  | 18   |
| 6250-6255  | 3                   | 1.502     | 0.3                                 | 6250-6255                        | 1.3  | 10   |
| 6707-6710  | †                   | 1.506     | 0.6                                 | 7070-7075                        | 1.4  | 14   |
| 7750-7755  | 2                   | †         | †                                   | 7305-7310                        | 1.3  | 14   |
| 9000-9005  | †                   | 1.502     | 0.3                                 | 8020-8025                        | 1.0  | 13   |
| 10,000-10,005                                      | 5                   | 1.501     | 0.1                                 | 9400-9405                        | 1.3  | 10   |
| 11,102-11,105                                      | †                   | 1.503     | 0.4                                 | 10,200-10,205                    | 1.3  | 9  |
| 12,040-12,045                                      | †                   | 1.502     | 0.3                                 | 11,255-11,260                    | 1.7  | 9  |
| 13,000-13,005                                      | 5                   | 1.502     | 0.3                                 | 12,240-12,245                    | 1.5  | 8  |
| 13,886-13,889                                      | 3                   | 1.504     | 0.5                                 | 13,250-13,255                    | 1.5  | 6  |
|  |                     |           |                                     | 13,625-13,630                    | 1.5  | 10   |
| Omami No. 1 Borehole                               |                     |           |                                     | Omami No. 1 borehole*            |  |  |
| depth  |                     |           |                                     | depth                            |  |  |
| 10,544-10,554                                      | 9                   | 1.504     | 0.5                                 | 10,544-10,554                    | 1.4  | 10   |
| 10,994-11,004                                      | †                   | 1.504     | 0.5                                 | 10,800-10,810                    | 1.3  | 10   |
| 11,700-11,707                                      | †                   | 1.504     | 0.5                                 | 12,012-12,017                    | 1.2  | 10   |
| 12,012-12,017                                      | 0                   | 1.500     | 0.1                                 | 13,110-13,118                    | 1.4  | 8  |
| 13,110-13,118                                      | †                   | 1.497     | 0.0                                 | 13,723-13,743                    | 1.3  | 9  |
| 13,514-13,524                                      | 2                   | 1.499     | 0.1                                 | 14,120-14,130                    | 1.4  | 8  |
| 13,910-13,920                                      | 0                   | 1.503     | 0.4                                 | 14,331-14,344                    | 1.1  | 12   |
| 14,339-14,344                                      | 3                   | 1.500     | 0.1                                 |                                  |  |  |
| Shales, Eocene Wilcox Formation, Louisiana, U.S.A. |                     |           |                                     |                                  |  |  |
| Siberman well*                                     |                     |           |                                     |                                  |  |  |
| depth  |                     |           |                                     |                                  |  |  |
| 5040   | 18                  | 1.503     | 0.4                                 |                                  | 1.7  | 8  |
| 5325   | 68                  | 1.503     | 0.4                                 |                                  | 1.7  | 9  |
| William Edwards well*                              |                     |           |                                     |                                  |  |  |
| depth  |                     |           |                                     |                                  |  |  |
| 10,045   | 47                  | 1.503     | 0.4                                 |                                  | 1.6  | 8  |
| 10,097   | 28                  | 1.502     | 0.3                                 |                                  | 1.8  | 7  |
| 10,115   | 35                  | 1.502     | 0.3                                 |                                  | 2.4  | 7  |
| 10,180   | 20                  | 1.504     | 0.5                                 |                                  | 2.0  | 8  |
| 10,210   | 40                  | 1.504     | 0.5                                 |                                  | 1.6  | 8  |
| 10,265   | 41                  | 1.503     | 0.4                                 |                                  | 2.0  | 7  |
| 10,507   | 60                  | 1.504     | 0.5                                 |                                  | 2.6  | 7  |
| Luma Darbonne well*                                |                     |           |                                     |                                  |  |  |
| depth  |                     |           |                                     |                                  |  |  |
| 12,113   | 61                  | 1.503     | 0.4                                 |                                  | 2.6  | 8  |
| 12,151   | 30                  | 1.502     | 0.3                                 |                                  | †  | †  |
| 12,285   | 30                  | 1.504     | 0.5                                 |                                  | 1.7  | 9  |
| 12,312   | 28                  | 1.502     | 0.3                                 |                                  | 2.1  | 7  |
| 12,368   | 100                 | 1.502     | 0.3                                 |                                  | 1.8  | 8  |
| 12,690   | 40                  | 1.499     | 0.0                                 |                                  | 2.2  | 7  |
| 12,728   | 45                  | 1.504     | 0.5                                 |                                  | 1.9  | 8  |
| 13,888   | 39                  | 1.498     | 0.0                                 |                                  | 1.8  | 8  |
| 15,539   | 41                  | 1.502     | 0.3                                 |                                  | 1.1  | 6  |
| 15,870   | 42                  | 1.503     | 0.4                                 |                                  | 2.1  | 7  |

\*Complete set of diffractograms.

†Not determined.

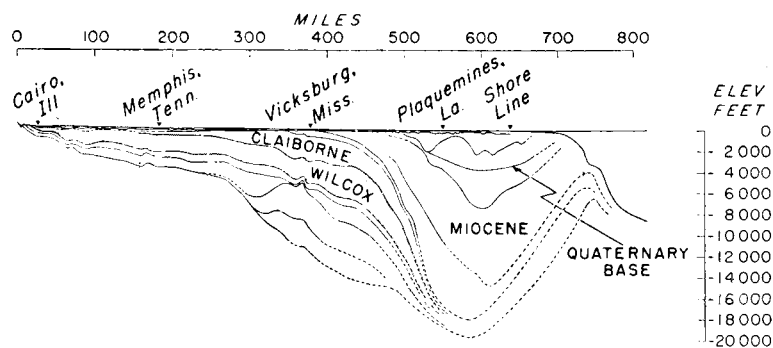


Fig. 7. Cross section of the Mississippi Embayment, Tertiary sediments (after Fisk, 1944).

X-ray fluorescence. The presence of soluble salts and their influence on total rock chemistry was tested by extraction in the ratio 1 g finely hand ground sample to 5 ml distilled water. Samples were mechanically shaken for 1 hr and subsequently filtered. The extractions were analyzed for Na and K by flamephotometry and after addition of lanthanum chloride for Ca and Mg by atomic absorption spectrophotometry.

#### ANALYTICAL RESULTS

The diffractograms of the Papuan samples show some systematic changes with depth (Figs. 8, 9 and 11, Table 2). Following ethylene glycol treatment diffractograms of the Barikewa material show a weak peak at about 17.6 Å for depths down to 6250 ft. The peak decreases gradually in strength

and is absent below this level. The diffractograms of the Omati material do not show any peak at about 17 Å. A characteristic change can also be observed in the diffractograms of the Mg<sup>2+</sup> saturated airdried samples. Samples from the upper part of the Barikewa Mesozoic sequence show a strong diffraction peak at about 14 Å. This peak, still present for the 6250 ft level decreases rapidly in intensity and shifts also *grosso modo* in position from 14 Å at the high levels to 11.2 Å at the lower levels. In the Omati material no strong 14 Å occurs but a similar erratic peak shift occurs. The diffractograms of the airdried K<sup>+</sup> saturated material show for Barikewa large peaks at about 10 Å down to 6250 ft. These 10 Å peaks are slightly asymmetrical to the lower angle side down to about 10,000 ft. These features cannot be observed

Table 2. Major peak changes for diffractograms in relation to sample depth

| Barikewa No. 1 section   |   |
|--|---|
| Ethylene glycolated  | Decreasing intensity small 17.6 Å peak down to 6250 ft; peak disappears farther down. Minor 9.3 Å peak for 3500 ft level shifts to 9.8 Å for 9400 ft; peak disappears beyond. Minor 4.7 Å peak in higher levels disappears below 6250 ft. |
| Mg <sup>2+</sup> airdried  | Strong 14 Å peak down to 6250 ft, shifts then to 11.2 Å.  |
| K <sup>+</sup> airdried  | Very big 10 Å peak down to 6250 ft; asymmetrical down to 10,200 ft.   |
| Omati No. 1 section  |   |
| The diffraction of the sample at 10,544 ft depth, highest in the sequence, is similar to the diffractogram for the Barikews 9400 ft level (9.8 Å peak, etc). Samples of lower levels show diffractograms similar to Barikewa diffractograms of corresponding depths. |   |
| Louisiana sections   |   |
| Ethylene glycolated  | Decreasing intensity small 17.6 Å peak down to 10,015 ft; peak disappears farther down. Minor 9.1 Å peak down to 10,045 ft.   |
| Mg <sup>2+</sup> airdried  | Bad separation of the 14 Å and 10 Å peak down to 10,045 ft. Small 11.9 Å peak for 5040 ft shifts to 10.8 Å for 10,079 ft and stays there for deeper levels.   |
| K <sup>+</sup> airdried  | Asymmetrical 10 Å peak down to 10,045 ft level.   |
| All treatments   | Decrease from 7 Å from 12,368 ft downwards.   |



## BARIKEWA

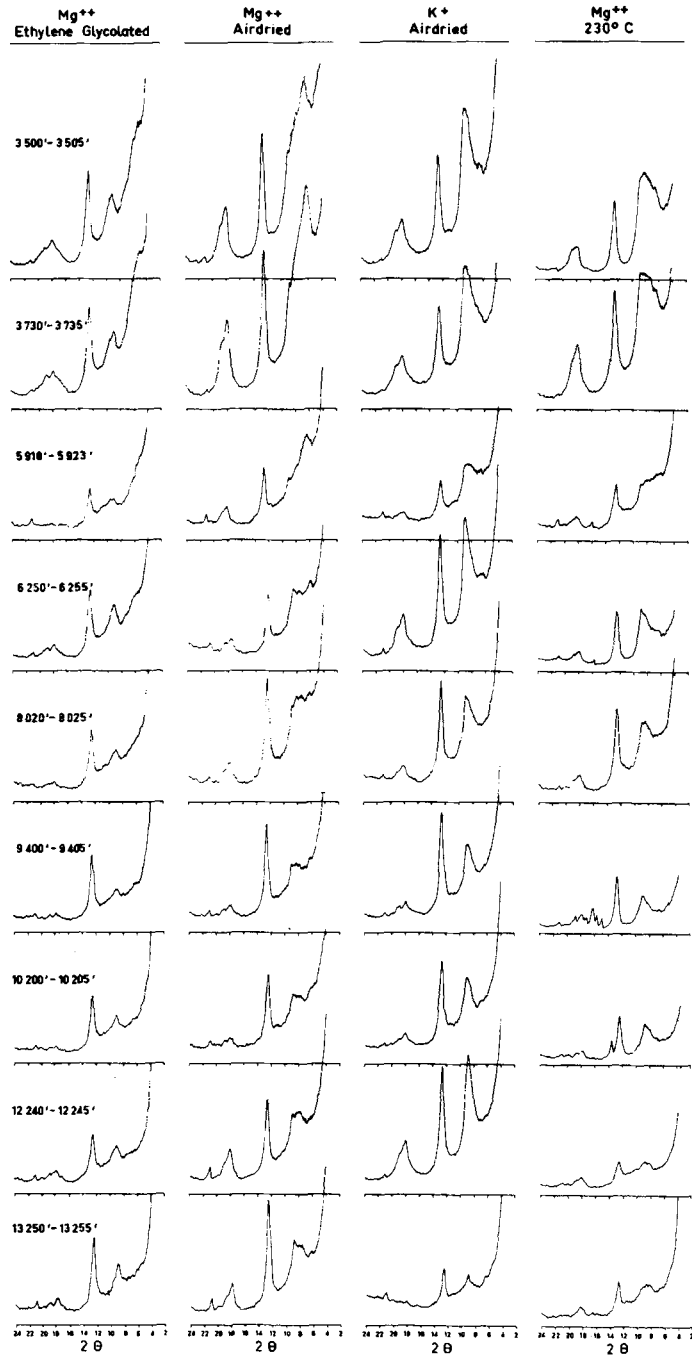


Fig. 8. Diffractograms of oriented aggregates,  $<2\mu$  fraction, from Jurassic and Cretaceous shales, Barikewa No. 1 borehole. Papua.

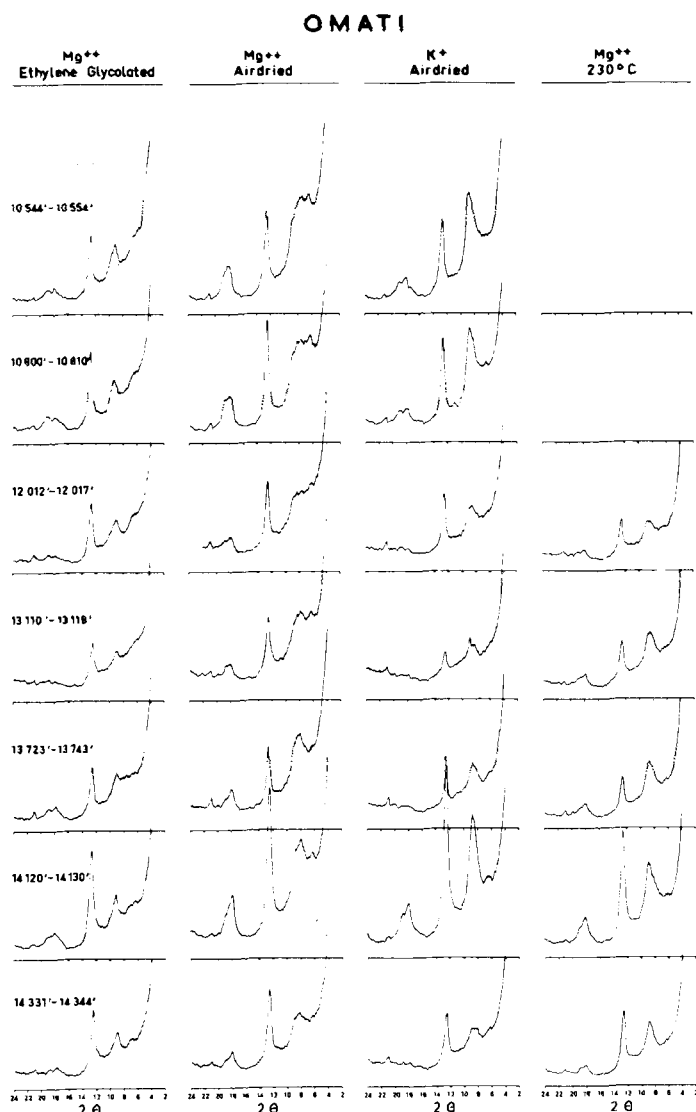


Fig. 9. Diffractograms of oriented aggregates,  $< 2\mu$  fraction, from Jurassic and Cretaceous shales, Omati No. 1 borehole, Papua.

for the Omati shales. Another feature of the Barikewa diffractograms is the presence of a small satellite peak at the higher angle side of the  $10\text{\AA}$  peak for the glycolated material. This peak shifts from  $9.3\text{\AA}$  in the higher levels to  $9.8\text{\AA}$  at 9400 ft and disappears beyond. Less obvious is the presence of a  $4.7\text{\AA}$  peak in the Barikewa levels down to 6250 ft. Only the diffractogram of Omati uppermost sample at 10,544 ft shows a peak at  $9.3\text{\AA}$ .

The interpretation of these peak shifts seems to

be the following. As no (002) or higher order peak of montmorillonite is present in the diffractograms, no pure montmorillonite is present in noticeable amount in any of the specimens, not even in those which show a  $17.6\text{\AA}$  peak. The complete diffraction curves for  $10/17.7\text{\AA}$  or  $10/17.5\text{\AA}$  random interstratification calculated by Hendricks and Teller's (1942) method for infinite crystallites or by MacEwan's method (1958) for smaller crystallites respectively (see MacEwan, Ruiz Amil and Brown, in Brown, 1961, Fig. XI. 12 and 11) show that the

CLAY MINERALS IN MESOZOIC SHALES

GULF COAST

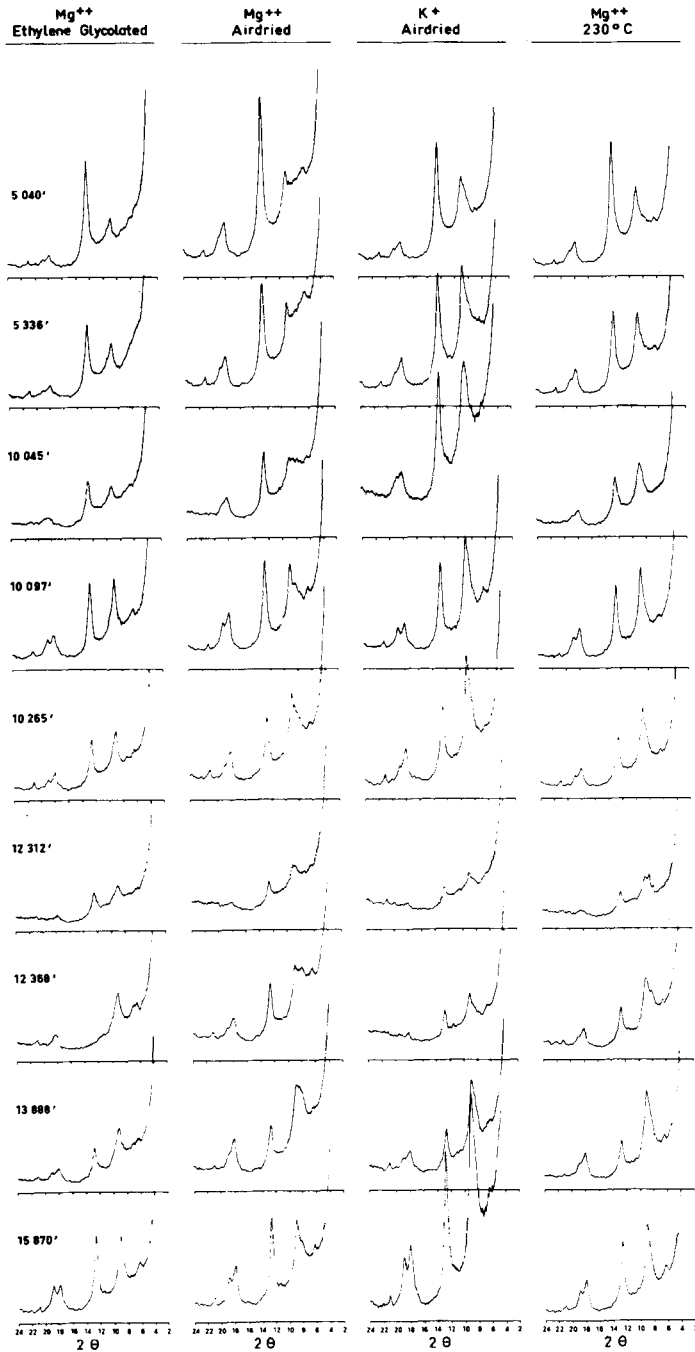


Fig. 10. Diffractograms of oriented aggregates,  $<2\mu$  fraction, from Eocene shales, Wilcox Formation, Louisiana, U.S.A.

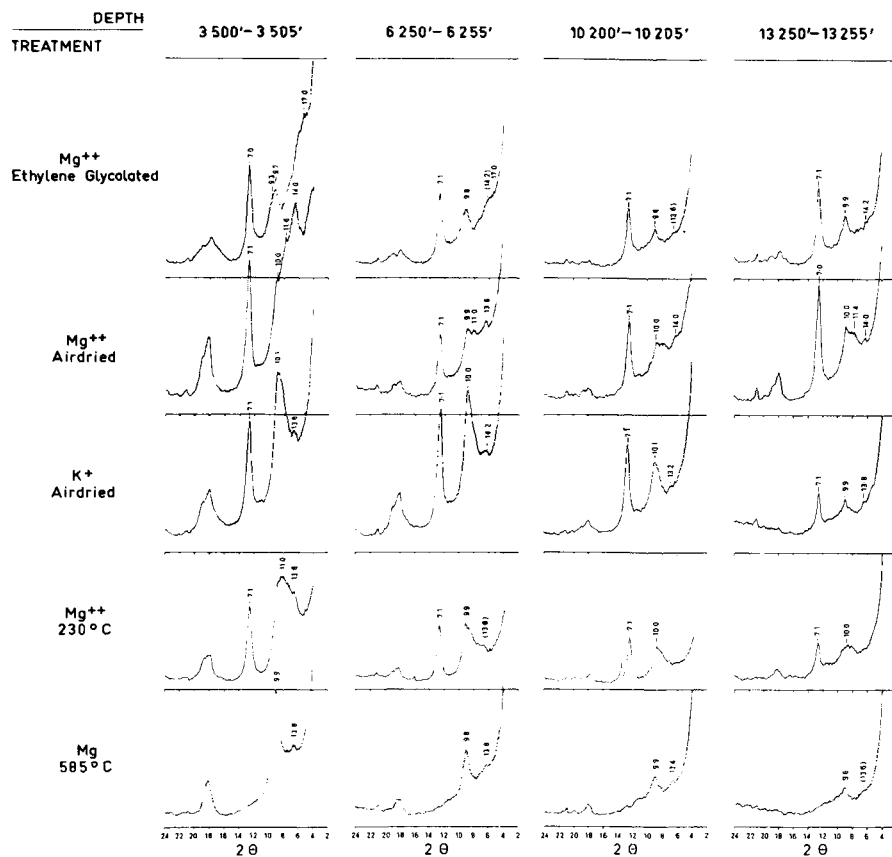


Fig. 11. Diffractograms of some oriented aggregates,  $<2\mu$  fraction, from Jurassic and Cretaceous shales, Barikewa No. 1 borehole, Papua.

17Å peak persists without shifting but with decreasing intensity down to about 40% 17Å layers. The 9.3Å peak for the higher Barikewa levels corresponds to 60% montmorillonite/40% illite composition of a randomly interstratified clay. The 9.8Å peak at the 9400 ft level of the same section corresponds to 20% montmorillonite/80% illite or even less. The change in composition is confirmed by the shift of the (001) peak in the  $Mg^{2+}$  treated airdried samples. As magnesium saturated airdried montmorillonite has a basal spacing of about 14Å the system can be treated here as a mixture of 14Å and 10Å layers. The movement of the combined (001) peak for this mixture is ill defined (see MacEwan, Ruiz Amil and Brown, Fig. XI. 6, in, Brown, 1961). A 14 Å peak may correspond to anything between 50% and 100% 14Å material. The basal spacing of 11.2Å for the deeper levels may correspond to 10–30 per cent expandable material, depending on whether Hendricks and Teller's (1942) or

MacEwan's (1958) method is taken. The presence of a 4.67Å peak down to 6250 ft is not well understood. It is not caused by the very small amounts of chlorite and is not quite in the right position to represent the (004) basal reflection of 60% montmorillonite/40% illite random interstratified clay.

The Omati glycolated material does not show 17Å peaks and generally no satellite peak on the higher side of the 10Å peak; only for 10,544 ft a small peak at 9.8Å is observable. Evaluation of the primary peak position in diffractograms in  $Mg^{2+}$  airdried material shows a shift from about 11.8Å at 10,544 ft down to 11Å at deeper levels. This corresponds to a decrease of 20–40% expandable material down to 10–20% expandable layers, using the same graph XI.16 in Brown. The Omati diffractograms are similar to the Barikewa diffractograms at similar depths.

Besides illite/montmorillonite randomly interstratified minerals considerable amounts of illite (9.96Å and 4.98Å peak), and kaolinite (7Å peak,

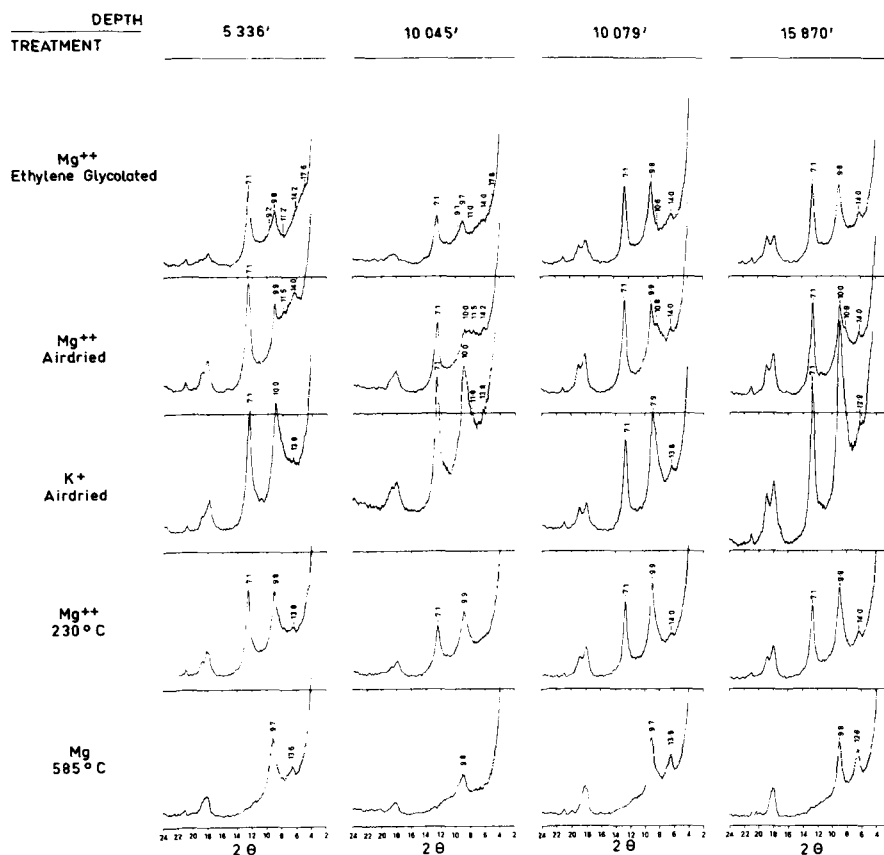


Fig. 12. Diffractograms of some oriented aggregates,  $<2\mu$  fraction, from Eocene shales, Wilcox Formation, Louisiana, U.S.A.

disappearing after heating at 585°C, persisting after HCl treatment) are present in both sections. Chlorite (stable 14Å peak) is virtually absent in most of the Barikewa material and very minor in the Omati material. The Greene-Kelly test (1953) for samples of the higher levels of Barikewa demonstrates that montmorillonite/illite rather than beidellite/illite interstratifications are present. Diffractograms of Mg<sup>2+</sup> and K<sup>+</sup> saturated samples heated up to 230° or 585°C do not show peaks between 10Å and 14Å. Consequently no chlorite/montmorillonite/illite interstratifications (see Weaver, 1956) are present in the Papuan material.

Vermiculite was identified in the Barikewa 9680 ft and Omati 14,120 ft levels (Mg<sup>2+</sup>, 12 hr 110°C, N<sub>2</sub> atmosphere, 11Å peak) and was confirmed by Alexiades and Jackson's method (1966), involving measurement of the cation exchange capacity after saturation and fixation with various cations. Paragonite was looked for systematically but was not found.

The diffractograms of the Eocene shales from

Louisiana (Figs. 10 and 12) are in many aspects similar to the diffractograms described above. The two samples from the Silberman well at about 5000 ft depth and the sample at the top of the Wilcox Formation in the William Edwards well at 10,045 ft show 17.6Å diffraction peaks when glycolated. The absence of the 8.8Å peak shows that no montmorillonite is present at these levels. 9.1Å satellite peaks off the 10Å peaks at these levels suggest the presence of randomly interstratified 50% montmorillonite/50% illite. The presence of interstratified material is confirmed by asymmetrical development of the 10Å peak for K<sup>+</sup> saturated material and very bad separation of the 14Å and 10Å peaks for Mg<sup>2+</sup> treated airdried material from the three levels. At deeper levels, most diffractograms for Mg<sup>2+</sup> treated and glycolated material show a 10.8Å peak as lower angle satellite of the 10Å peak. MacEwan's curves imply that at these deeper levels there is 10–25% of montmorillonite in the randomly interstratified illite/montmorillonite.

The Gulf Coast materials shows in addition a regular shift of a small peak from 11.9 Å at 5040 ft to 10.8 Å at 10,079 ft in ethylene glycol treated material and a shift over the same range in Mg<sup>2+</sup> airdried material. Study of the very asymmetrical 10 Å peak for K<sup>+</sup> airdried material is inconclusive; no special 400° test, causing collapse of Mg<sup>2+</sup> montmorillonite to 10 Å has been carried out (Weaver, 1956). Probably these peaks are caused by the presence of randomly interstratified chlorite/illite/montmorillonite with minor amounts of montmorillonite only and a chlorite/illite ratio changing from about 30/70 to 15/85. The 10.8 Å peak at lower levels can be considered as the (001) reflection of the previously discussed illite/montmorillonite interstratification.

Variations in the 7 Å/10 Å peak ratio, 7 Å peak height for K<sup>+</sup> 230°C material and 14 Å peak height for Mg<sup>2+</sup> 585°C diffractograms are plotted together with the MgO content of the bulk rock in Fig. 13. From this figure and the X-ray information, completed for some samples with diffractograms of HCl treated material, it can be concluded that the first three samples contain more kaolinite and that in particular the kaolinite content from 12,360 ft down is much lower than at the higher levels. The chlorite content also increases from this level down.

High scattering at lower angles is typical for all the diffractograms. This feature was predicted for montmorillonite/illite random interstratification by MacEwan *et al.* (1961) and such clay minerals are present in all the samples analyzed. High scattering at low angles was not observed in a reference diffractogram from a pure 2M muscovite sample.

The polymorphs distribution, magnesium and iron content, sharpness ratio, and crystallinity index of the illites in the samples are listed in Table 1. The higher proportion of 2M illite polymorphs, the higher sharpness ratio and related lower crystallinity index of the illites in the Louisiana samples when compared with the Papuan samples will be discussed below.

The bulk chemical composition of the shales, water extractable (earth) alkalis and derived Niggli values are listed in Table 3. The extractable salts consist essentially of sodium salts, contributing up to 0.3 weight per cent Na<sub>2</sub>O in the bulk rock composition, where Na<sub>2</sub>O ranges from 1 to 4 per cent. The influence of the composition and concentration of the extractable salts on the bulk rock composition is limited. The chemical data will be discussed in more detail below.

#### INTERPRETATION AND DISCUSSION

##### *Chemical composition—mineralogical composition*

The clay mineralogical differences within the Papuan and the Louisiana sections can in principle

be explained by either changes in the pattern of sedimentation or by post-depositional alterations. Examination of the bulk rock analyses from the Papuan samples (Table 3) does not reveal the significant variations in chemical composition which would usually follow differences in the pattern of sedimentation. Variation in silica values occurs but can be explained by differences in quartz content in relation to grain size. This variation can be ruled out by expressing the rock composition in Niggli values, as these parameters are based on the ratio of the oxides of aluminium, iron plus magnesium, calcium, and alkalis. The Niggli values listed in Table 3, and in particular the *al* values, suggest a stable pattern of sedimentation. Variations in CaO and FeO and the related *c* and *fm* values seem to be due essentially to the presence of some calcite and siderite and do not affect variations in the chemical composition of the silicate phase.

The shales from Louisiana, although somewhat different in composition from the Papuan samples, show also little variation in their chemistry. The magnesium content however of the samples downwards from 12,368 ft, expressed in oxide form and as a Niggli value, is significantly and abruptly higher than in the upper part of the section. The positive correlation of the chlorite 14 Å peak intensity with the magnesium content of the rock (Fig. 13), and the abrupt decrease of kaolinite at the 12,368 ft level suggest a change in the pattern of sedimentation. The chemical analyses of the samples from higher levels are all very similar. There is no chemical evidence of important changes in sedimentary facies at these higher levels, although it is here that the important mineralogical change occurs.

Minor mineralogical changes in the composition of the Wilcox sediments have been recorded by Burst in the form of the 7 Å/10 Å peak height ratio. This ratio correlates well with the environment log as Burst demonstrated for the Luma Darbonne section between about 12,000 and 13,000 ft. The value of the 7 Å/10 Å peak ratio is, according to Burst, essentially due to the chlorite content. The chlorite content is higher in the marine and beach deposits than in the deltaic and lagoonal deposits. Kaolinite is only of subordinate importance at these levels, in contrast with the situation at higher levels; general use of the ratio is impossible with varying kaolinite content.

The gradual change from 60% montmorillonite/40% illite to 20% montmorillonite/80% illite randomly interstratified minerals in the Papuan material is completed at comparable depths of about 10,200 ft in the Barikewa section and at 10,800 ft in the Omati section. The stratigraphic

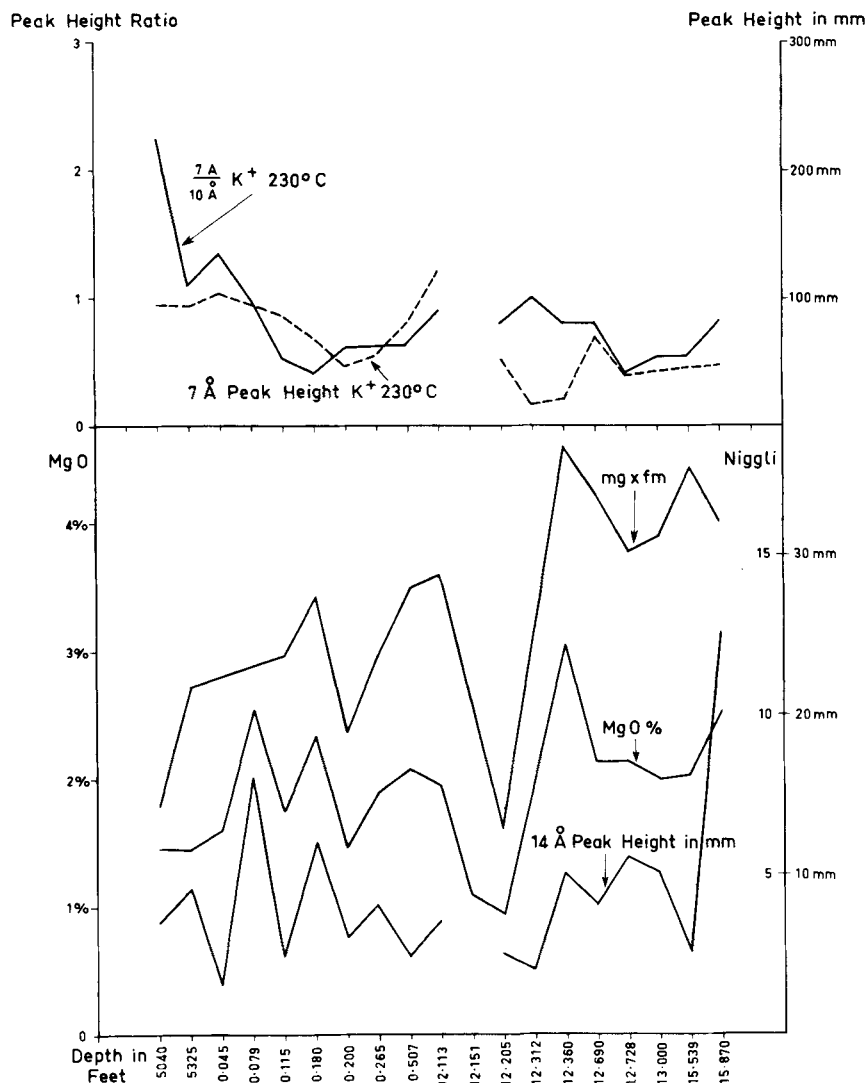


Fig. 13. Correlation of 14 Å peak of chlorite in the  $<2\mu$  fraction with the magnesium content of the bulk rock composition. The values of the 7 Å peak and the 7 Å/10 Å peak ratio are vaguely reciprocal to the magnesium and chlorite content. Eugene shales, Wilcox Formation, Louisiana, U.S.A.

levels however are very different and give additional support to a diagenetic origin of the alterations.

The somewhat abrupt mineralogical change in the analyzed Louisiana samples from 50% montmorillonite/50% illite to 25%–10% montmorillonite/75%–90% illite at levels lower than 10,045 ft seems again to be caused by diagenesis, involving the disappearance of most of the expandable material. The second mineralogical change in this material at a depth of 12,368 ft, the increase of chlorite and decrease of kaolinite, coincides with a

chemical change and is thought to be caused by changes in sedimentation.

These observations are in general agreement with Burst's (1959) general conclusion that in the Wilcox sediments montmorillonite structures are commonly interstratified with illite components below depth of 3000 ft and that pure montmorillonite is not very evident below that depth. Burst stated: "Montmorillonite becomes less evident below 3000 ft and is not found in an unmixed state below 9000–10,000 ft overburden level. At depths

Table 3. Chemical composition of shales

|                       |                    | Jurassic and Cretaceous, Central Foothills, Papua |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |
|-----------------------|--------------------|---|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|------------------|-------------------------------|------------------|-----------------|-------------------------------|-------------------------------|--------|--------|---------------------|-------------------|------------------|---------------|------|------|------|------|---------|---------|-----|
|                       |                    | Chemical Analysis                                 |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |
|                       |                    | SiO <sub>2</sub>                                  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | H <sub>2</sub> O | CO <sub>2</sub> | H <sub>2</sub> O <sup>+</sup> | H <sub>2</sub> O <sup>-</sup> | Total  | Excr.  | (excrH) alkalis-ppm |                   |                  | Niggli values |      |      |      |      |         |         |     |
|                       |                    |   |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        | MgO    | CaO                 | Na <sub>2</sub> O | K <sub>2</sub> O | si            | al   | fu   | c    | alk  | mg x fm | k x alk |     |
| Sarawak No 1 Borehole | 3500'-3505'        | 57.5  | 16.5                           | 1.83                           | 4.49 | 1.64 | 1.22 | 2.31              | 1.81             | 0.96             | 0.18                          | 0.01             | 1.61            | 5.64                          | 3.08                          | 98.78  | < 1    | < 1                 | 2140              | 30               | 261           | 44.3 | 34.7 | 5.7  | 25.3 | 11.2    | 5.2     |     |
|                       | 3748'-4750'        | 68.0  | 13.5                           | 1.92                           | 2.76 | 1.04 | 1.73 | 1.75              | 1.41             | 0.96             | 0.15                          | 0.01             | 1.64            | 4.07                          | 2.97                          | 99.86  | < 1    | < 1                 | 1674              | 35               | 412           | 44.1 | 32.0 | 11.3 | 15.6 | 9.5     | 5.5     |     |
|                       | 3918'-3923'        | 65.3  | 15.1                           | 0.88                           | 3.46 | 1.03 | 0.95 | 2.19              | 1.70             | 0.58             | 0.13                          | 0.01             | 0.95            | 4.46                          | 2.07                          | 98.81  | < 1    | < 1                 | 1630              | -                | 366           | 46.8 | 31.0 | 5.6  | 16.8 | 8.2     | 4.9     |     |
|                       | 6350'-6355'        | 63.1  | 16.6                           | 2.37                           | 3.04 | 1.02 | 1.21 | 1.92              | 2.22             | 0.75             | 0.09                          | 0.03             | 1.42            | 3.24                          | 1.69                          | 98.80  | < 1    | 2                   | 2174              | 279              | 333           | 45.3 | 33.0 | 6.6  | 17.1 | 8.2     | 7.3     |     |
|                       | 7750'-7755'        | 68.6  | 10.4                           | 3.36                           | 4.38 | 0.87 | 0.96 | 1.80              | 1.52             | -                | 0.18                          | 0.01             | 1.36            | 4.73                          | 1.62                          | 99.88  | -      | -                   | 292               | 25.1             | 43.8          | 5.8  | 15.5 | 3.2  | 2.6  |         |         |     |
|                       | 9204'-9206'        | 61.3  | 15.6                           | 0.63                           | 5.20 | 0.39 | 2.44 | 1.76              | 1.79             | 0.79             | 0.21                          | 0.12             | 3.50            | 5.39                          | 1.95                          | 101.07 | < 1    | 2                   | 1172              | 271              | 306           | 45.8 | 27.2 | 12.9 | 16.1 | 3.0     | 3.6     |     |
|                       | 9405'-9410'        | 52.6  | 15.0                           | 4.70                           | 5.50 | 0.95 | 0.99 | 4.18              | 1.42             | 1.00             | 0.21                          | 0.21             | 3.31            | 3.11                          | 1.83                          | 98.28  | -      | -                   | -                 | -                | 396           | 36.0 | 39.2 | 6.4  | 20.6 | 5.9     | 3.7     |     |
|                       | 10200'-10205'      | 49.8  | 18.4                           | 5.00                           | 7.23 | 0.15 | 3.47 | 1.61              | 1.63             | 0.77             | 0.48                          | 0.05             | 5.30            | 3.26                          | 1.55                          | 98.10  | < 1    | 3                   | 1332              | 134              | 178           | 32.4 | 17.6 | 20.3 | 7.6  | 0.9     | 3.8     |     |
|                       | 11102'-11005'      | 51.7  | 15.7                           | 4.02                           | 7.16 | 1.23 | 1.71 | 2.48              | 2.09             | 1.00             | 0.24                          | 0.07             | 7.18            | 4.17                          | 1.88                          | 100.61 | < 1    | -                   | -                 | 203              | 36.2          | 42.4 | 7.1  | 14.3 | 7.1  | 4.9     |         |     |
|                       | 11255'-11240'      | 57.7  | 16.3                           | 1.35                           | 5.62 | 1.53 | 0.95 | 1.74              | 1.94             | 0.88             | 0.17                          | 0.05             | 1.40            | 5.50                          | 2.16                          | 98.67  | < 1    | 1                   | 1620              | 74               | 277           | 44.8 | 37.0 | 4.8  | 13.6 | 10.7    | 5.4     |     |
|                       | 12050'-12045'      | 57.3  | 16.1                           | 1.16                           | 6.43 | 1.69 | -    | 2.87              | 1.12             | 0.48             | 0.15                          | 0.10             | 1.10            | 3.07                          | 1.44                          | 100.05 | < 1    | 2                   | 1368              | 109              | 256           | 42.5 | 39.2 | 0.0  | 18.3 | 11.1    | 5.8     |     |
|                       | 13220'-13215'      | 60.0  | 16.7                           | 0.83                           | 4.80 | 1.45 | 0.81 | 1.53              | 2.28             | 0.97             | 0.19                          | 0.01             | 1.03            | 5.37                          | 1.85                          | 98.62  | < 1    | 1                   | 1361              | 60               | 276           | 45.3 | 32.0 | 3.8  | 18.8 | 10.9    | 7.3     |     |
| 13866'-13859'         | 68.9               | 13.3  | 1.19                           | 2.52                           | 1.05 | 0.44 | 0.09 | 1.95              | 0.62             | 0.03             | 0.04                          | 1.05             | 2.17            | 1.10                          | 98.57                         | < 1    | 1      | -                   | -                 | 378              | 62.9          | 26.1 | 2.6  | 28.4 | 8.6  | 6.2     |         |     |
|                       |                    | Analyses: S.E. Hill and R.B. Reid, April 1968.    |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |
|                       |                    | Eocene Wilcox Formation, Louisiana (U.S.A.)       |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |
|                       |                    | SiO <sub>2</sub>                                  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | H <sub>2</sub> O | CO <sub>2</sub> | H <sub>2</sub> O <sup>+</sup> | H <sub>2</sub> O <sup>-</sup> | Total  | Excr.  | (excrH) alkalis-ppm |                   |                  | Niggli values |      |      |      |      |         |         |     |
|                       |                    |   |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        | MgO    | CaO                 | Na <sub>2</sub> O | K <sub>2</sub> O | si            | al   | fu   | c    | alk  | mg x fm | k x alk |     |
| Billman Well          | Depth 5040'-5044'  | 62.70   | 17.34                          | 2.42                           | 1.77 | 1.41 | 0.71 | 1.13              | 1.91             | 0.88             | 0.01                          | 0.01             | -               | 9.78                          | 1.94                          | 100.29 | -      | -                   | -                 | -                | 369           | 60.1 | 26.5 | 0.0  | 13.4 | 7.1     | 7.1     |     |
|                       | 5325'              | 62.71   | 16.64                          | 2.12                           | 1.77 | 1.38 | 0.69 | 1.56              | 2.38             | 0.93             | 0.01                          | 0.01             | -               | 9.66                          | 2.06                          | 101.69 | < 1    | < 1                 | 1210              | 137              | 359           | 53.4 | 27.5 | 2.6  | 16.4 | 10.8    | 8.2     |     |
| William Edwards Well  | 10045'             | 58.88   | 20.37                          | 3.29                           | 2.78 | 1.66 | 0.71 | 0.94              | 2.18             | 1.13             | 0.03                          | 0.01             | -               | 9.03                          | 1.80                          | 102.09 | < 1    | < 1                 | 2850              | 163              | 273           | 53.9 | 32.6 | 3.2  | 10.3 | 11.1    | 6.1     |     |
|                       | 10079'             | 59.10   | 19.57                          | 2.61                           | 3.48 | 0.93 | 1.09 | 1.11              | 2.41             | 0.84             | 0.04                          | 0.05             | -               | 7.01                          | 1.81                          | 101.29 | -      | -                   | -                 | -                | 253           | 69.0 | 23.2 | 3.0  | 14.6 | 8.4     |         |     |
|                       | 10115'             | 59.28   | 18.98                          | 2.68                           | 2.15 | 1.74 | 1.19 | 1.47              | 2.45             | 0.87             | 0.03                          | 0.01             | -               | 7.00                          | 1.89                          | 99.53  | -      | -                   | -                 | -                | 271           | 51.1 | 29.6 | 5.8  | 13.7 | 13.8    | 7.3     |     |
|                       | 10180'             | 53.63   | 20.57                          | 3.10                           | 4.30 | 2.37 | 1.75 | 1.74              | 3.20             | 0.81             | 0.05                          | 0.02             | -               | 11.00                         | 0.48                          | 100.85 | < 1    | 1                   | 1810              | 67               | 213           | 46.9 | 31.1 | 7.3  | 14.6 | 13.7    | 6.2     |     |
|                       | 10210'             | 59.17   | 20.93                          | 0.68                           | 3.89 | 1.43 | 1.60 | 1.59              | 3.59             | 0.74             | 0.03                          | 0.01             | -               | 1.68                          | 1.06                          | 100.37 | < 1    | < 1                 | 1770              | 112              | 266           | 52.0 | 27.6 | 8.7  | 12.2 | 9.6     | 10.2    |     |
|                       | 10285'             | 59.17   | 19.39                          | 1.41                           | 3.29 | 1.76 | 0.77 | 1.79              | 2.39             | 0.78             | 0.03                          | 0.01             | -               | 7.97                          | 1.59                          | 101.36 | -      | -                   | 1920              | 322              | 280           | 52.3 | 29.5 | 3.6  | 14.6 | 11.8    | 4.8     |     |
|                       | 10507'             | 56.73   | 21.93                          | 1.30                           | 2.78 | 2.17 | 0.14 | 1.44              | 2.95             | 0.87             | 0.06                          | 0.01             | -               | 8.33                          | 1.28                          | 98.98  | -      | -                   | 680               | 201              | 264           | 56.6 | 28.6 | 0.5  | 16.5 | 13.9    | 8.4     |     |
|                       | Luna Darbonne Well | 12133'  | 67.50                          | 17.22                          | 1.34 | 2.67 | 1.87 | 0.42              | 1.66             | 2.06             | 0.71                          | 0.04             | 0.01            | -                             | 5.12                          | 1.02   | 101.57 | -                   | -                 | -                | -             | 349  | 52.5 | 30.1 | 2.2  | 15.2    | 16.3    | 6.8 |
|                       |                    | 12151'  | 67.26                          | 16.84                          | 1.85 | 1.52 | 1.16 | 0.71              | 0.80             | 2.00             | 0.94                          | 0.02             | 0.01            | -                             | 5.98                          | 0.81   | 100.16 | < 1                 | < 1               | 240              | 37            | 447  | 60.7 | 26.8 | 0.0  | 12.5    | 10.3    | 7.8 |
|                       |                    | 12205'  | 62.10                          | 19.76                          | 2.44 | 1.39 | 0.86 | 0.98              | 1.59             | 2.33             | 0.87                          | 0.01             | 0.01            | -                             | 7.18                          | 0.78   | 100.40 | -                   | -                 | -                | -             | 335  | 59.0 | 21.3 | 5.1  | 14.6    | 8.4     |     |
| 12312'                |                    | 56.48   | 21.88                          | 1.24                           | 4.05 | 1.97 | 0.62 | 1.06              | 1.90             | 0.85             | 0.08                          | 0.01             | -               | 7.49                          | 1.27                          | 100.68 | -      | -                   | -                 | -                | 353           | 56.7 | 31.7 | 1.8  | 9.8  | 12.7    | 5.3     |     |
| 12368'                |                    | 56.55   | 24.37                          | 0.76                           | 3.79 | 2.07 | 0.71 | 1.13              | 1.74             | 1.02             | 0.07                          | 0.01             | -               | 7.86                          | 0.67                          | 99.38  | -      | -                   | -                 | -                | 223           | 57.7 | 33.6 | 0.0  | 8.7  | 18.6    | 6.4     |     |
| 12480'                |                    | 63.87   | 20.04                          | 1.32                           | 3.89 | 1.32 | 0.88 | 1.18              | 2.46             | 0.74             | 0.06                          | 0.01             | -               | 4.83                          | 0.63                          | 100.92 | -      | -                   | -                 | -                | 315           | 51.3 | 27.6 | 0.0  | 6.9  | 16.0    | 7.0     |     |
| 12728'                |                    | 58.83   | 20.49                          | 1.60                           | 3.34 | 2.32 | 1.33 | 1.21              | 2.63             | 0.88             | 0.10                          | 0.01             | -               | 5.95                          | 1.12                          | 100.00 | -      | -                   | -                 | -                | 256           | 48.6 | 30.8 | 5.8  | 14.8 | 14.0    | 10.2    |     |
| 13088'                |                    | 60.53   | 15.81                          | 1.35                           | 2.91 | 1.87 | 1.12 | 1.09              | 2.82             | 0.91             | 0.09                          | 0.01             | -               | 6.22                          | 0.94                          | 98.17  | -      | -                   | -                 | -                | 288           | 55.9 | 31.4 | 5.9  | 16.8 | 14.5    | 9.2     |     |
| 15339'-15350'         |                    | 68.71   | 12.42                          | 0.46                           | 3.41 | 2.01 | 1.05 | 1.84              | 1.95             | 0.73             | 0.07                          | 0.01             | -               | 5.67                          | 0.87                          | 99.17  | -      | -                   | -                 | -                | 379           | 60.7 | 36.0 | 6.3  | 17.0 | 17.7    | 7.0     |     |
| 15870'                |                    | 57.48   | 18.02                          | 0.56                           | 6.45 | 2.52 | 1.33 | 1.68              | 2.18             | 0.78             | 0.07                          | 0.46             | -               | 7.57                          | 0.99                          | 100.29 | < 1    | 1                   | 2560              | 57               | 227           | 41.9 | 39.6 | 5.7  | 12.8 | 16.9    | 5.5     |     |
|                       |                    | Analyses: T. Ramachandra Rao, November, 1967      |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |
|                       |                    | Excr. = traces ** not present - = not determined  |                                |                                |      |      |      |                   |                  |                  |                               |                  |                 |                               |                               |        |        |                     |                   |                  |               |      |      |      |      |         |         |     |

between 6000 and 14,000 ft montmorillonite structures are commonly interspersed with illite, and frequency of which increases with depth to a virtual elimination of montmorillonite characteristics below 14,000 ft."

Burst also illustrated the decrease of swelling characteristics essentially by a gradual shift of the diffraction peak of untreated material from 12.5Å to 10 Å and a shift in glycolated material from 17Å down to equally 10Å. These shifts shown for four samples in his Fig. 5, are for minor peaks also observable in our diffractograms for the few samples analyzed in the range from 5000 to 10,000 ft.

According to MacEwan, Ruiz Amil and Brown in Brown (1961) or Weaver (1956) these shifts are typical for mixtures of 10Å/14Å and/or 17Å/10Å randomly interstratified material respectively. Similar peak shifts have been observed by Dunoyer de Ségonzac (1964) in diffractograms from shales in a deep Cretaceous section from Cameroon and have been interpreted by him also as a montmorillonite-interstratified 10-14-illite sequence. The author is inclined to explain the shifts observed by Burst and Dunoyer as being caused by combined disappearance of montmorillonite, change of composition and disappear-

ance of interstratified chlorite/illite/montmorillonite, and change in composition of illite/montmorillonite randomly interstratified clay minerals. There is no indication of presence of interstratified chlorite/illite/montmorillonite in the Papuan samples. These minerals are according to Weaver (1956) quite common in shales and are according to our interpretation also present in the Louisiana and Cameroon samples. The low chlorite content of the Papuan sediments may have prevented their development. Because of the somewhat irregular shift of vague peaks the interstratified clays are not thought to have one specific composition at a certain level, but to show a certain range in composition.

One would expect that the changing proportions of expandable material in the randomly interstratified montmorillonite/illites expresses itself in the chemistry of the shales. This is not the case (Table 3), although lower K<sub>2</sub>O values may be present in samples from the higher levels of the Barikewa and Wilcox sections. High magnesium and iron content of montmorillonite may be inherited by illites, also rich in these elements (Hower and Mowatt, 1966 and Maxwell and Hower, 1967). Absence of systematic variations in Al<sub>2</sub>O<sub>3</sub> may be explained by variations in kaolinite content.



### *Factor of diagenesis*

No systematic sedimentary facies changes are likely to have caused the mineralogical changes, and metamorphic processes do not appear to have been responsible for them either. Burial, time, and the composition of interstitial brines are more likely to be the factors that have determined the final mineral assemblages. An inventory of the clay minerals in ancient sediments by Grim (1953) shows that montmorillonite is generally absent in sediments older than the Mesozoic and that kaolinite is relatively rare in Pre-Carboniferous sediments. It is likely that these differences in composition of sediments are caused by diagenesis.

Because of the complex history of the sediments inventoried by Grim time is not necessarily the only factor operating in diagenesis. Outcropping Wilcox sediments are montmorillonite-rich and buried Wilcox material is montmorillonite-poor; consequently time is not an important factor in the diagenesis of these sediments, if at all.

Depth of burial and temperature are necessarily related. Because of a lack of information from various sedimentary basins, no firm conclusion can be drawn as yet about the relative importance of these factors. Burst (1966) claims that pore water and excessive (more than two) clay-water interlayers are removed by the action of overburden pressure after the first few thousand feet and that temperature (105°C) removes the next to last water interlayer.

Influence of brines was discussed by Whitehouse and McCarter (1958) who observed alteration of montmorillonite to illite or chlorite during long run experiments in artificial seawater. The nature of the mineral formed depended on the Mg/K ratio in the water. Interstitial water in sediments is much more concentrated and often shows a higher K/Mg ratio than seawater where the ratio is 1/3 (White, 1965). The high K/Mg ratios observed, 100/1 or higher, in the extractions from the shales analysed (see Table 3) could explain why the montmorillonite components seem to alter gradually into illite in the rocks analysed.

### *Illite polymorphs*

The Papuan and Louisiana sediments show some marked differences in the type of illite polymorphs present, (Table 2), the sharpness of the illite peaks (Table 2) and the chemistry (Table 3). The relative amount of the illite 1Md polymorphs in the Papuan shales is constant and usually higher than 95 per cent. The Gulf Coast samples show a much lower proportion of 1Md polymorphs, averaging only at 57 per cent. Yoder and Eugster (1955) determined on synthetic and natural material the stability relations of the muscovite polymorphs. They

found that the 1Md polymorph formed metastably at all temperatures and that it was succeeded by 2M at higher temperatures (>200°–350°C) and by 1M at low temperatures. Velde's (1965) re-examination of the system showed that 2M is the stable polymorph at temperatures as low as 125°C at 4.5 kb, and he concluded that the 1M polymorph is also metastable at muscovite composition. In spite of this, 1Md seems to remain the typical low temperature polymorph.

Data on illite polymorphs in Mesozoic and Cainozoic sediments are scarce. Velde and Hower (1963) found for most Palaeozoic shales from North American that 1Md is by far the more abundant polymorph. Maxwell and Hower (1967) demonstrated for high grade diagenetic and low grade metamorphic illites in the Precambrian Belt Series that increasing temperature and pressure conditions accompanying deep burial and deformation apparently cause a transformation of the 1Md to the 2M polymorph.

The high proportion of the 2M illite polymorph in the Wilcox shales seems at first sight surprising as one would rather suspect a high proportion of 1Md. A clastic origin for at least part of the clays in recent Mississippi sediments is certain. Hurley *et al.* (1960) found an average K/Ar age of 166 million yr for the clay fraction size from recent Mississippi sediments and an average of 280 m.yr for whole samples of essentially silt-size material. A ready source for this largely illitic material can be found in the Appalachian system, drained to the Mississippi via tributaries of the Ohio. The age of the Appalachian rocks is 400 m.yr. It is postulated that the high proportion of 2M polymorphs as observed in this paper is caused by detrital material. Mixing with other sediments or stripping of potassium during weathering can explain the 166 m.yr age of the clay fraction observed by Hurley *et al.* Bailey (1961) observed higher K/Ar ages for 2M, illite polymorphs than for 1Md polymorphs in a Pennsylvanian shale.

The illites of the Papuan shales show a very low proportion of 2M polymorphs. It is unlikely that they have been derived immediately from metamorphic or igneous rocks and it is assumed that they are derived from highly weathered soils or that they are formed anathigenetically.

### *Sharpness of the illite (001) diffraction peak*

A second difference between the illites of both rock suites is the difference in sharpness ratio and crystallinity index of the 10Å illite peak. It is assumed that the higher sharpness ratio and related lower crystallinity index for the Louisiana samples corresponds to a higher proportion of fresh detrital material. This is a second order

difference as the sharpness of the 10Å peak is related to the illite polymorph type (Maxwell and Hower, 1967). The sharpness ratio has been used by Weaver (1961) as a parameter for degree of diagenesis and metamorphism for shales from the Ouichita belt in Texas. The crystallinity index has been used by Kubler (1966) on a more general base as an indicator of degree of diagenesis and metamorphism. If used as an absolute measure this factor may be dangerous.

### Geochemistry

The third difference between the two suites of rocks consists of the chemical differences. The Papuan samples are much poorer in MgO and K<sub>2</sub>O than the Louisiana samples. The higher magnesium content can be explained by the higher chlorite content of the Wilcox sediments while the Papuan samples contain little or no chlorite, in agreement with Eckhardt's (1958) observation that chlorite-rich sediments are richer in MgO. The difference in K<sub>2</sub>O content can be explained by differences in illite composition. Illite differs in bulk composition from ideal muscovite and contains more H<sub>2</sub>O, SiO<sub>2</sub> and MgO but less K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>. Variation in composition can be considerable (Hower and Mowatt, 1966). According to Maxwell and Hower (1967), 1Md illites are more potassium deficient than 2M illites. Consequently the K<sub>2</sub>O deficiency of the 1Md rich Papuan sediments can be explained.

It would be interesting to re-examine the Cretaceous shales in the Cameroun section described by Dunoyer de Ségonzac (1964). The average MgO content of fifteen samples without or with very little chlorite from the uppermost part of the section is 1.46 ± 0.08 per cent, as calculated from his partial total rock analyses; the average MgO content of nine chlorite-containing samples in the lower part of the section is 2.25 ± 0.13 per cent. Dunoyer claims, and uses the argument, that no significant chemical variations occur with depth as a proof for the diagenetic origin of the chlorite. The possibility of a direct relation between the chemistry of the clay fraction of recent sediments and factors such as relief and degree of weathering of the hinterland and speed of sedimentation was demonstrated by Porrenga (1967). The clay fractions of sediments from the Niger delta (flat weathered drainage basin), the Orinoco Shelf (partly flat and weathered partly mountainous drainage basin of the Orinoco), and the Sarawak Shelf (mountainous hinterland with igneous and metamorphic rocks nearby) are characterised by increasing MgO and K<sub>2</sub>O content in the order mentioned. The analogy with the magnesium and potassium poor Papuan samples and the Louisiana sediments rich in these elements

is strong. Thus chemical evidence supports the evidence given by illite 10Å peak sharpness ratio and polymorph type that the Papuan shales are derived from a flat weathered source and that the Louisiana samples are at least partly derived from fresh rocks.

*Acknowledgments*—The author acknowledges the support of the Australian Research Grants Committee for the project "Geochemistry and Mineralogy of Diagenesis" and wishes to thank the Australasian Petroleum Company Pty., Sydney, and the Bureau of Mineral Resources, Geology and Geophysics, Canberra, A.C.T., for their permission to work on the sample materials and for their kind co-operation during the study in general. Special thanks are due to the Shell Development Company, Houston, Texas, and Dr. J. F. Burst, General Refractories Company, Philadelphia, Pa., for sending located samples of the original Wilcox suite. Discussions of the work with Mr. A. J. Gaskin, Chief of the Division of Applied Mineralogy, C.S.I.R.O., Melbourne and with Professor M. L. Jackson, Department of Soil Science, University of Wisconsin, Madison, were most useful.

Miss S. E. Hill and Mr. R. B. Reid, Geology Department, University of Tasmania, analysed chemically the Papuan material. Thanks are due to Dr. T. R. Rao, Andhra University, India, for providing the data of chemical analyses of the Wilcox Formation samples.

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**Résumé**—Le changement graduel de minéraux argileux en couches interstratifiées en désordre, passant de 60% de montmorillonite et 40% de chlorite à 1000 mètres de profondeur, à 20% de montmorillonite et 80% d'illite à 3100 mètres de profondeur, peut être observé dans une section complète de schistes mésozoïques à Barikewa, en Nouvelle Guinée. La partie supérieure d'une section similaire complète de type mésozoïque, à 3200 mètres, à proximité du trou de mine d'Omati, contient 20–40% de montmorillonite dans des couches de montmorillonite/illite interstratifiées en désordre. A partir de 3290 mètres de profondeur, on ne trouve que de 10 à 20% de matériaux dilatables. En conséquence, c'est la profondeur de la couche plutôt que le niveau stratigraphique qui contrôle la proportion de matériaux dilatables présents. Des modifications diagénétiques similaires se produisent dans la formation Wilcox, en Louisiane, également contrôlées par la profondeur.

La quantité de polymorphes illite 2M dans les prélèvements papous est normalement inférieure à 5%, le taux d'acuité de crête de l'illite 10Å est d'environ 1,4. Les valeurs correspondantes pour les prélèvements de Louisiane sont de 43% de polymorphes 2M et d'un taux d'acuité d'environ 2,0. Les analyses chimiques des schistes papous montrent de faibles valeurs MgO et K<sub>2</sub>O par rapport aux prélèvements de Louisiane. Ces derniers dépôts contiennent un peu de chlorite, les premiers presque pas. Les différences démontrent une proportion plus élevée de matériaux relativement inaltérés dans les prélèvements américains.

La hausse de la teneur en chlorite, la hausse de la teneur en magnésium et la baisse de la teneur en kaolinite à partir de 3700 mètres, dans les prélèvements de Louisiane, suggèrent une altération du modèle de sédimentation.

**Kurzreferat**—Eine allmähliche Veränderung von 60% Montmorillonit/40% Chlorit, der mit unregelmässigen Zwischenschichten von Tonmineralen durchzogen ist auf 3500 Fuss Tiefe in 20% Mont-

morillonit/80% Illit auf 10200 Fuss kann in einem vollständigen Schnitt mesozoischer Schiefer in Barikewa, Neu Guinea beobachtet werden. Die Spitze eines ähnlich gearteten vollständigen mesozoischen Schnittes auf 10544 Fuss in dem unweiten Bohrloch von Omati enthält 20–40% Montmorillonit in unregelmässig zwischengeschichtetem Montmorillonit/Illit. Ab 10800 Fuss abwärts besteht nur 10–20% ausdehnbares Material. Es folgt, dass die Tiefe der Eingrabung und nicht so sehr das stratigraphische Niveau den Anteil des vorhandenen ausdehnbaren Materials bestimmen. Ähnliche diagenetische Veränderungen treten in der Wilcox Formation in Louisiana auf und auch sie werden durch die Vergrabung bestimmt.

Die Menge von Illit 2M Polymorphen in the Papua Proben is meist weniger als 5%, das Illit 10Å Scheitelwert Schärfeverhältnis ist etwa 1,4. Die entsprechenden Werte für die Louisiana Proben sind 43% 2M Polymorphe and etwa 2,0 Schärfeverhältnis. Die chemische Analyse der Papua Schiefer ergibt im Vergleich mit den Proben aus Louisiana niedrige MgO und K<sub>2</sub>O Werte. Die letzteren Ablagerungen enthalten etwas Chlorit, die erstgenannten beinahe keinen. Die Unterschiede deuten auf einen hohen Anteil an verhältnismässig unverwittertem Material in den amerikanischen Proben hin.

Die Zunahme im Chloritgehalt, sowie die Zunahme im Magnesium- und Abnahme im Kaolinitgehalt von 12368 Fuss an abwärts deuten Veränderungen im Ablagerungsbild an.

**Резюме** — В полном разрезе мезозойских сланцев близ Барикева (Новая Гвинея) наблюдался постепенный переход от неупорядоченного смешаннослойного образования, содержащего 60% монтмориллонита и 40% хлорита (на глубине 3500 фт) к смешаннослойному образованию из 20% монтмориллонита и 80% иллита (на глубине 10200 фт). Верхняя часть аналогичного полного мезозойского разреза на глубине 10544 фт в скважине близ Оматти содержит неупорядоченное смешаннослойное образование монтмориллонит-иллит с 20–40% монтмориллонита. Ниже 10800 фт наблюдается лишь 10–20% разбухающего материала. Следовательно, от глубины залегания, скорее чем от стратиграфического уровня, зависит содержание разбухающего компонента. Аналогичные диagenетические изменения в формации Вилкоккс (Луизиана) также определяются глубиной залегания.

Количество иллита модификации 2M в образцах из Папуа обычно не превышает 5%; относительная величина, характеризующая остроту пика иллита 10 Å, составляет около 1,4. Соответствующие значения для образцов из Луизианы составляют: содержание иллита 2M — 43% и острота пика — 2,0. Химический анализ сланцев из Папуа обнаружил низкое содержание MgO и K<sub>2</sub>O по сравнению с их содержанием в образцах из Луизианы. В последних имеется также некоторое количество хлорита, в то время как в образцах из Папуа он почти не встречается. Найденные различия демонстрируют высокое содержание относительно невыветрившегося материала в американских образцах.

Увеличение содержания хлорита и MgO, а также уменьшение содержания каолинита на глубинах ниже 12368 фт в образцах из Луизианы указывает на изменение условий осаждения.