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CLAY MINERAL BURIAL DIAGENESIS IN TERTIARY SEDIMENTS FROM THE EASTERN FLANK OF THE NIGER DELTA

University of Cincinnati PH.D. 1982

CLAY MINERAL BURIAL DIAGENESIS IN TERTIARY SEDIMENTS FROM THE EASTERN FLANK OF THE NIGER DELTA

A dissertation submitted to the

Division of Graduate Education and Research
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1982

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October 13 19 82

I hereby recommend that the thesis prepared under my supervision by Sokari Percival Braide

entitled CLAY MINERAL BURIAL DIAGENESIS IN TERTIARY SEDIMENTS FROM THE EASTERN FLANK ON THE NIGER DELTA

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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ABSTRACT

Detailed mineralogic and chemical analyses of well cuttings of Tertiary sediments from two wells, Uruan-1 and Uda-1, on the eastern flank of the Niger delta, have been made in an attempt to investigate clay mineral burial diagenesis.

The clay mineralogy of one well, Uruan-1, indicates a transformation of smectite to illite via a mixed-layer illite/smectite (I/S) phase. The occurrence of discrete smectite below 3,675 m, a depth for which calculated geothermal temperatures range between 100 - 120 ^{o}C, is enigmatic, but interpreted to be detrital. The chemical data of the <0.1-μm size fraction shows a net gain in K_2O and Al_2O_3 and a net loss in SiO_2 with depth. This observation, together with the observed clay mineralogy between 1,312 m and 3,642 m can be explained by the clay mineral burial diagenesis hypothesis of Perry and Hower (1970). The results of this study also indicate that neither temperature nor the availability of potassium is the principal factor controlling the clay mineralogy of the sediments below a depth of 3,675 m in well Uruan-1. Other factors that may have influenced the observed clay mineral suite are debated. These include inherited smectite charges, tectonics, climate, transgression and regression and formation of other diagenetic products like calcite.

In the second well studied, well Uda-1, random and ordered interstratified mixed-layer I/S occurs from 1,719 m to total depth at 3,688 m. There is a drastic drop in percentage of smectite layers in the mixed-layer I/S from 80% in the random interstratified phase at a depth of 2,730 m to 10% in the ordered interstratified phase observed at 3,031 m. This sharp drop in the amount of smectite layers in the mixed-layer I/S, over a relatively short stratigraphic interval, may be a manifestation of differences in the original clay mineral suite before burial. In other words, it may be may be an indication of some form of stratigraphic or facies control. The chemical data of the <0.1-μm size fraction show a net loss in SiO_2 and a net gain in K_2O, with depth.

The distribution of kaolinite and chlorite in both wells Uruan-1 and Uda-1, appear to be unrelated in any systematic way to smectite - illite transformation. They are considered to be either the products of other diagenetic reactions affecting various stratigraphic levels, or the result of primary sediment deposition. In well Uda-1 however, kaolinite decreases in relative abundance with depth. This trend has been interpreted elsewhere (Brown et al., 1977), to be indicative of a transition from nonmarine to marine facies.

What is apparent from this study is that the clay mineral burial diagenesis of Tertiary sediments from the eastern flank

of the Niger delta is complex and difficult to characterise in a simple model, based only on mineralogic and geochemical considerations. For instance, in well Uda-1, although the mineralogic and chemical data, in part, can be characterised by the clay mineral burial diagenesis hypothesis of Perry and Hower (1970), the mineralogic data can also be interpreted in terms of facies. The observation of discrete smectite, in both wells Uruan-1 and Uda-1, under conditions considered prohibitive to smectite's existence according to the Perry and Hower hypothesis, is enigmatic. If the hypothesis is applicable to the Tertiary sediments in the eastern flank of the Niger delta, could it be that it works in certain cases and not in others ? If so, under what conditions is the hypothesis valid ? These are key questions that need to be answered for a better understanding of clay mineral burial diagenesis.

This study recognises the possibility of using clay mineral burial diagenesis in indexing stratigraphic packages. Such an exercise would be useful in exploratory work for fossil fuels and groundwater, especially where clay mineral data from virgin territory can be correlated to nearby proven reserves. Such a correlation would be useful in reducing exploration expenses and time, by aiding in targeting certain strata for other conventional geological means of exploration.

Key words. clay mineral burial diagenesis, sedimentary geochemistry, stratigraphy, geothermal temperature, Tertiary sediments, Niger delta.

Once again, this dissertation is dedicated to my mother, VIRTUE HELEN BRAIDE, who was very supportive when the decision to give it one more try was made.

ACKNOWLEDGEMENT

I am indebted to Dr. Warren D. Huff whose constructive suggestions formed the framework on which this study has been based. Discussions, on the kinetics of mixed-layer clay transformations, with Dr. J. Barry Maynard were most fruitful. Dr. Wayne A. Pryor helped with the interpretation of electric logs from the two wells studied, and in deciphering the stratigraphy. Drs. Huff, Maynard and Pryor (members of my advisory committee) critically read the manuscript.

I would also like to thank Dr. Paul Edwin Potter for editing an earlier version of the proposal for this study. Communication with Dr. Harry F. Shaw of the Department of Geology, Imperial College of Science and Technology, University of London, England, is appreciated. Technical discussions with Mr. Dan Joyce were useful in the operation of some of the analytical equipments.

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Samples for this study were provided through the courtesy of Shell Petroleum Development Company of Nigeria.

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INTRODUCTION

The present Niger delta (Fig. 1) was formed during an Eocene regression, and is still building out into the Atlantic Ocean at this present time. During its relatively short geological history, there have been minor transgressions (Stonely, 1966, p.390; Short and Stauble, 1967, p.761). Much of the deltaic sediments may reach a maximum thickness of about 8 km. according to gravity measurements (Hospers, 1965, p.421; Walcott, 1972, p.1845). The Niger delta, owing to its unstable clay and shale base that overlies the basement (Emery et al., 1975, p. 2243; Mercki, 1972, p.637), has undergone a varied structural history culminating in numerous growth faults and diapiric structures. Another major structural feature in the region, that probably helped determine the geometry of the delta, is the Benue trough (Burke et al., 1971, p.51; Grant, 1971, p.2295).

The Niger delta may be divided into three broad sedimentary environments which are: a continental environment, a transitional environment, and a marine environment. Based on this sedimentary environmental classification, three rock-stratigraphic subdivisions are used in the literature in describing the subsurface sedimentary sequences: Benin, Agbada and Akata Formations which respectively correspond to the continental, transitional/paralic and marine environments (Fig. 2).

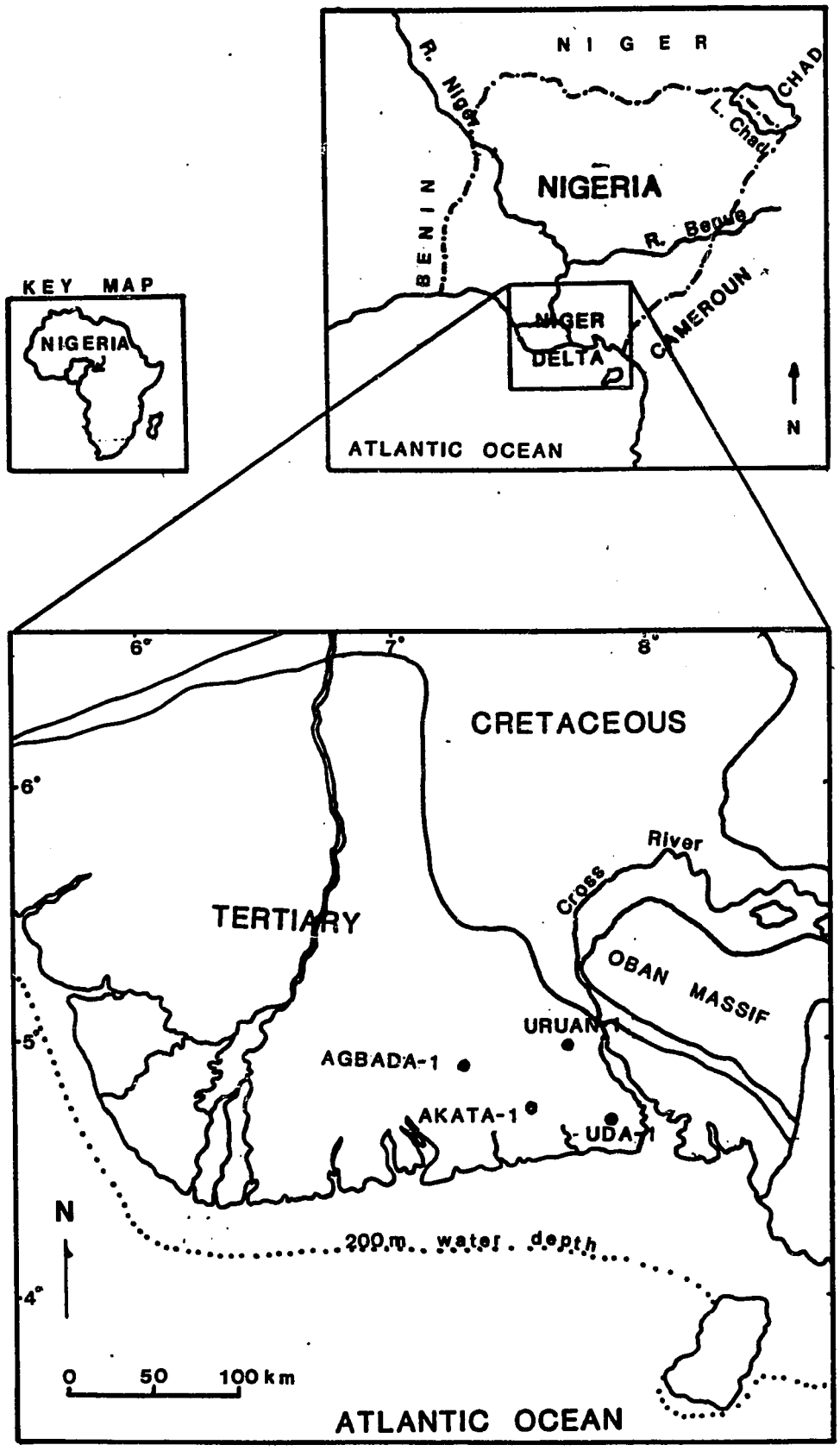

FIG. 1. Index map of the Niger delta showing the locations of wells studied and the type locality of Agbada and Akata Formations.

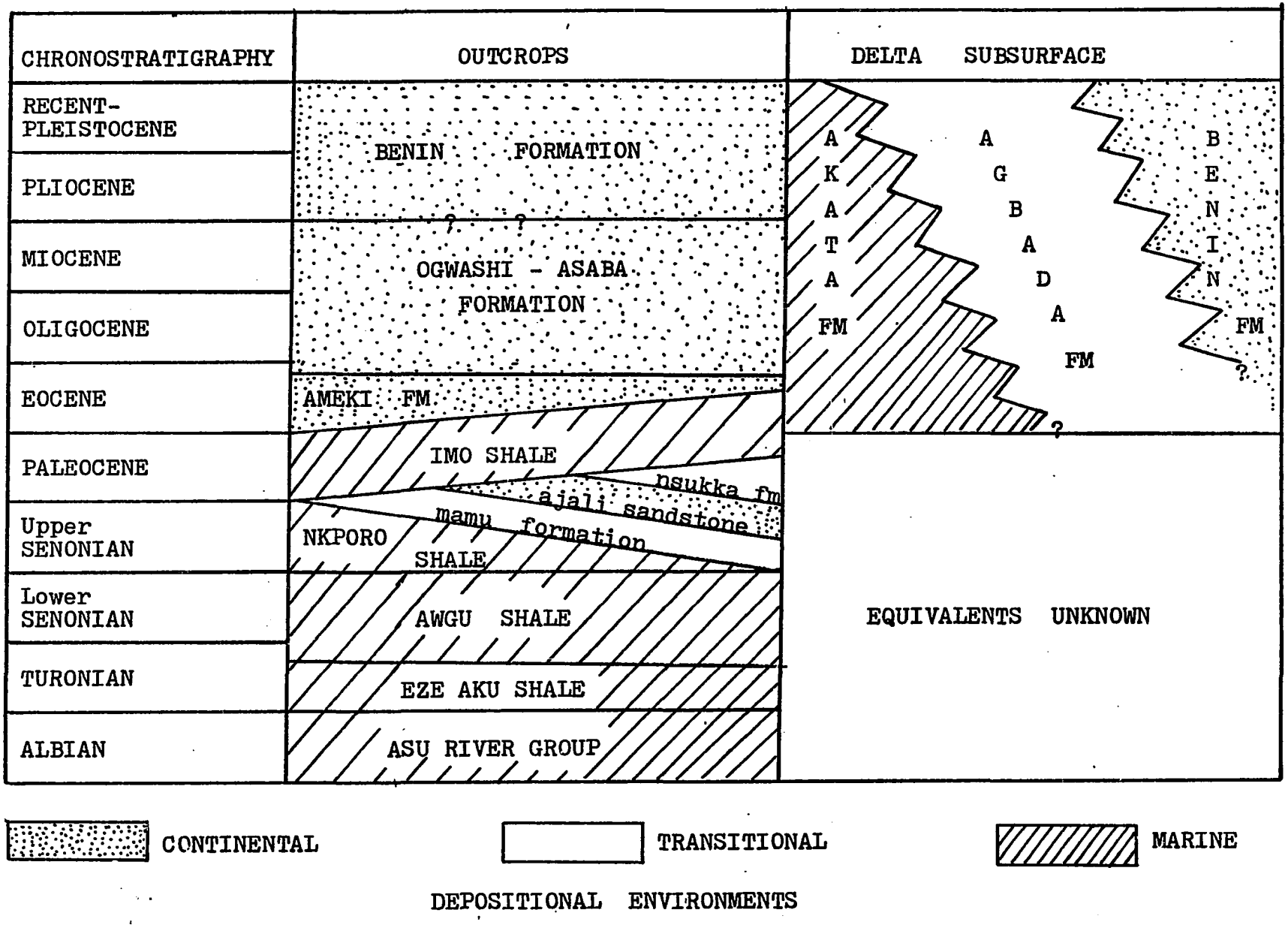

Fig. 2. Type sketch of the Niger Basin stratigraphy and depositional environments.
(After Schlumberger's Well Evaluation Conference, Nigeria, 1974, p. I-3).

Purpose and scope of study.

The purpose of this study is to investigate the clay mineral burial diagenetic history of the eastern Niger delta. Choice of the Niger delta was based on the fact that the region has had similar geological histories and sediments of the same geological age, as the Tertiary U.S. Gulf Coast, where similar studies on clay mineral burial diagenesis have been carried out, and characteristic mineral transformations described (Perry and Hower, 1970).

The problem focusses on one area of the delta (the eastern flank), and involves a systematic investigation of the vertical clay mineralogic changes that take place with increasing depth of burial. It also involves a documentation of the change in the major chemical constituents of the clays with respect to their stratigraphic position. Information thus obtained should provide the criteria for speculating on the salient factors that control the pattern of clay mineral burial diagenesis in the eastern Niger delta.

Previous work.

Previous studies of clay mineral diagenesis in the U.S. Gulf Coast have established the chemical and mineralogic changes in the conversion of smectite toward illite with increasing depth and temperature. However, this hypothesis has not been tested in a similar geological setting elsewhere.

Lambert-Aikhionbare and Shaw (1982) carried out a study of a related nature on the Niger delta, but their work was not primarily aimed at investigating clay mineral burial diagenesis. They studied the significance of the clays to the petroleum geology of the Niger delta. Burst (1959, p. 327) concluded that in the U.S. Gulf Coast, increasing burial depth resulted in the transformation of smectite to illite which he considered to be temperature dependent. Perry and Hower (1970, 1972) as well as Heling (1974) noted that the alteration process from smectite to illite includes the incorporation of potassium ions which are initially absorbed in exchange positions and later fixed at interlayer positions, thereby replacing the interlayer water. Van Olphen (1963) showed experimentally that this process of replacement of the interlayer water cannot be accomplished by pressure alone. Burst (1959, 1969) pointed out that temperature rather than pressure has to be considered the main controlling factor, in the dehydration of smectite. The dehydration reaction could be represented thus:

$$S(H_2O)x = I + xH_2O + Hr$$

where S is the hydrated clay lattice, $(H_2O)x$ is the water held within the hydrated lattice, I is a dehydrated lattice and Hr is the heat of reaction. The heat of reaction is negative and must be supplied geothermally.

Hower et al. (1976) suggested that the smectite to illite

transformation occurs via a mixed-layer illite/smectite phase, and involves chemical changes in the concentration of major elements with depth, in the clay fraction and whole rock component. Heling (1978, p. 211) concluded that although the alteration of smectite to illite primarily depends on the cumulative energy supply , i.e. temperature x time, small grain size and high potassium concentrations in the pore solutions shorten the time necessary to complete the alteration. Both Heling (1978) and Hower et al. (1976) noted that the potassium required for the dehydration of smectite is supplied by the decomposition of feldspar within the sediment. The replacement of feldspar by secondary calcite increases the availability of potassium. Because of the low potassium concentration of the pore solutions in the U.S. Gulf Coast, the potassium supply from outside the clayey sediment is considered unlikely (Powers, 1959). The significant role played by potassium in the conversion of smectite to illite is supported by Foscolos and Kodama (1974, p. 332) who observed the K_2O content of interstratified clays in the Buckinghorse Formation of Lower Cretaceous age, in north eastern British Columbia, increases as the burial depth increases.

According to Dunoyer de Segonzac (1970) the alteration of smectite to illite includes the increase of the layer charge by substitution of tetrahedral Si by Al. It appears that the necessary Al is derived from octahedral layers. Heling (1978,

p. 219) noted that the inherited layer charge of the initial smectite possibly has some bearing on illite diagenesis. Higher charged smectite with more tetrahedral Si substituted by Al would more readily alter to illite than lower charged smectites.

Significance of study.

This study adds to the basic theoretical knowledge of clay mineral burial diagenesis. The clay mineral data obtained suggest the occurrence of stratigraphic packages which can be correlated. Such an exercise would be usefull in exploratory work for fossil fuels and groundwater, especially where fossils are absent or poorly preserved, and clay mineral data can be correlated from virgin territory to nearby proven reserves. With a compilation of data on clay mineral burial diagenesis from other future studies of this kind in the area, a role for clay mineral burial diagenetic studies in the economic development of the region can be forseen. Finally, an accurate documentation of clay mineral burial diagenesis in the eastern Niger delta, as has been done in this study, will encourage active research in this area of Niger delta geology, which has sadly been neglected in the past.

Method of study.

Samples for this study were supplied through the curtesy of Shell Petroleum Development Company of Nigeria Limited, and consisted of 1,079 well cuttings from three wells, two of which

reached depths beyond 3,280 m. In the U.S. Gulf Coast studies, this depth of 3,280 m. (10,000 ft.) has commonly been mentioned as the depth at which a change from randon to ordered interstratification in the mixed-layer I/S is observed (Hower, 1981, p.64, Fig. 4.2). This study has systematically investigated variations in clay mineralogy and major element constituents, with increasing depth of burial in the two deeper weels (Uruan-1 and Uda-1). The data is compared to those obtained for other parts of the world. Analytical tools used for this investigation are a General Electric XRD-5 X-ray diffractometer, and a Perkin-Elmer atomic absorption spectrophotometer, model 403. Sand/shale ratios were obtained by visual inspection, with the aid of a binocular microscope, according to the method described by Swanson (1981).

(i) X-ray powder diffraction.

Only the < 0.1-um size fraction clays were investigated by X-ray powder diffraction because this size range is the most sensitive to burial diagenetic changes (Hower et al., 1976). Heling (1978, p. 212) also noted that the alteration of smectite to illite is most evident in the < 0.1-um size fraction where smectite and mixed-layer I/S are concentrated, while quartz, feldspar, carbonate, and organic matter are absent.

Effective disaggregation of the well cuttings was achieved with the aid of a Heat Systems-Ultrasonics' sonifier cell disruptor, model W 185. Between 10 - 20 gm. of sample was

initially hand disaggregated to pea size, and soaked in 250 - 300 ml. of deionized water for about 12 hours. The soaked sample was then subjected to the sonifier for 15 minutes. Suspended particles after this time period, were decanted and the ultrasonic treatment repeated until a sufficient volume of suspended particles, about 600 ml., had been accumulated.

Separation into the < 0.1-um size fraction was then made by centrifuging in an International centrifuge, model CM, at 2,000 r.p.m. for 1 hour. The suspended particles after centrifuging under these conditions were < 0.1-um (Jackson, 1975), and were decanted for X-ray powder diffraction and atomic absorption analysis.

X-ray powder diffraction patterns were obtained from the oriented < 0.1-um size fraction prepared on ceramic plates by centrifugation. Several rounds of centrifuging successive aliquots on to the same ceramic plate was necessary inorder to achieve an optimum thickness of sample on plate. The optimum thickness was found to be a thickness which would prevent the direct diffraction of X-rays by the ceramic plate, but at the same time not too thick as to flake off on drying. Definite measurements cannot be suggested, but what is optimum is achieved by trial and error. Advantage in using the ceramic plate method is realised in the ethylene glycol treatment, which is essential for expandable clay identification. The preferred

method of glycol treatment that was favored in this study involved dropping about three drops of ethylene glycol directly on the sample, and smearing the glycol with a glass slide (Shaw, 1973, personal communication). Excess glycol was absorbed by the ceramic plate. Treated samples were stored in a desicator jar, with some glycol at its base, at room temperature for 12 hours before diffracting.

Air-dried samples were initially diffracted, then heated for 1 hour at 550 ^{o}C, and diffracted again. A duplicate set of samples was solvated with glycol before diffracting. The three sets of X-ray data obtained for each sample were interpreted following the guidelines of Carroll (1970), Reynolds and Hower (1970) and Reynolds (1980.

(ii) Atomic absorption spectrophotometer.

Portions of the < 0.1-um size fraction, segregated by centrifuging, were dried in an oven at 60 ^{o}C. Time periods required for complete drying varied from a day to three days. The dried out < 0.1-um size fraction was then scraped from their glass beakers and stored in plastic vials. Atomic absorption spectrophotometric studies for major chemical constituents was carried out on two size ranges, < 0.1-um size fraction and whole rock. The sample preparation method adopted was fusion employing Lithium metaborate ($LiBO_2$), as described by Medlin et al. (1969). Six USGS rock standards were used for

calibration of absorbance vs. concentration curves for each of the seven chemical constituents investigated. These rock standards are:

BHVO-1	Basalt
MAG-1	Marine mud
STM-1	Nepheline syenite
SCo-1	Cody shale
SDC-1	Mica schist
RGM-1	Rhyolite

Blank solutions were also prepared for all the elements investigated. Blank A was prepared for SiO_2, and consisted of 50% MgO, 20% Fe_2O_3, 10% CaO and 20% Al_2O_3. Blank B was prepared for Al_2O_3, and consisted of 40% MgO, 10% Fe_2O_3, 10% CaO and 40% SiO_2. For Fe_2O_3, MgO and CaO, blank C was prepared and consisted of 50% SiO_2 and 50% Al_2O_3. The blank for K_2O and Na_2O was deionised water.

Absorbance rather than concentration was read off the atomic absorption spectrophotometer. It was therefore necessary to draw up calibration curves of absorbance vs. concentration for each of the elements of interest. This was achieved by reading a series of absorbances, approximately 5, for each element of interest in the USGS rock standards, and plotting these against their published concentration values. These calibration curves, as well as the raw absorbance data obtained for both the USGS rock standards and samples in this study, are presented

in the appendix at the back of this dissertation. The research procedures are summarised in Fig. 3.

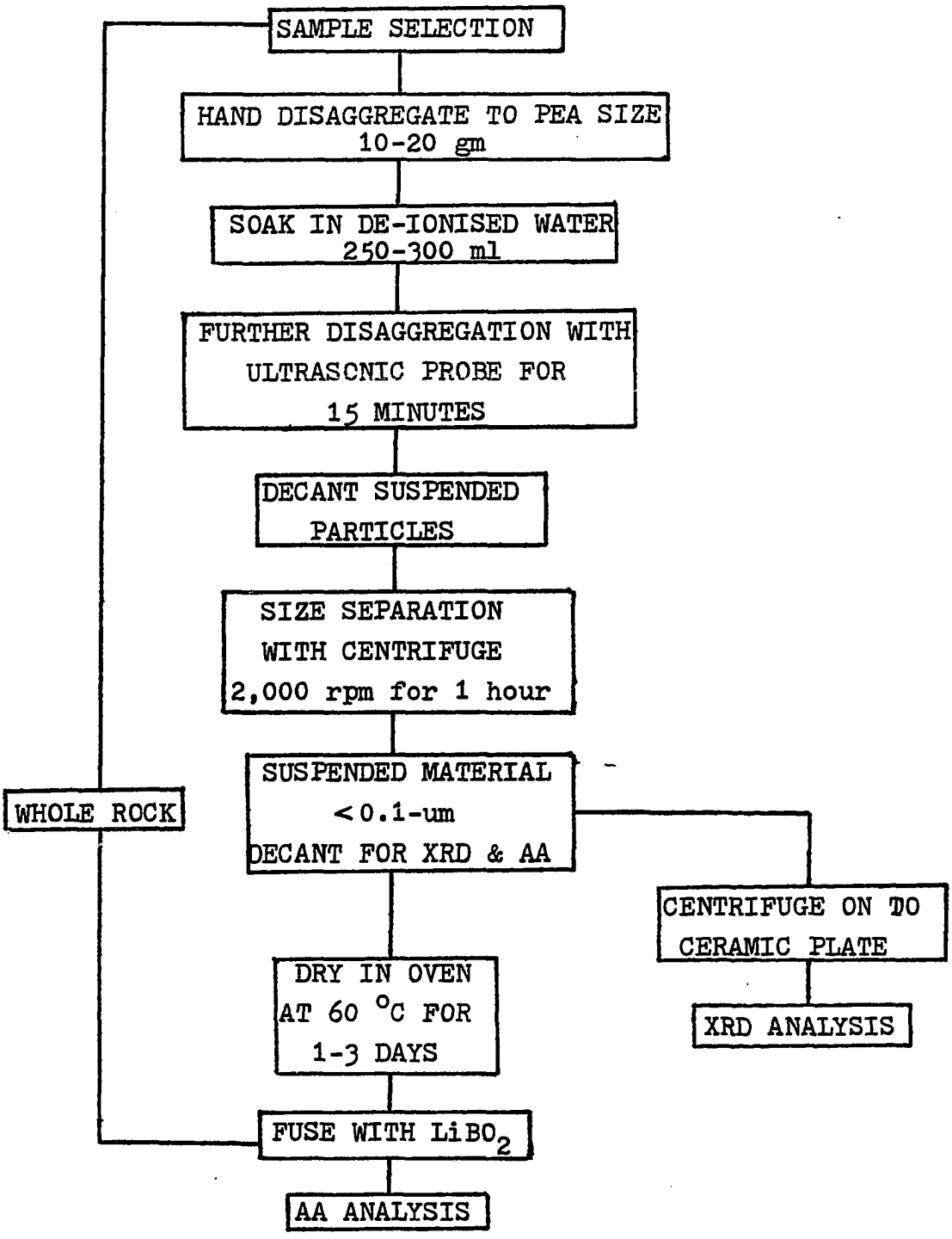

FIG. 3. Flow chart of research procedures in sample preparation for XRD and AA.

STRATIGRAPHY

of the eastern flank of the Niger delta

This chapter is largely a review of the literature on the stratigraphy of the eastern Niger delta. The two wells investigated (Uruan-1 and Uda-1) are compared by means of electric logs, and their stratigraphy is inferred from published studies and visual inspection of well cuttings. The most notable published stratigraphic reviews on the Niger delta include studies by Short and Stauble (1967), Murat (1970), Mercki (1970), Weber (1971), Asseez (1974), Avbovbo (1978) and Evamy et al. (1978).

The Tertiary Niger delta is predominantly composed of regressive clastic sequences, and its geometry is controlled by various basement blocks. Hospers (1965) pointed out the predominance of a northeast - southwest and northwest - southeast trend in the megatectonic framework (Fig. 11). These two trends can be linked to the openning of the south Atlantic (Emery et al., 1975)

Evamy et al. (1978, p.3) vertically subdivided the delta into broad facies units, which consist of massive sands and gravels, deposited under continental conditions. Underlying these units are sands with some shales, considered to be a transitional series. They grade into an alternation of sand-

stone and shale deposited under paralic conditions. Below this series are marine shales with some turbidites. Evamy et al. (1978) also recognised evidence of varied provenance for the sediments of the Niger delta. They reported the restriction of paralic and marine/paralic sediments to the eastern flank during the Paleocene - Eocene, and considered these to be deposits of the incipient Cross River, whose watershed is in the Oban Massif, in close proximity to the volcanic Cameroun Mountains.

During this early period in its development, the delta lay west of the present course of the Niger River. In the Oligocene and earliest Miocene, Evamy et al. (1978, p.5) reported that successive depocenters in the western part of the delta considerably overlapped, thus reflecting a pronounced subsidence and a relatively slow advance of the delta front toward the west and southwest. This is supported by isopach maps of the Benin and Agbada Formations, and a structure contour map to the top of the Akata Formation (Figs. 4, 5 and 6 respectively). In contrast, successive depocenters in the east generally do not overlap, and thus reflect a more rapid advance of the delta front. In the Miocene to present, both depocenters merged and an enlarged delta prograded simultaneously although a more rapid subsidence and consequently slower rate of advance of the delta continued to be characteristic of the western part (Short and Stauble, 1967).

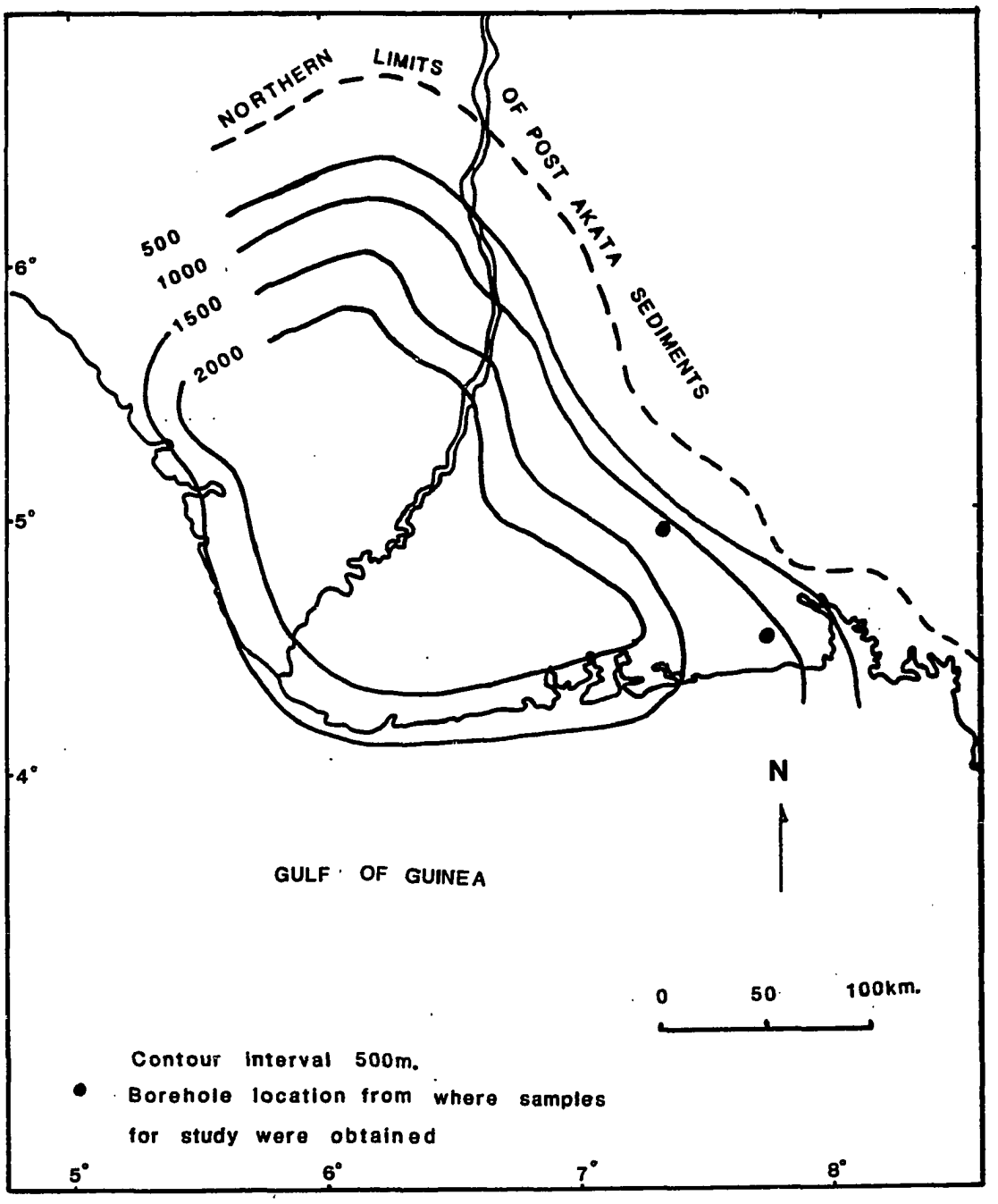

FIG. 4. Isopach map of Benin Formation, Niger delta (Adapted from Avbovbo, 1978).

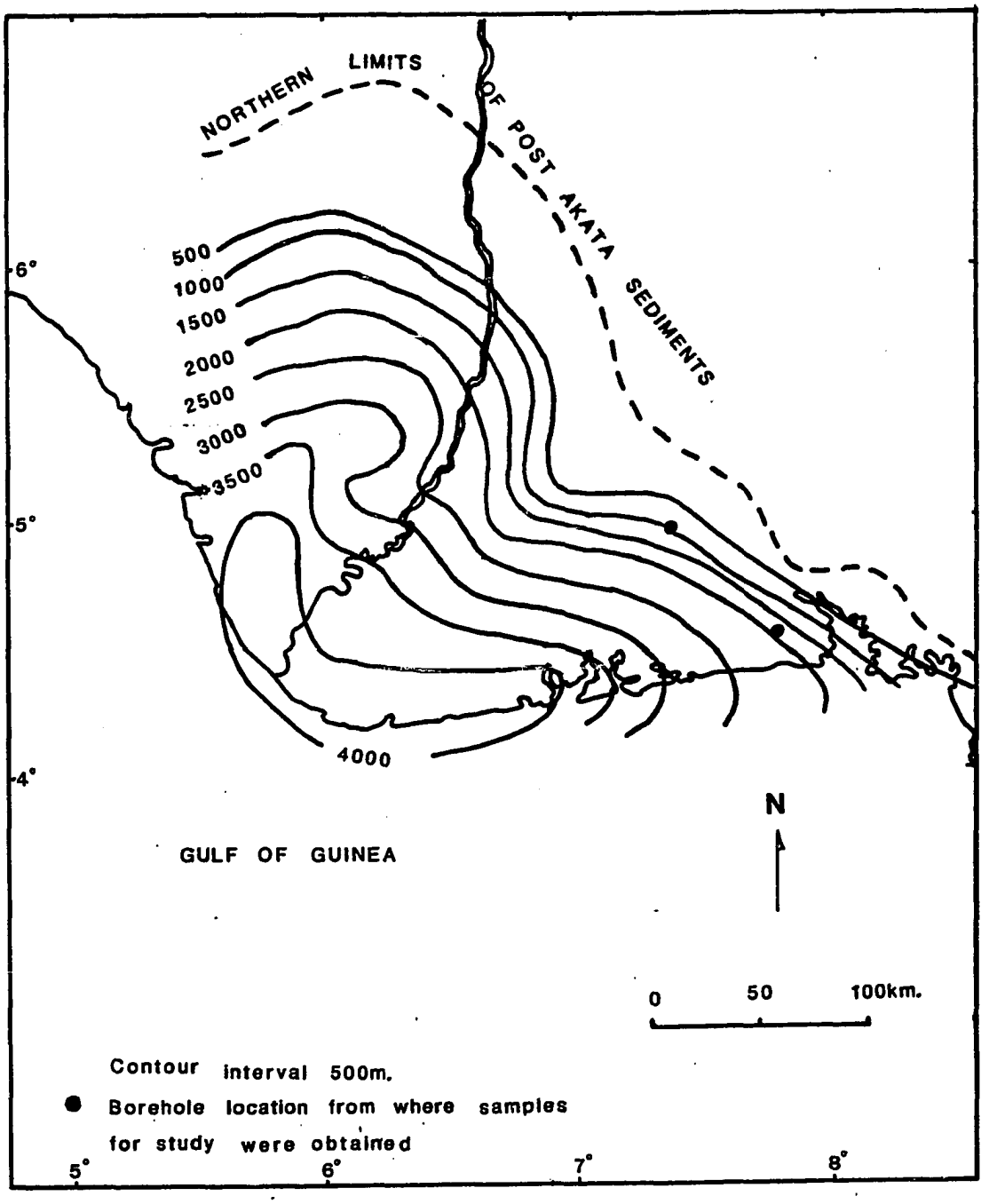

FIG. 5. Isopach map of Agbada Formation, Niger delta (Adapted from Avbovbo, 1978).

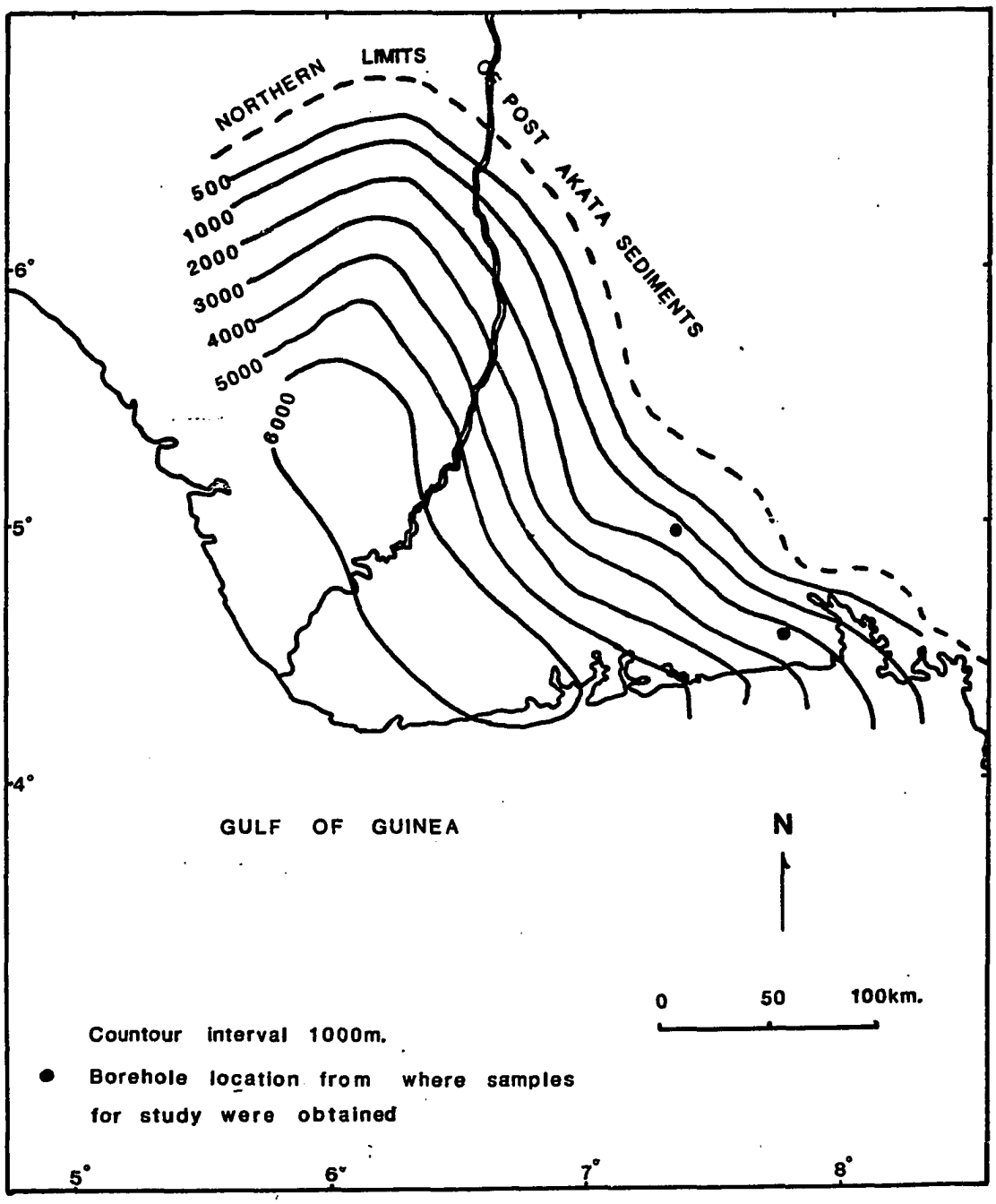

FIG. 6. Structural map of top of Akata Formation, Niger delta (Adapted from Avbovbo, 1978).

During the Miocene, Evamy et al. (1978) recognised periods of sedimentation hiatuses in the eastern flank of the Niger delta, and they considered these to be one evidence of the existence of megaunits, in the delta, which are entities with respect to the stratigraphy.

Lithology

Owing to the objective of this study, which is to investigate the burial diagenesis of clays in the eastern flank of the Niger delta, lithologic description was restricted to the depth interval from 1,312 m. to total depth in both wells Uruan-1 (3,773 m.) and Uda-1 (3,688 m.). Within these depth intervals, both the Agbada and Akata Formations are recognised. Above the depth of 1,312 m., the sediments have not been subjected to a high enough geothermal temperature to have imparted any burial diagenetic characteristics on the clays.

Uruan-1 (1,312 m. - 3,773 m., Fig. 7)

Agbada Formation (1,312 m. - 2,100 m.)

The base of the Agbada Formation is recognised at 2,100 m., and the lithology to this depth is characterised by an alternation of sand bodies with shale sequences. In places, the shale sequences are considerably thicker than the sand units. The Agbada Formation can be subdivided, in this well, into an upper and lower part. The boundary is put at a depth of 1,509 m. The upper part consists predominantly of sands which are very

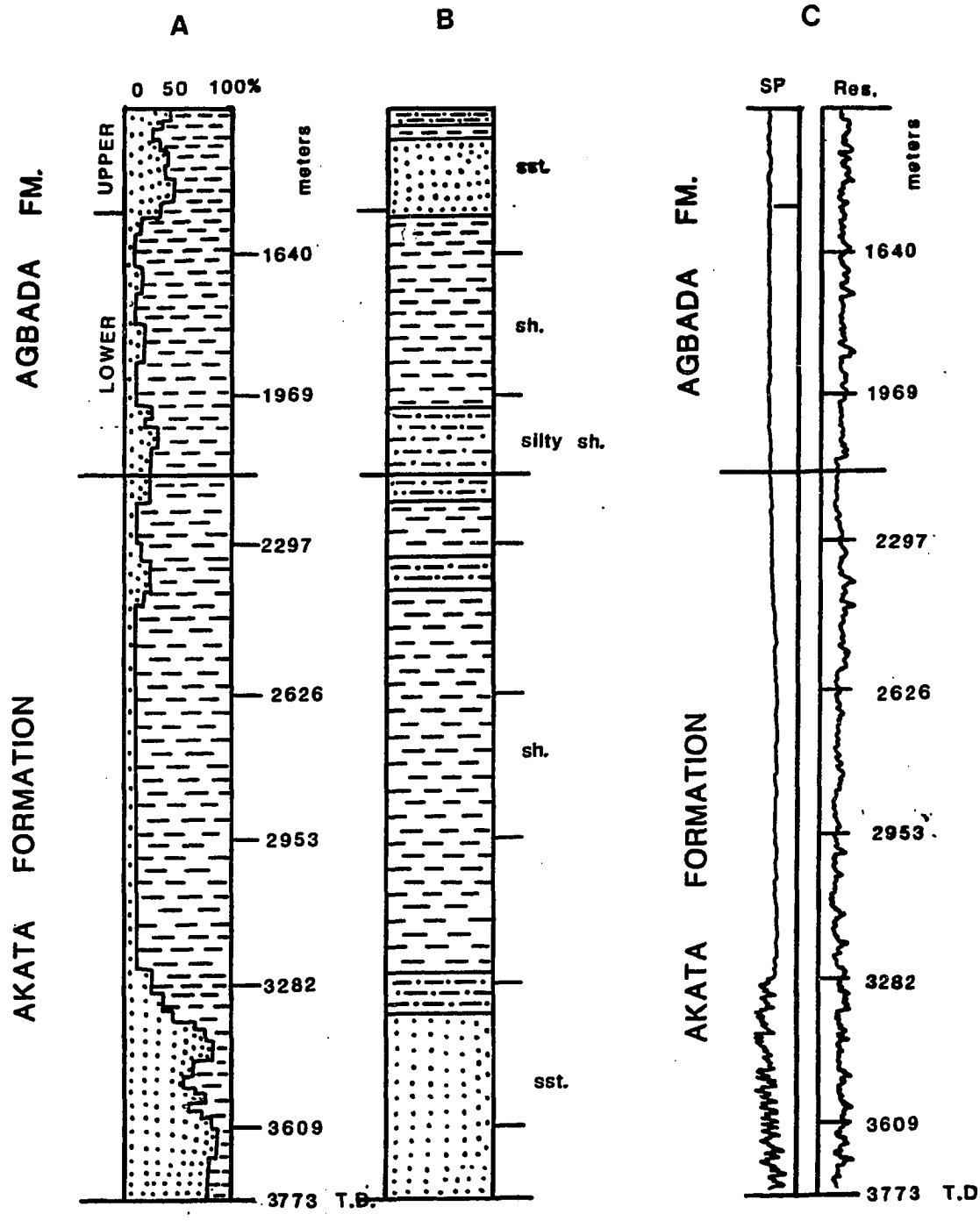

FIG. 7. Logs for well Uruan-1, eastern Niger delta.
(A) Percentage lithology.
(B) Interpretation of log A.
(C) SP and Resistivity.

coarse to very fine-grained, and are mostly unconsolidated . Sorting is very poor, but improves where the shale percentage increases. Shales predominate in the lower part. They are grey and dense, but those from the upper part tend to become more silty. Short and Stauble (1967, p.769) interpreted the prominent shale units in the lower part of the Agbada Formation in the type section, as being suggestive of localized non-deltaic conditions at the onset of a transgression, and the coarseness and poor sorting of some of the sand units in the upper part, was interpreted to indicate their fluviatile origin. Short and Stauble (op. cit.) further suggested that the well-sorted (and in general finer-grained) sands represent beach or coastal barrier sand deposits. The paleogeographic position of these coastal barrier sands has varied throughout the Tertiary (Fig. 8). A plausible explanation for the alternation of sands and shales in the Agbada Formation, may be a variation in sediment supply and sediment provenance, shifts in the delta depocenters, differential subsidence or a combination of all these factors.

Akata Formation (2,100 m. - 3,773 m.)

The depth interval from 2,100 m. - 3,346 m. has a uniform shale development with no more than 25 percent sand at certain horizons. The shale is generally dark grey. Below 3,346 m., thick sand units occur (Fig. 7), with intercalation of shale layers. These units are interpreted as turbidi-

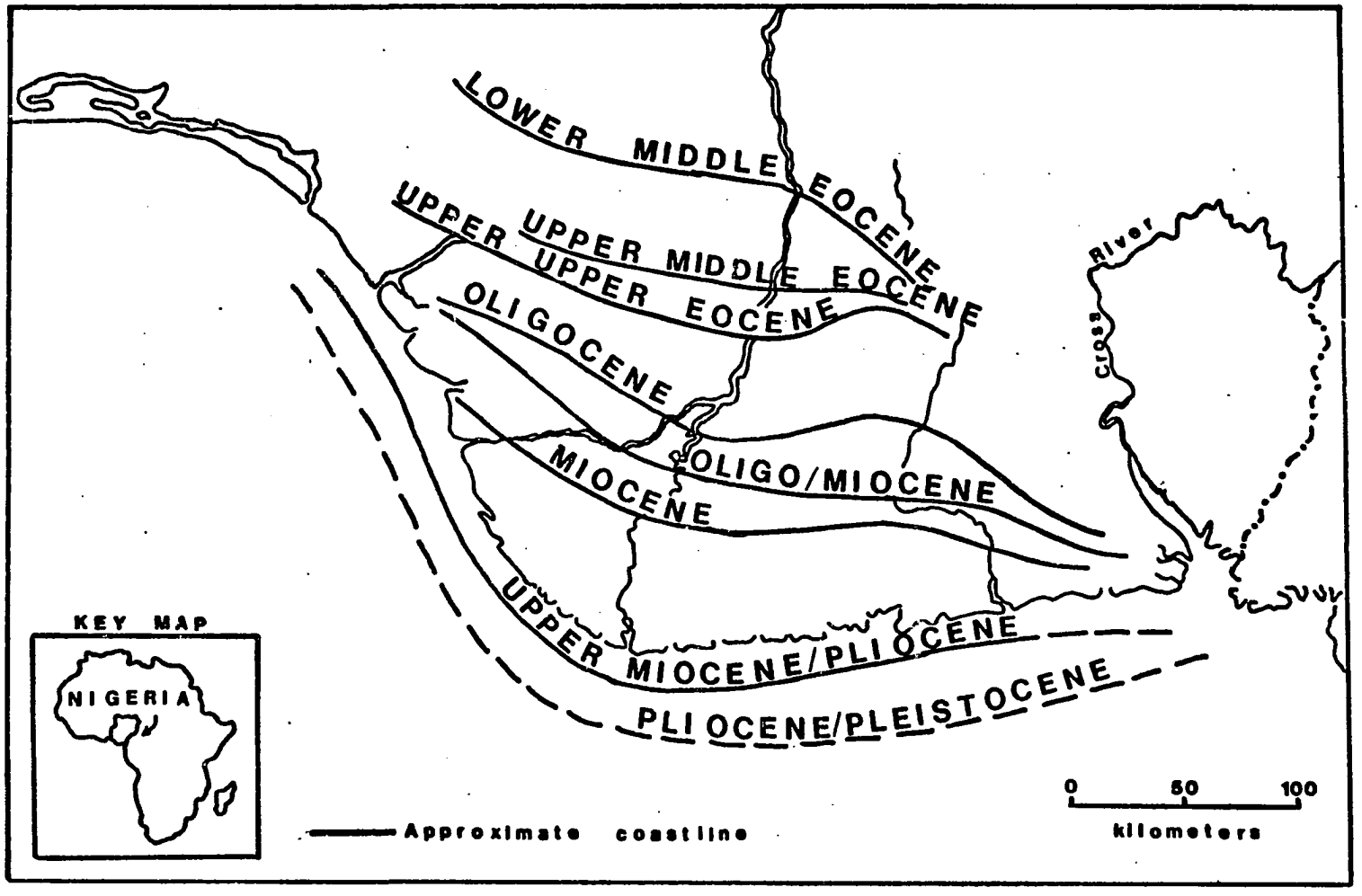

FIG. 8. Paleogeography of the Tertiary Niger delta illustrating stages of delta growth (After Short and Stauble, 1967, Fig. 6).

tes from electric log signature and stratigraphic position, and are therefore suggestive of a deeper-water environment.

Uda-1 (1,312 m. - 3,688 m.)

Agbada Formation (1,312 m. - 2,149 m. Fig. 9)

Three batches of well cutting samples were missing from this well. These batches are from 1,886 m. - 1,895 m. (a gap of 9 m.); 1,913 m. - 2,064 m. (151 m.); and 2,070 m. - 2,720 m. (650 m.). Thus, for a total depth of 810 m., there is no sand/shale percentage determinations (nor any mineralogical and chemical data). The lithology for this missing portion is inferred from electric logs.

The Agbada Formation is again recognised in two parts. The upper part (1,312 m. - 1,854 m.) has a higher sand percentage than the lower part (1,854 m. - 2,149 m.) which is predominantly shaly, but with two distinct sand bodies which are noticeable on electric logs. The sands in the upper part are coarse, generally unconsolidated, and are poorly sorted.

Akata Formation (2,149 m. - 3,688 m.)

The Akata Formation in this well is predominantly of a uniform dark grey shale, with a prominent sandy horizon (up to 50 percent sand), around a depth of 2,953 m. This sand unit however, is not detectable on the SP curve probably because of freshwater invasion (Schlumberger, 1974, p. II-1). The thick sand sequence with intercalating shale units observed

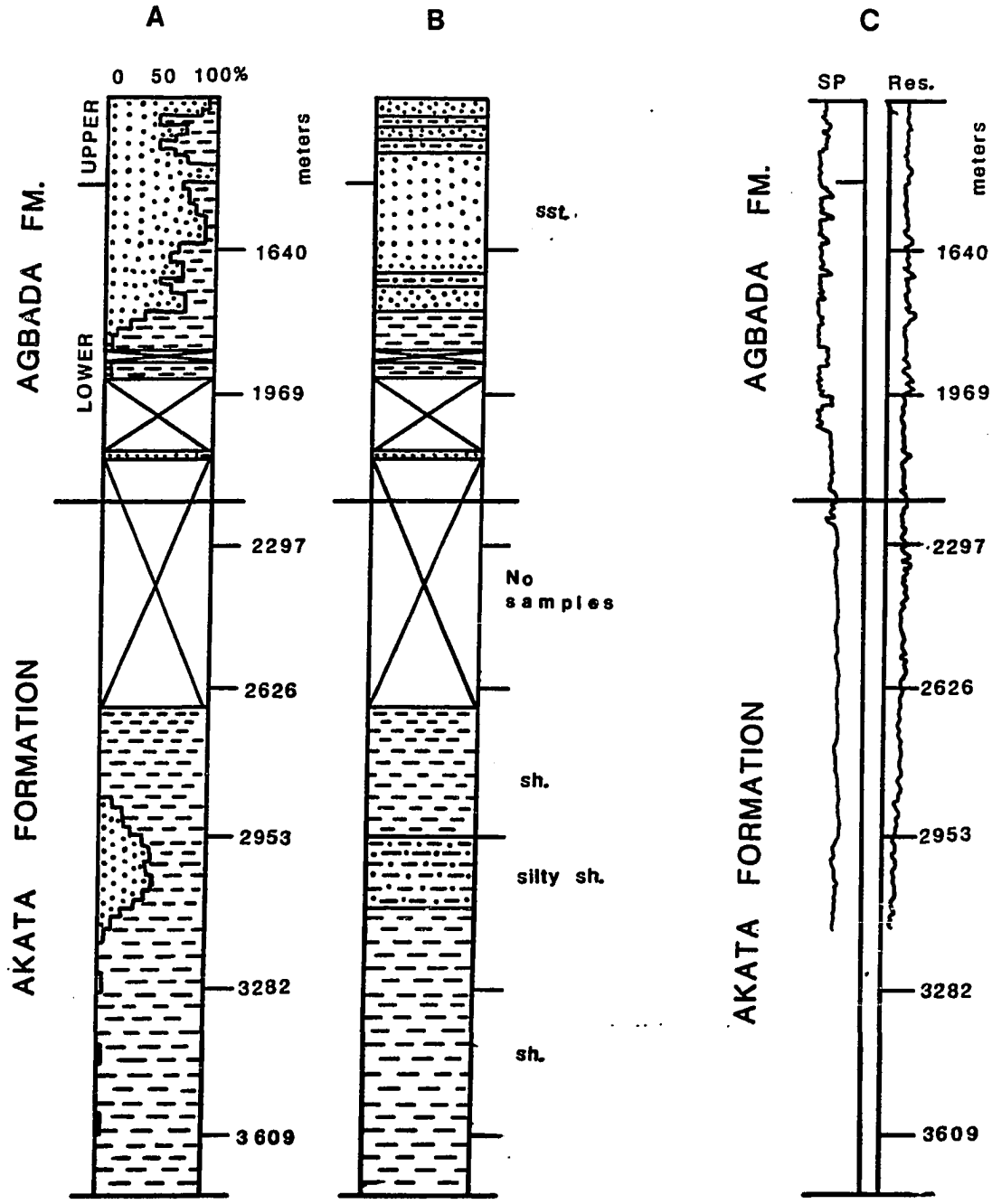

FIG. 9. Logs for well Uda-1, eastern Niger delta.
(A) Percentage lithology.
(B) Interpretation of log A.
(C) SP and Resistivity.

at the base of well Uruan-1, and considered to be turbidites, are not observed in well Uda-1. However, their occurrence may possibly exist at depths in excess of the total depth (3,688 m.) drilled in well Uda-1. Figure 10 is a comparison of electric logs from wells Uruan-1 and Uda-1 to the type section of the Agbada and Akata Formations.

Structural Features

The Niger delta is characterised by approximately east - west trending growth faults (Fig. 11), and the deltaic sequence is schematically illustrated in Fig. 12. A time stratigraphic unit of such a deltaic sequence is characteristically S-shaped (Mercki, 1970). The growth faults are initiated by the differential loading of the underlying and undercompacted Akata shales, and are typically crescent shaped in both plan and section (Fig. 13). The Agbada Formation is intensively deformed as a result of these growth faults whiles the Akata Formation is only superficially deformed.

Geotemperatures in the Niger delta.

Evamy et al. (1978, p.19) suggested that plots of subsurface temperature against depth and lithology show a distinct relation between temperature gradient and sandstone/shale ratio in the Niger delta (Fig. 14). They showed that the

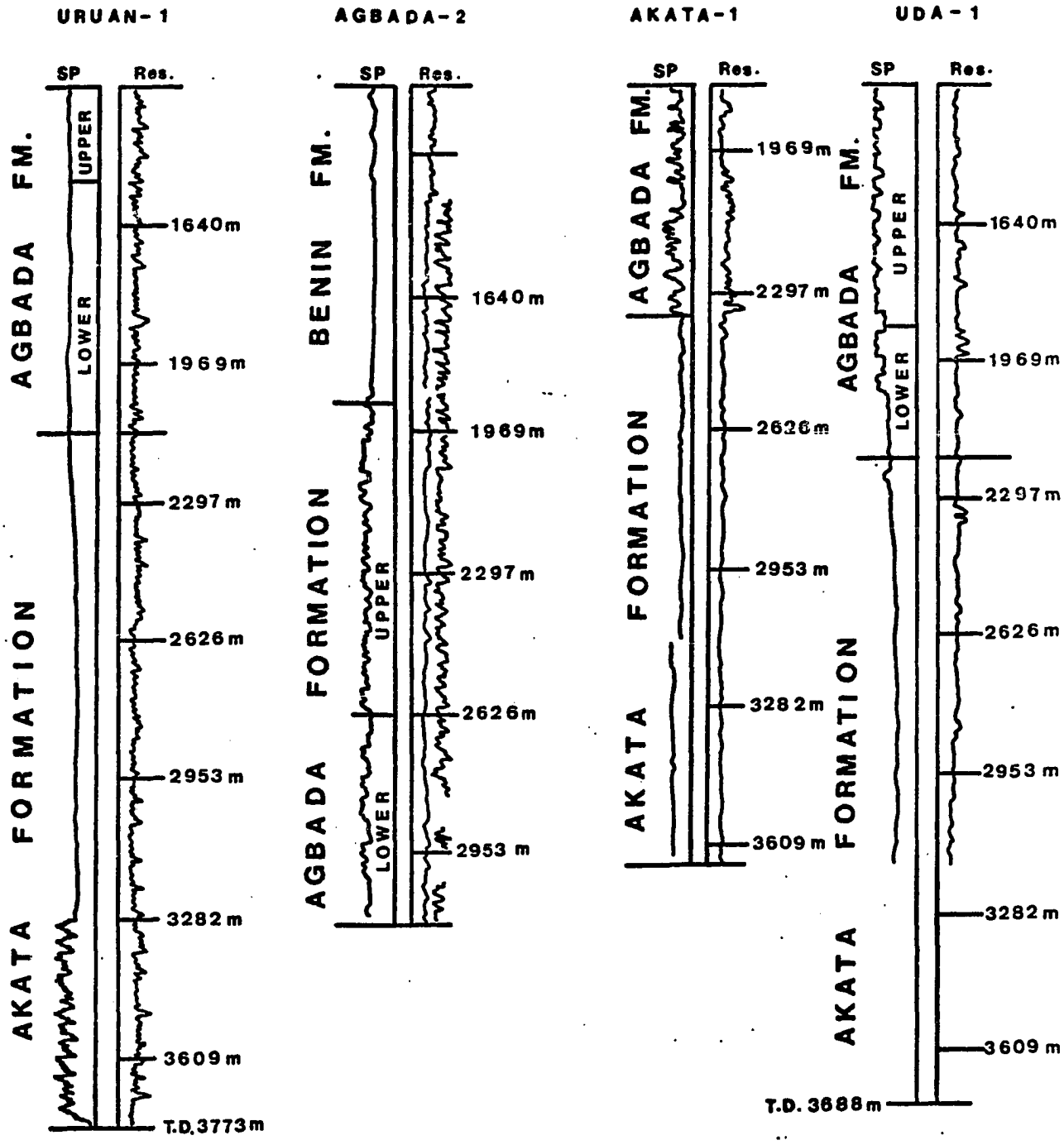

FIG. 10. Comparison of electric logs from wells Uruan-1 and Uda-1 to electric logs from the type sections of Agbada and Akata Formations. (Agbada-2 and Akata-1 electric logs are after Short and Stauble, 1967).

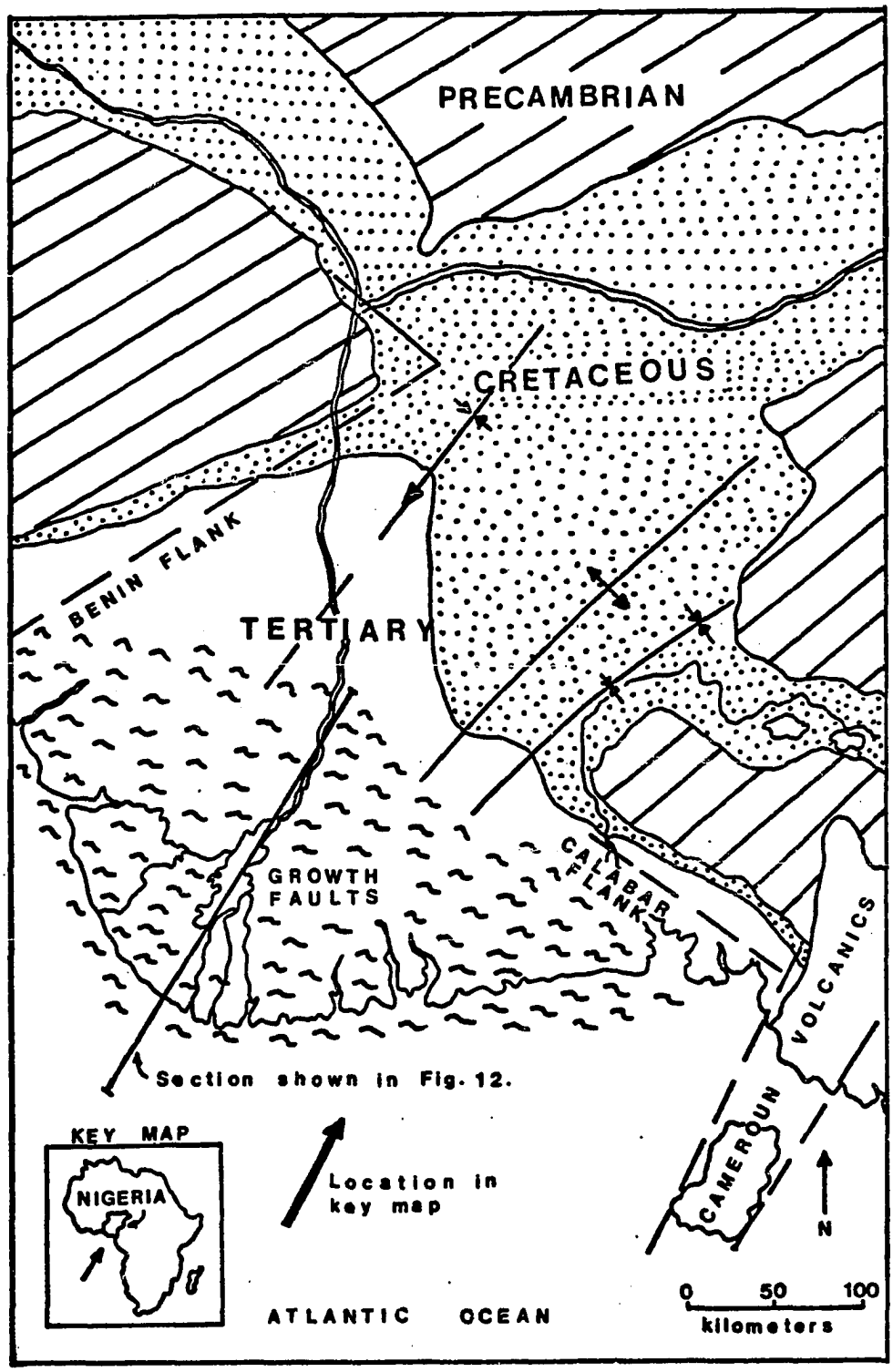

FIG. 11. Niger delta megatectonic elements and growth faults area (Adapted from Weber, 1971, Fig. 2a).

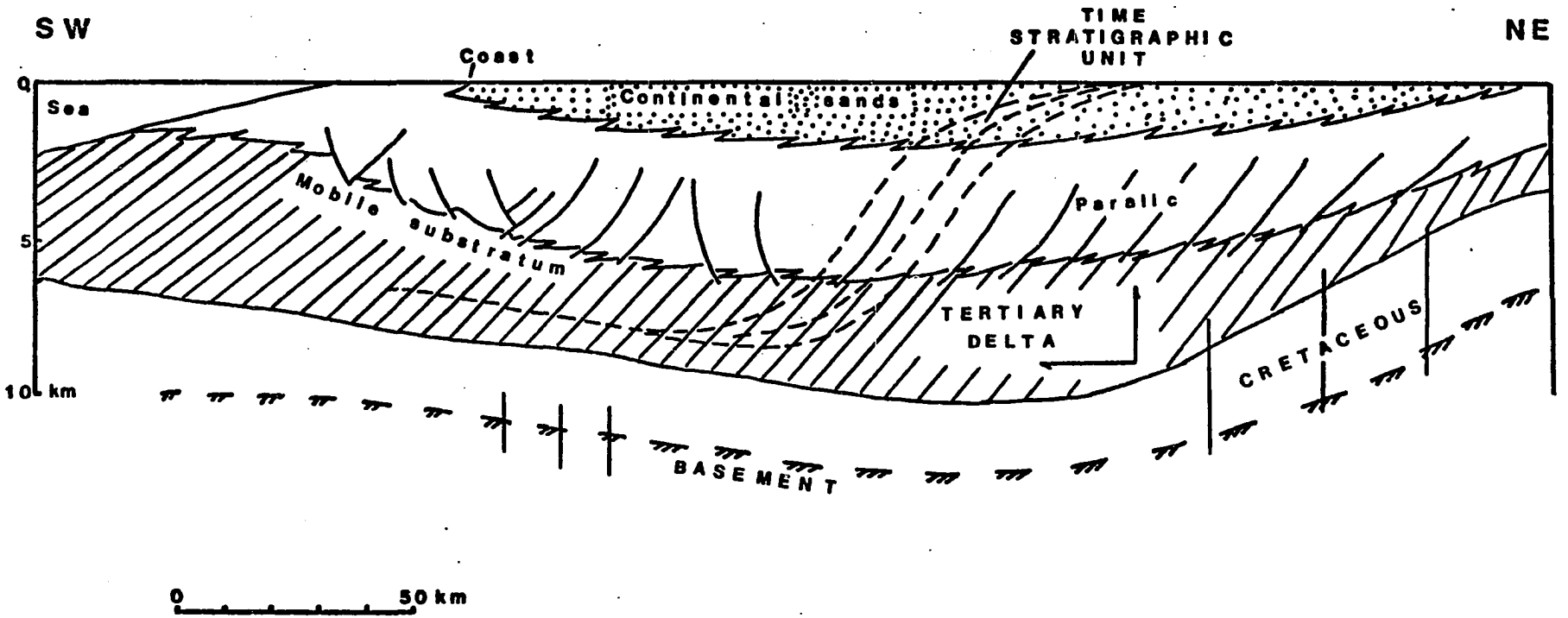

FIG. 12. Schematic section perpendicular to the Niger delta coastline (After Weber, 1971, Fig. 2b).

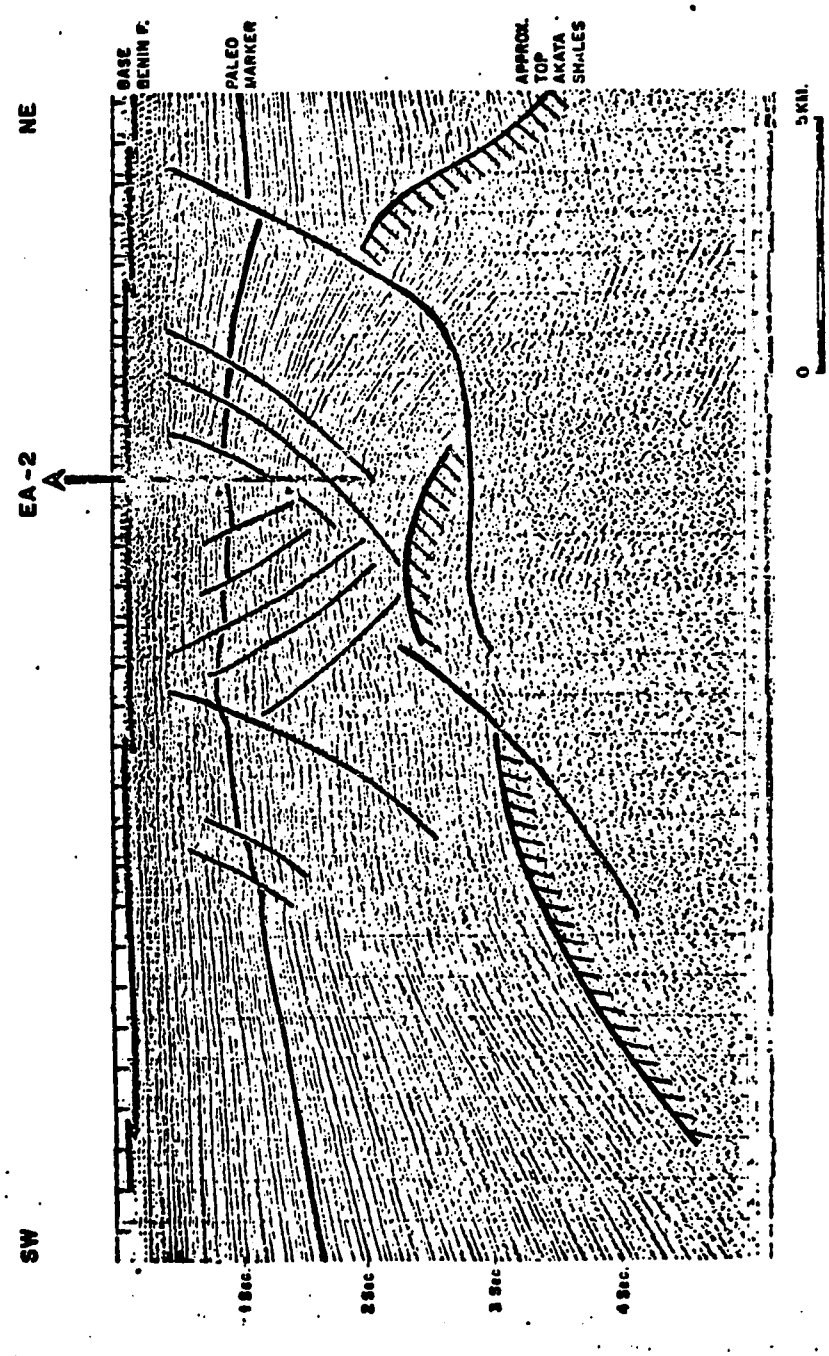

FIG. 13. Seismic dip-section illustrating growth faulting, and a clay upheaval structure, offshore Niger delta (After Mercki, 1970, Fig. 6).

temperature gradient increases with diminishing sand percentage from less than 1.84 °C/100 m. in the continental sands, to about 2.73 °C/100 m. in the paralic section, to about 5.47 °C/100 m. in the continous shales of the Niger delta. Using this relationship (Fig. 14) between geotemperature gradient and sand percentage, and the equation :

$$T = a - bS^2 + cD$$

(After Evamy et al., 1978, p.19) which reflects the observed slight increase of the temperature gradient with depth, the calculated temperature profiles for wells Uruan-1 and Uda-1 are illustrated in Figure 15.

T is the temperature gradient (°F/100 ft),
S is the sand percentage of the selected interval,
D is the average depth of the selected interval.
$a = 1.811 \pm 0.161$; $b = (1.615 \pm 0.146) \times 10^{-4}$
$c = (7.424 \pm 1.749) \times 10^{-5}$.

The calculated temperature profiles for wells Uruan-1 and Uda-1 compare favorably to plots of geotemperatures at 2,591 m. and of subsurface depth to 116 °C by Evamy et al., (1978, Fig. 15) reproduced here as Figs. 16 and 17. The calculated profiles also compare favorably to Niger delta geotemperature data by Nwachukwu (1976) and Avbovbo (1978).

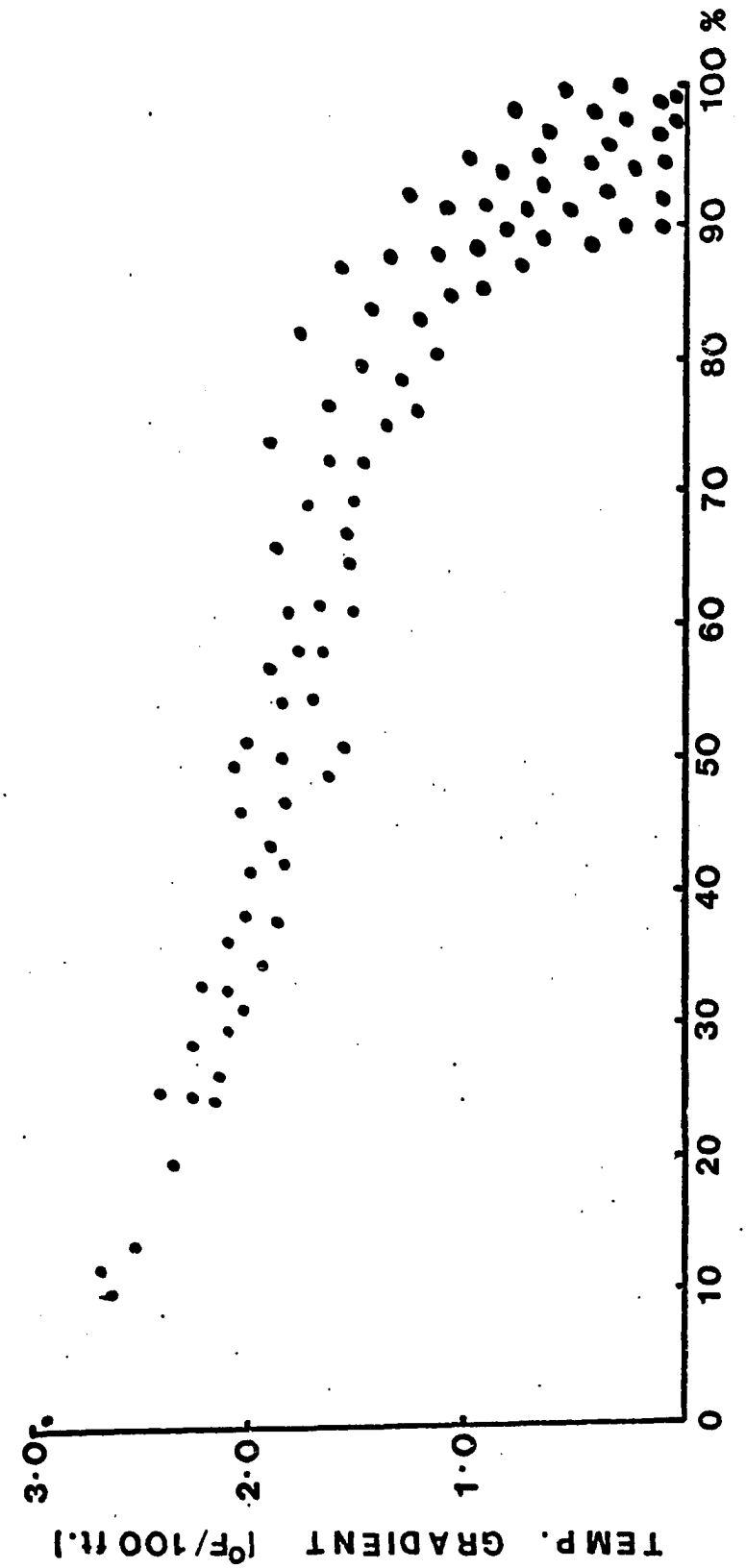

FIG. 14. Relation between geotemperature gradient and sand percentage. Niger delta (After Evamy et al., 1978, Fig. 14).

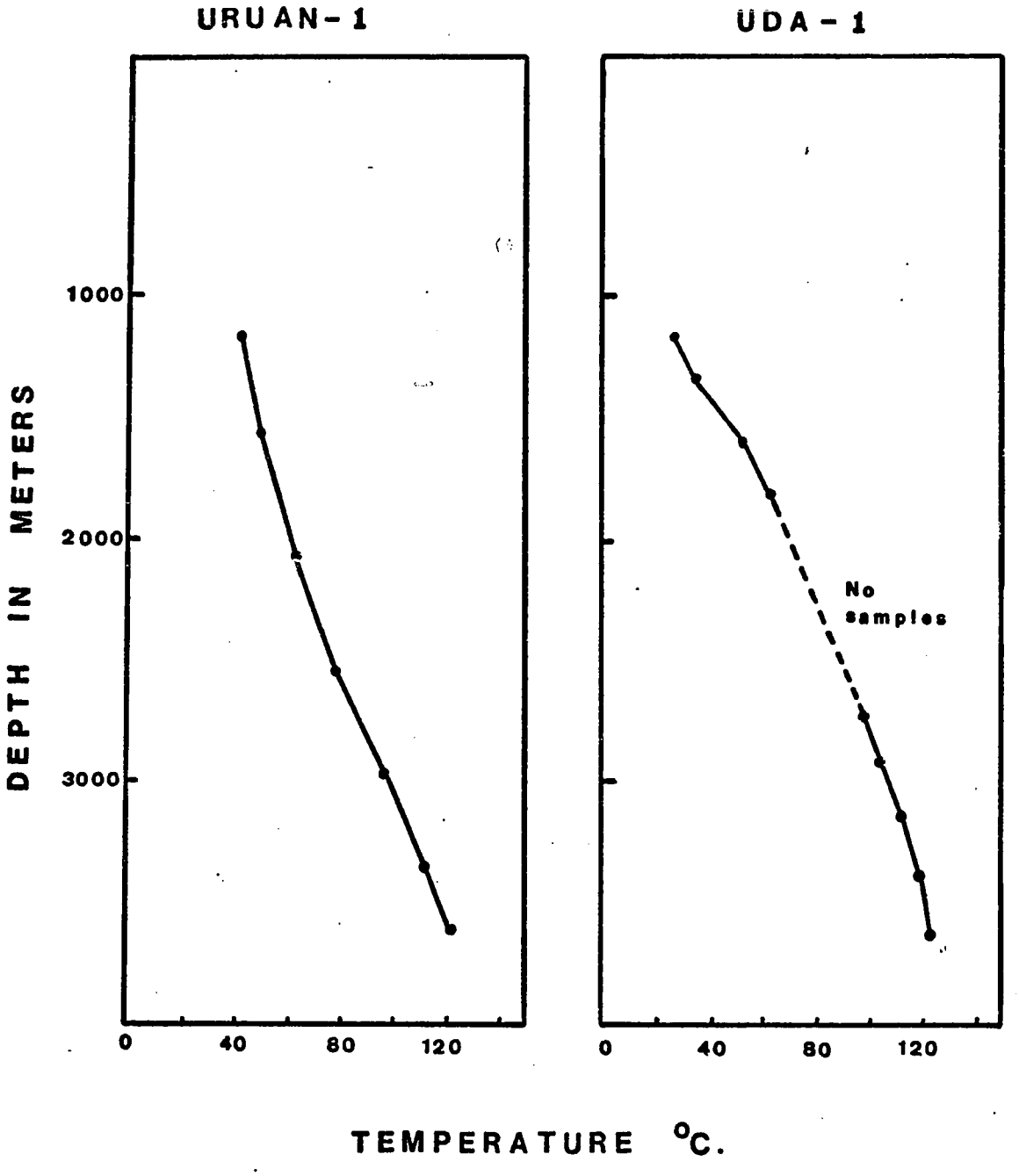

FIG. 15. Calculated temperature profiles for wells Uruan-1 and Uda-1, Niger delta.

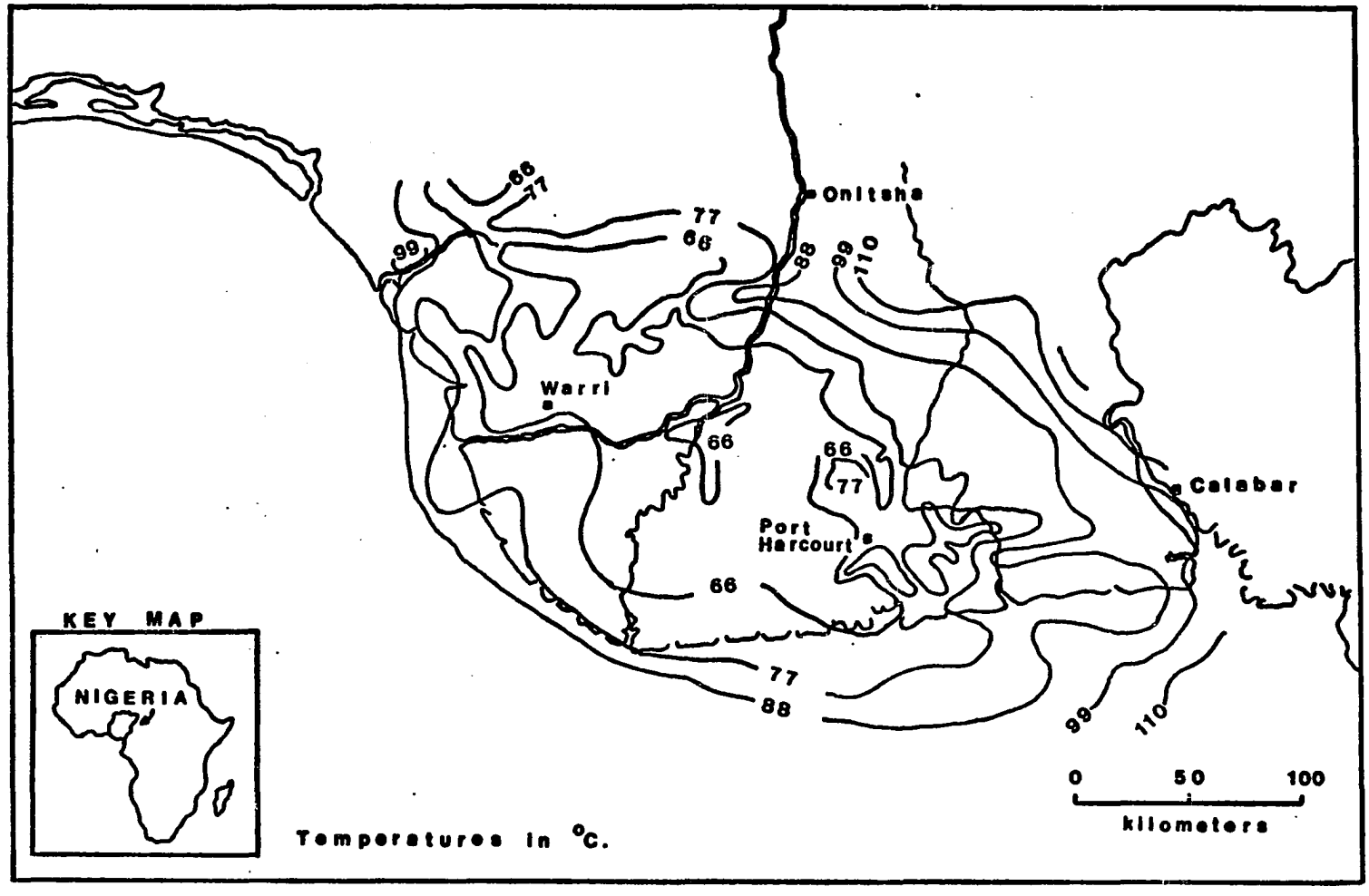

FIG. 16. Geotemperatures at 2,591 m. in the Niger delta (After Evamy et al., 1978, Fig. 15a).

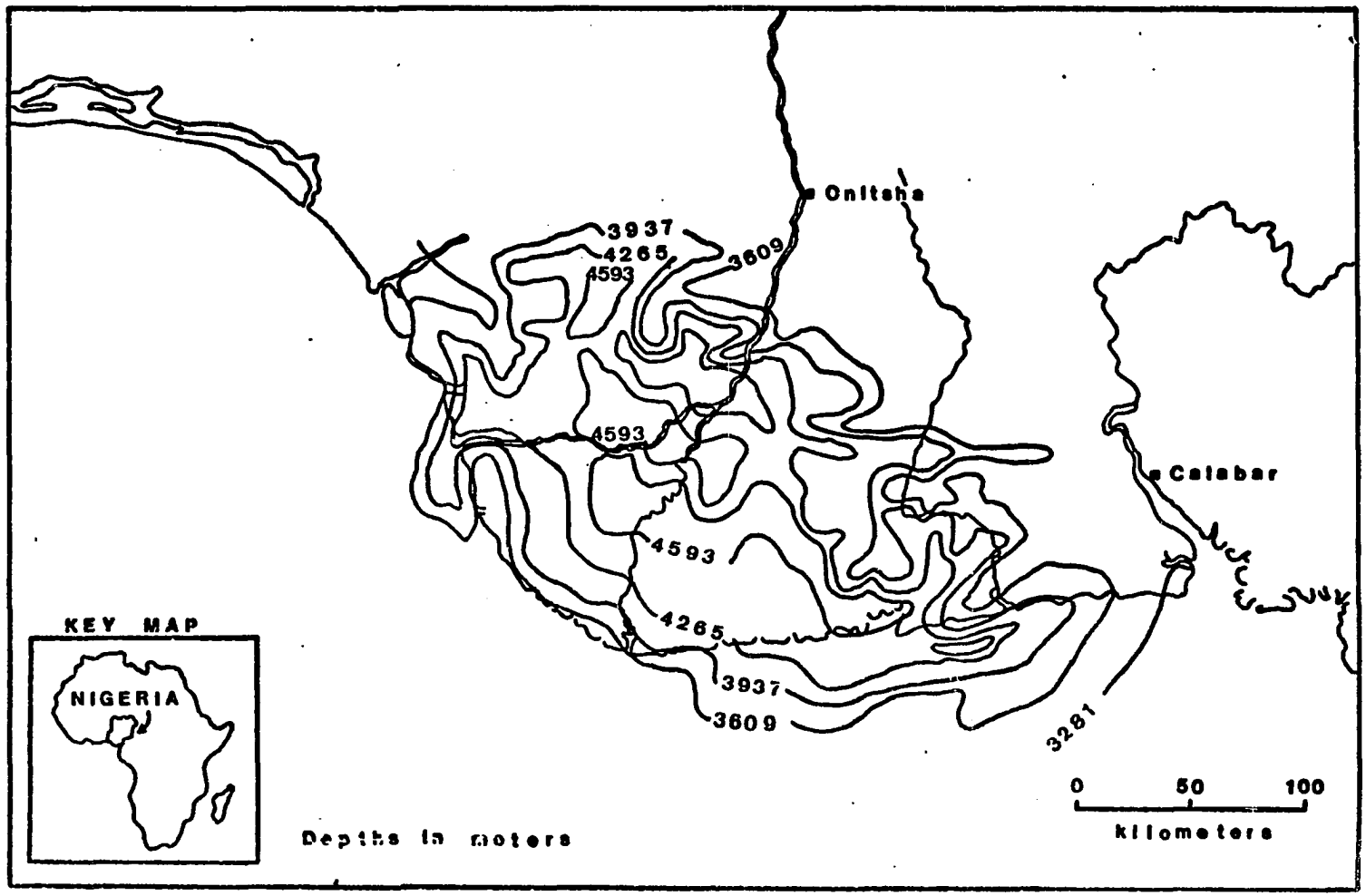

FIG. 17. Subsurface depth to 116 ^{o}C temperature in the Niger delta (After Evamy et al., 1978, Fig. 15b).

MINERALOGIC DATA

Introduction

Investigation of the variation of the clay mineralogy versus depth was limited to the < 0.1-um size fraction, because it is the size fraction most sensitive to burial diagenesis (Hower et al., 1976). In addition, x-ray powder diffraction analysis of this size fraction shows no crystalline phases other than clay minerals.

Five principal clay minerals were identified in this study. They are smectite, illite, kaolinite, chlorite and mixed-layer illite/smectite. The first four minerals were identified by methods described by Carroll (1970) and summarised in Table 1, and by Brown and Brindley (1980). Mixed-layer illite/smectite (I/S) was identified by methods described by Reynolds and Hower (1970), and Reynolds (1980). Since this study is primarily to investigate clay mineral burial diagenesis, both the distinction between random and ordered interstratification of mixed-layer illite/smectite and the estimation of the amount of each component are critical to the principal conclusion to be drawn.

Smectite

Brindley (1980, p.169-182), among many others, has discussed the various cation substitutions in both the tetrahedral

TABLE 1. X-ray identification of principal clay minerals observed in this study. (Adapted from Carroll, 1970, Table 9).

Mineral	Basal d spacings (001)	Glycolation effect	Heating effect
Kaolinite	7.15 Å (001);3.75(002)	No change	Becomes amorphous @ 550 °C.
Smectite	15 Å (001) and integral series of basal spacings	(001) expands to 17 Å with rational sequence of higher orders	At 300 °C (001) becomes 9 Å
Illite	10 Å (002), broad, other basal spacings present but small	No change	(001) noticeably more intense on heating as water layers are removed
Chlorite, Mg-form	14 Å (001) and integral series of basal spacings	No change	(001) increases in intensity
Chlorite, Fe-form	14 Å (001) less intense than in Mg-form; integral series of basal spacings	No change	(001) scarcely increases

and octahedral positions of the smectite group. He noted that substitutions of ions of the same valence, notably Mg - Fe (II) and Al - Fe (III) substitutions, are common in octahedral positions. In addition, coupled substitutions may also occur, such as $Fe^{3+} + O^{2-}$ replacing $Fe^{2+} + (OH)^-$, which is equivalent to a combined oxidation - dehydration process. Therefore substitution by ions of lesser charge, notably Si^{4+} by Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, would lead to a charge deficiency on the layers. Charge neutrality is achieved by incorporation of exchangeable interlayer cations, normally Na^+, Ca^{2+} and Mg^{2+} (Brindley, 1980, p.169). The general formulae for di- and trioctahedral smectites, according to Brindley (op. cit.) are as follows:

Dioctahedral $(M^+_{x+y}\ nH_2O)(R^{3+}_{2-y}\ R^{2+}_{y})(Si_{4-x}\ Al_x)O_{10}(OH)_2$

Trioctahedral $(M^+_{x-y}\ nH_2O)(R^{2+}_{3-y}\ R^{3+}_{y})(Si_{4-x}\ Al_x)O_{10}(OH)_2$

$(M^+_{x+y}\ nH_2O)(R^{2+}_{3-y}\ Li_y)(Si_{4-x}\ Al_x)O_{10}(OH)_2$

The end-member compositions of the more important dioctahedral smectites are:

Montmorillonite: $(M^+_y\ nH_2O)(Al_{2-y}Mg_y)Si_4O_{10}(OH)_2$

Beidellite: $(M^+_x\ nH_2O)Al_2(Si_{4-x}Al_x)O_{10}(OH)_2$

Nontronite: $(M^+_x\ nH_2O)Fe^{3+}_2(Si_{4-x}Al_x)O_{10}(OH)_2$

and the following are the more important trioctahedral smectites:

Saponite: $(M^+_{x-y}\ nH_2O)(Mg_{3-y}(Al,Fe)_y)(Si_{4-x}Al_x)O_{10}(OH)_2$

Hectorite: $(M^+_y\ nH_2O)(Mg_{3-y}Li_y)Si_4O_{10}(OH)_2$

With such a wide variety of mineral species in the smectite group, their identification by x-ray diffraction is usually an approximation within the expected range of their basal reflections (spacings). These depend on the nature of the interlayer cations, the degree of hydration of the cations, and the presence of liquids other than water purposely introduced as part of the identification process (Brindley, 1980, p.170). An important step in their identification, therefore, is the use of ethylene glycol to expand the basal reflections to a constant value around 17 Å. Air-dried basal reflections sometimes do not conform to integral orders of diffraction as stipulated by the Bragg reflection law, because of the effects of ambient humidity or the variability of interlayer hydration. In this study the term smectite is used as agroup name and no effort has been made to identify individual species.

Illite

The name illite also does not refer to a single mineral specie, but rather to a group of essentially non-swelling clays, the most common representative being a potassium-rich 2:1 layer type together with small amounts of interstratified smectite (Reynolds, 1980, p.275). However, most authors generally use the term illite for a 10 Å clay mica end member, a precedence adopted in this study.

Identification is made on the basis of a rational series of basal reflections with d(001) = 10 Å (Reynolds, 1980). The

001 reflection is asymetrical and has a low angle tail. Upon ethylene glycol solvation, the 001 reflection shows no change.

Mixed-layer illite/smectite (I/S)

When various amounts of smectite component are present in the I/S the 001 peak is near 8.5° 2θ (CuKα), corresponding to an interplanar spacing of 10.4 Å, in the air-dried condition. Upon ethylene glycol solvation the peak shifts to 8.8° 2θ(10 Å) or 8.9° 2θ(9.9 Å) and becomes more asymmetrical (Reynolds, 1980).

Figures 18 and 19 show CuK x-ray powder diffraction tracings of interstratified illite-smectite(glycol) for random and ordered sequences respectively. These figures are after Reynolds (1980) who also noted that no reflection is found for any composition in the random series in the 2θ range between the illite 001 and the smectite 001. Instead, increasing proportions of smectite cause the increased intensity of a reflection near the smectite 001, which is first recognizable in a mixed-layer interstratification with about 60% illite layers. For ordered structures the illite + smectite 002 maximum is present at about $\underline{d}$ = 13 Å, and it migrates toward the position of the smectite 001 with increasing smectite content. The migration, however, is not linear with respect to composition as was originally demonstrated by MacEwan (1958). Reynolds (1980) also noted that the only other evidence of order is manifested by a weak but

FIG. 18

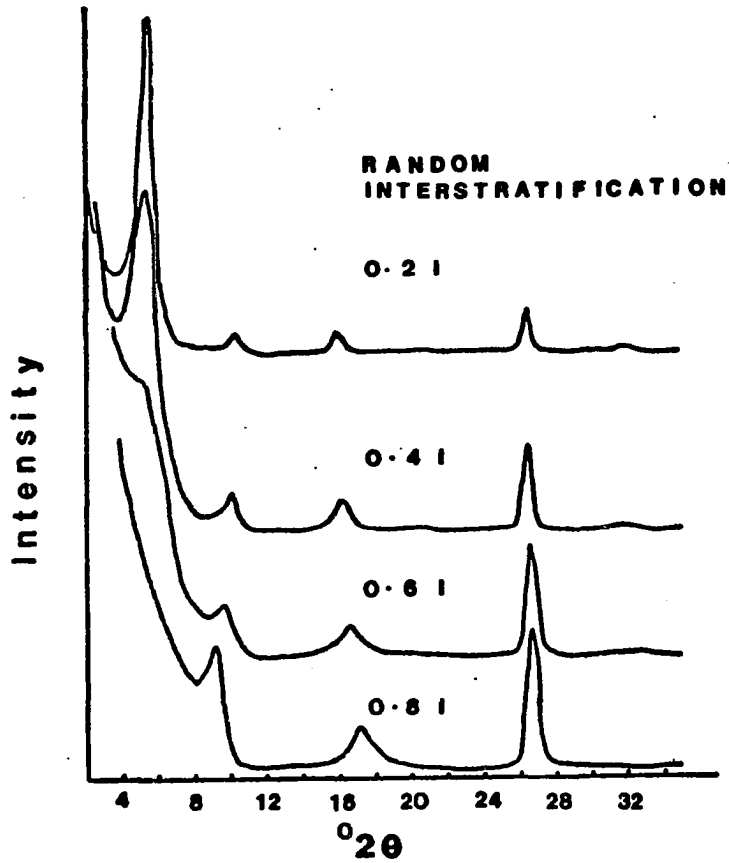

FIG. 18. Calculated diffractometer patterns of randomly interstratified illite-(glycol) smectite. 0.2 I = 20% illite, e.t.c. (After Reynolds, 1980, Fig. 4.7)

FIG. 19

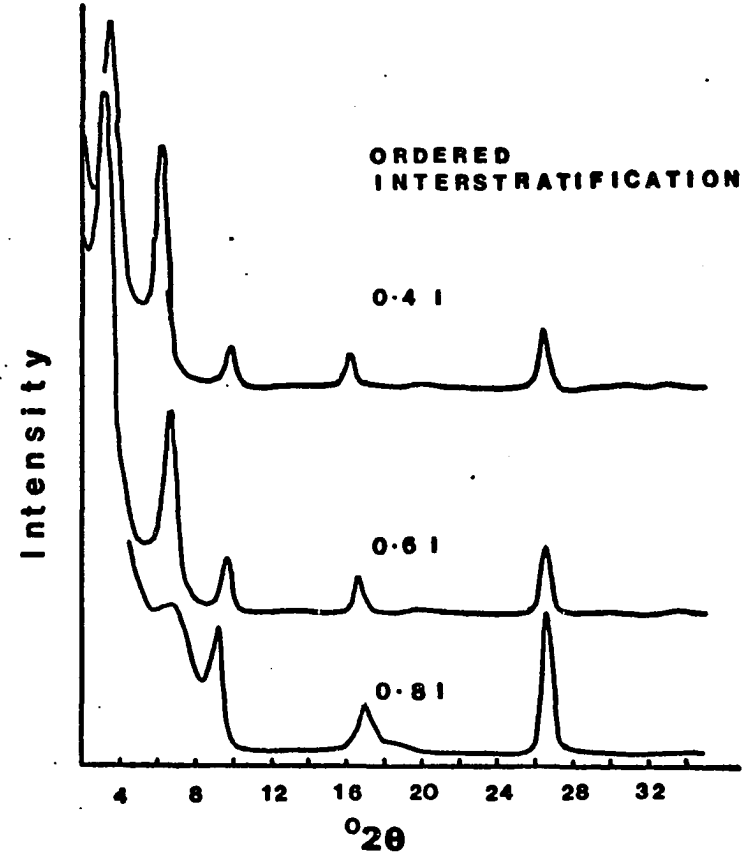

FIG. 19. Calculated diffratometer patterns for fully ordered (IS) interstratified illite-(glycol) smectite. 0.4 = 40% illite, e.t.c. (After Reynolds, 1980, Fig. 4.8).

distinct reflection at about d = 4.6 Å, and that as the composition approaches that of the end member with the largest d(001), the differences between manifestations of random and ordered interstratification become minimal.

The presence or absence of mixed-layer illite/smectite and, when present, the type of interstratification (i.e. random or ordered) as well as an approximate percentage of each component mineral was determined by curve matching observed diffraction patterns to the calculated patterns of ideal compositions presented by Reynolds and Hower (1970) and Reynolds (1980). In ethylene glycolated ordered interstratification, there is a basal reflection at about 13 Å while in ethylene glycolated random interstratification the comparable basal reflection is at about 17 Å. In both cases, the (001) basal reflection of the illite component is less than that of a discrete illite (10.1 Å) at about 9. $\pm$ 0.3 Å. Once a distinction had been made between ordered and random interstratification, an approximate percentage of the component layers can be made by noting the d spacing of the $002_I/003_S$ peak (Table 2), because this peak shows sufficient migration characteristics with respect to composition. However, since the variation is on the order of hundredths of an angstrom unit, this region was slow scanned at a chart speed of 0.2° 2θ/minute. The peak obtained is usually domal. Where a projection from the low and high angle sides of the dome meet

TABLE 2. Relations between compositions and peak positions for illite-(glycol) smectite interstratifications; spacings in Å. (After Reynolds, 1980, Table 4.5A).

	Random		Ordered	
% Illite	d	d	d	d
0	8.52	5.62	8.52	5.62
10	8.60	5.59	8.60	5.59
20	8.67	5.57	8.71	5.55
30	8.76	5.54	8.82	5.50
40	8.90	5.50	8.93	5.44
50	9.06	5.44	9.03	5.39
60	9.26	5.37	9.21	5.34
70	9.25	5.28	9.40	5.28
80	9.83	5.16	9.66	5.22
90	10.00	5.07	9.99	5.09
100	10.16	5.01	10.16	5.01

is considered to be the peak position. This is the most precise graphical method of obtaining the peak position. Nevertheless, it is subject to one's judgement in drawing the low and high angle projections. Therefore at best, the data obtained can be in error by as much as 10%.

Kaolinite and chlorite

The recognition of kaolinite in the presence of chlorite poses a problem. The 002 and 004 reflections of chlorites (d approximately 7.1 Å and 3.55 Å) overlap the 001 and 002 reflections of kaolinite (d = 7.15 Å and 3.58 Å). Brown and Brindley (1980, p.322) suggest that 'if the minerals are well-crystallized and give sharp reflections, an indication of the presence of both may be given by the partial resolution of the 002 kaolinite and 004 chlorite reflections'. Sometimes the reflections are broad, and the method adopted in this study for distinguishing between kaolinite and chlorite in such cases is to heat the sample at 550 °C for an hour. Kaolinite is transformed to very poorly ordered metakaolin (Brown and Brindley, 1980, p.323) and shows little or no diffraction pattern. Chlorite survives this thermal treatment and shows increases in the intensity of the 14 Å reflection and decreases in the intensities of the second, third and fourth orders. However, this method of distinction between chlorite and kaolinite is not

infallible as Brown and Brindley (1980, p.323) noted that 'many clay-grade chlorites are altered at lower temperatures than well-crystallized materials, so reflections of both kaolite and chlorite may be affected by a 450-500 ^{o}C treatment'. The problem is further compounded by the fact that in sedimentary materials, the chlorite component is sometimes altered by heating at 400-500 ^{o}C while the kaolinite component survives (Johns, Grim and Bradley, 1954). Kodama and Oinuma (1963) also noted an overlap of the critical temperature ranges in which the thermal transformations occurred in various kaolinites and chlorites. They considered that infrared data could be used to identify kaolinite minerals in the presence of chlorite.

A separation of kaolinite from chlorite can sometimes be obtained by treating with warm dilute HCl in which many chlorites are soluble. Brown and Brindley (1980, p.323) noted that acid dissolution is likely to depend on particle size and chemical composition. Brindley and Edwards (1976) noted that even hot strong HCl did not dissolve high magnesium chlorites. Thus acid treatment is also not an infallible means of distinguishing between kaolinite and chlorite.

The thermal method used in this study is useful in giving some measure of distinction between kaolinite and chlorite, but since the method, is not infallible, the results ought to be regarded only qualitatively.

Determination of the qualitative estimation of the clay minerals.

Quantitative estimation of discrete phases of clay mineral groups is difficult because of the several variable factors that affect the shape of the basal reflections. Some of these factors include chemical composition, polytypism, differences in crystal perfection, hydration, evenness of the spread of the mixed minerals, weight of the clay sample X-rayed, thickness of the mount, orientation of the grains and mass absorption coefficients of the individual minerals. For these reasons a direct comparison of peak areas or peak heights is inadequate in evaluating the volumetric contribution of each component in a multicomponent clay system. Johns, Grim and Bradley (1954) and Biscaye (1965) resolved some of this difficulty by using a method of weighting measured peak areas to make them directly comparable. Huff (1981, personal communication) points out that this method 'assumes that the various weighting factors for each mineral apply equally to all the particles of that mineral in the sample, and to all the samples compared, and that the sum of the weighted peak areas accounts for 100 percent of the mineralogy of the sample'.

The weighting factors used in making a semiquantitative estimation of the clay minerals in this study are after Johns, Grim and Bradley (1954), and Biscaye (1965) and are:

1 x 17 Å glycolated peak for smectite (area)

4 x 10 A glycolated peak for illite (area)

2 x 7 Å air-dried peak for chlorite-kaolinite (area)
The sum of the combined weighting peak areas is used as a denominator in determining the percentages of the individual minerals. Accuracy is estimated to be between 5 and 10 percent.

Where mixed-layer illite/smectite minerals are present, there is a difficulty in determining their proportions in relation to other clay minerals. Although this problem is acknowledged in the literature, it has not been addressed. In view of a lack of precedence on solving this problem, one can treat each of the ethylene glycolated peaks of the components of the mixed-layer as discrete phases, using the appropriate weighting factor of Johns, Grim and Bradley (1954) and Biscaye (1965). The percentage of the mixed-layer clay is then regarded as the sum of the percentages of its components. It is worth stressing that these percentages of relative abundance of the various clay minerals are not empirical. They are at best only semi-quantitative and are therefore most usefull in detecting trends in relative abundances.

Mineralogical data.

Well Uruan-1.

Smectite.

Smectite occurs between a depth of 1,312 m. to 1,969 m. and between 3,675 m. to the well's total depth at 3,773 m. (Fig. 20). Its relative abundance decreases from 1,312 m. to

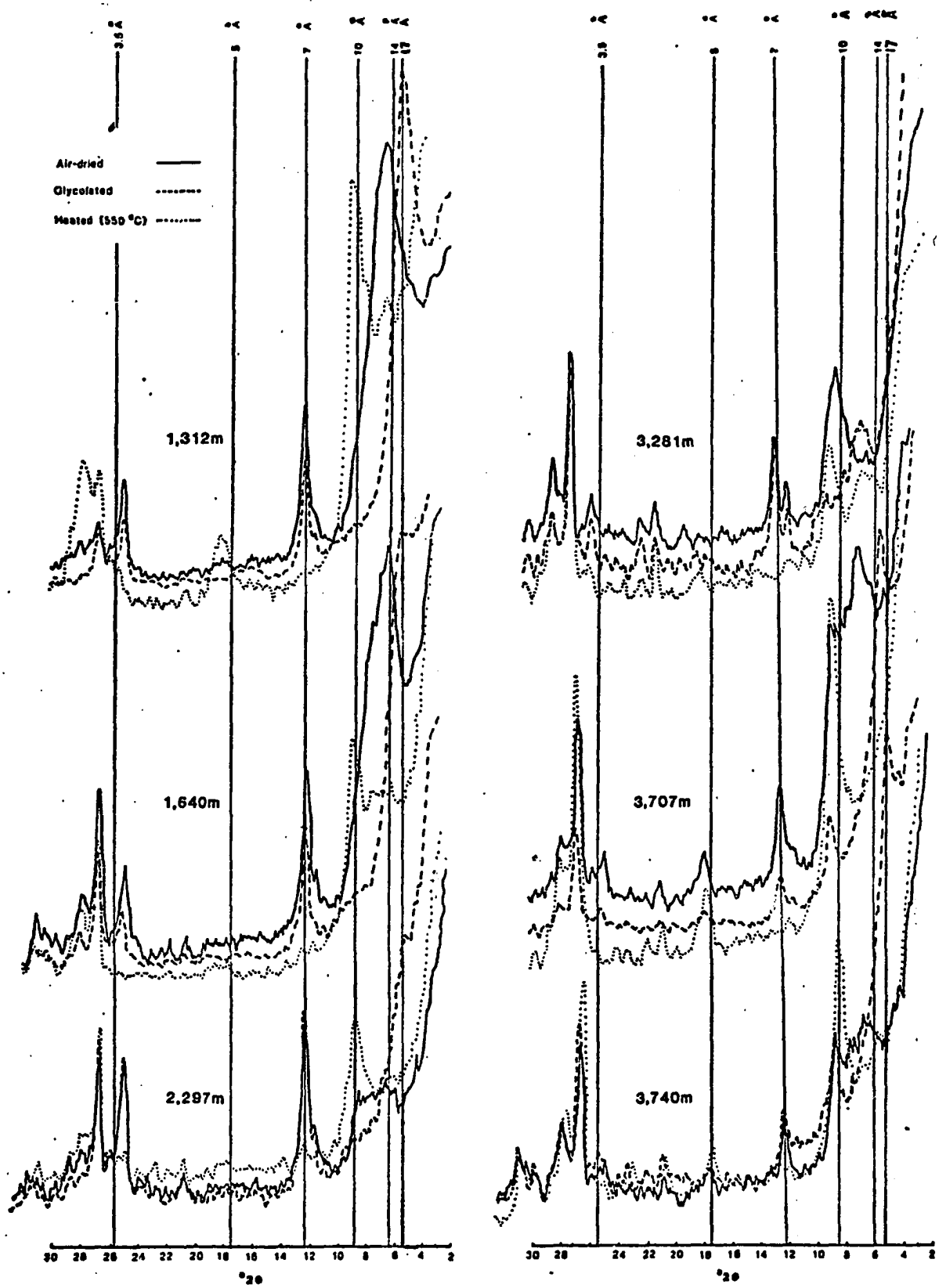

FIG. 20. X-ray powder diffractogram of samples from various depths in well Uruan-1, illustrating shifts in peak areas in response to three treatments of the clay minerals investigated.

1,969 m., but appears to be relatively constant between 3,675 m. to 3,773 m. (Table 3).

Illite

Illite was detected only between 3,642 m. and 3,773 m. (Fig. 20), and its relative abundance is fairly constant (Table 3).

Mixed-layer illite/smectite

Mixed-layer illite/smectite was detected between 1,969 m. and 3,675 m. (Fig. 20), and its relative abundance fluctuates between 90 and 28 percent (Table 3). Within this depth range, the mixed-layer illite/smectite from samples taken at depths 1,969 m. and 2,297 m. was randomly interstratified with 20% and 40% expandables (smectite) respectively (Table 4). Determination of percentage expandables is based on peak positions as outlined in Table 2. The mixed-layer illite/smectite between depths 2,625 m. and 3,675 m. all had ordered interstratification (Table 4). It is interesting to note that mixed-layer illite/smectite does not occur below a depth of 3,675 m.

Kaolinite and chlorite.

Kaolinite occurs sporadically throughout the depths investigated (Fig. 20 and Table 3). At certain depths, its relative abundance is as high as 62% while at other depths there is only a trace amount and even complete absence (Table 3).

Chlorite occurs in only a few samples and in relatively low abundances (Fig. 20 and Table 3). Chlorite probably might occur in a greater abundance than reflected in Table 3, but since its proportional quantity can only be determined in an air-dried diffractogram (Johns, Grim and Bradley, 1954; Biscaye,

TABLE 3. Semiquantitative estimate of clay mineral abundance (%) of < 0.1-um size fraction in well Uruan-1.

Depth (m.)	Smectite	I/S *	Illite	Kaolinite	Chlorite
1,312	71	0	0	29	0
1,640	28	0	tr	62	tr
1,969	31	69	0	0	tr
2,297	0	28	0	62	0
2,625	0	78	0	22	0
2,953	0	90	0	7	3
3,281	0	87	0	tr	13
3,642	0	39	55	tr	6
3,675	36	40	20	0	4
3,707	41	0	48	11	0
3,740	48	0	44	tr	8
3,773	48	0	42	10	0

* Mixed-layer illite/smectite.

tr = Trace amounts.

TABLE 4. Percentage expandables (smectite) in mixed-layer I/S, and type of interstratification in well Uruan-1.

Depth (m.)	Percentage expandable	Type of interstratification
1,312	-	-
1,640	-	-
1,969	20	Random
2,297	40	Random
2,625	35	Ordered
2,953	40	Ordered
3,281	40	Ordered
3,642	15	Ordered
3,675	10	Ordered
3,707	-	-
3,740	-	-
3,773	-	-

1965), chlorite peak may be masked in samples with appreciable amounts of smectite as exemplified in a sample from 1,640 m. (Fig. 20). The chlorite peak after heating to 550 ^{o}C cannot be used in quantitative estimations because it increases in intensity (Table 1). Hence, although it appears that there is a definite occurrence of chlorite in the sample from depth 1,640 m. as evidenced in the heated peak (Fig. 20), it has been reported as a trace amount in Table 3.

Well Uda-1

(Apart from a sample at 2,067 m., there were no samples between depths 1,913 m. and 2,720 m.).

Smectite

In this well, smectite was detected in only three samples from depths of 1,391 m., 3,031 m. and 3,360 m. (Fig. 21 and Table 5). The shallowest sample (1,391 m.) had a 50% abundance in smectite while the two other lower samples had 25 % and 23% smectite respectively. It therefore seems that the abundance of smectite decreases with depth.

Illite

Illite occurs only in the upper part of the well (i.e. from 1,391 m. to 2,730 m.) and appears to increase in abundance with depth (Fig. 21 and Table 5).

Mixed-layer illite/smectite

Mixed-layer illite/smectite occurs from 1,719 m. to the total depth of the well (3,688 m.), and appears to increase

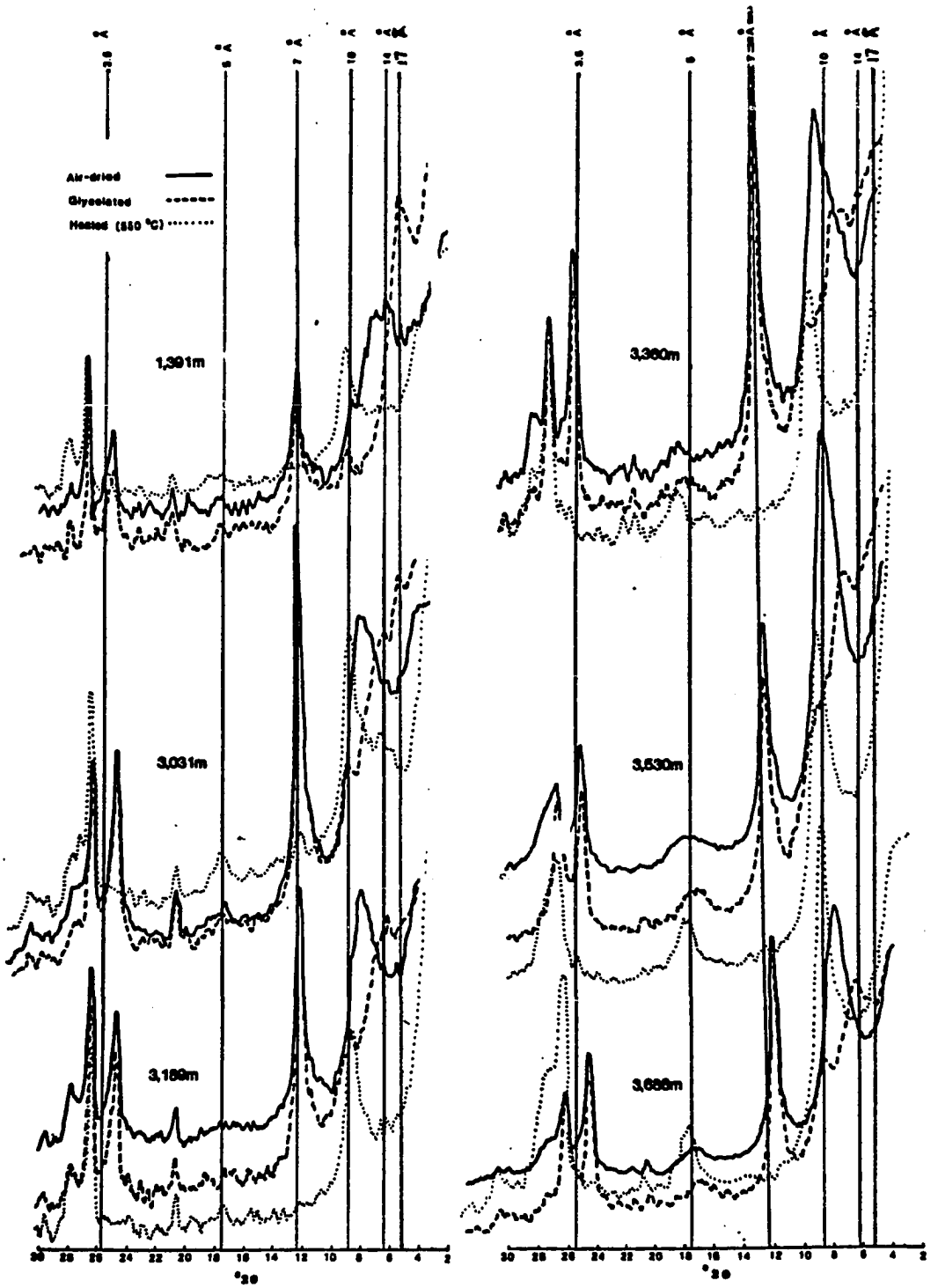

FIG. 21. X-ray powder diffractogram of samples from various depths in well Uda-1, illustrating shifts in peak areas in response to three treatments of the clay minerals investigated.

TABLE 5. Semiquantitative estimate of clay mineral abundance (%) of <0.1-um size fraction in well Uda-1.

Depth (m.)	Smectite	I/S *	Illite	Kaolinite	Chlorite
1,391	50	0	15	35	0
1,719	0	20	32	48	0
2,067	0	20	38	42	0
2,730	0	30	38	32	0
3,031	25	40	0	35	tr
3,189	23	50	0	27	0
3,340	0	88	0	22	tr
3,360	0	90	0	10	0
3,530	0	93	0	7	0
3,661	0	86	0	14	0
3,688	0	90	0	10	0

* Mixed-layer illite/smectite

tr = Trace amounts.

in abundance with depth (Fig. 21 and Table 5) The type of interstratification as determined from peak positions and Table 2, varies from random interstratification in samples from depths 1,719 m., 2,067 m. and 2,730 m., to ordered interstratification in the rest of the samples investigated from 3,031 m. to 3,688 m. (Table 6). An interesting observation is the abrupt decrease in percentage expandables between depths 2,730 m. and 3,031 m. (Table 6).

Kaolinite and chlorite.

Kaolinite occurs in every sample investigated from this well, but there is a decrease in its abundance with depth (Table 5). In contrast, chlorite is essentially rare except for trace amounts in two samples from depths 3,031m. and 3,340m.

Discussion.

The occurrence of smectite, illite and mixed-layer illite/smectite in well Uruan-1 (Table 3) suggest a transformation of smectite through a mixed-layer illite/smectite phase (Table 4) to illite (Fig. 23). This transformation illustrates clay mineral burial diagenesis as described for the the U.S Gulf Coast by Perry and Hower (1970), and Hower et al.(1976). However, the occurrence of smectite at a depth of 3,675 m. and below, is clearly an anomaly according to the hypothesis of Perry and Hower (1970). At these depths, which have been subjected to geothermal temperatures between 100 - 120 ^{o}C (Fig. 15),

TABLE 6. Percentage expandables (smectite) in mixed-layer I/S, and type of interstratification in well Uda-1.

Depth (m.)	Percentage expandable	Type of interstratification
1,391	-	-
1,719	90	Random
2,067	90	Random
2,730	80	Random
3,031	10	Ordered
3,289	10	Ordered
3,340	15	Ordered
3,360	10	Ordered
3,530	20	Ordered
3,661	20	Ordered
3,688	20	Ordered

smectite is not expected to occur in the discrete phase, especially if sufficient potassium had been available to the clayey sediments.

In well Uda-1, the distribution of smectite, mixed-layer illite/smectite, and illite, do suggest some form of transformation has taken place. Evidence for this is in the relative increase in abundance of the mixed-layer illite/smectite with depth (Table 5). However, it is difficult to relate these changes to the hypothesis of clay mineral burial diagenesis deviced for the U.S. Gulf Coast by Perry and Hower (1970), because of the stratigraphic positions of smectite and illite in relation to the mixed-layer illite/smectite (Fig. 23). For instance, the occurrence of smectite at depths 3,031 m. and 3,189 m. appear to be anomalous since it has been subjected to geothermal temperatures of 100 - 120 ^{o}C (Fig. 15), and therefore should have been converted to a mixed-layer illite/smectite phase according to the hypothesis of Perry and Hower (1970). Furthermore, the occurrence of illite at a stratigraphic position higher than the bulk of the mixed-layer illite/smectite do not suggest that it was derived from clay mineral burial diagenesis. The more likely explanation is that it is detrital and its distribution is a function of the pattern of sedimentation in the eastern Niger delta basin.

Another apparent anomaly, if we try to interprete the

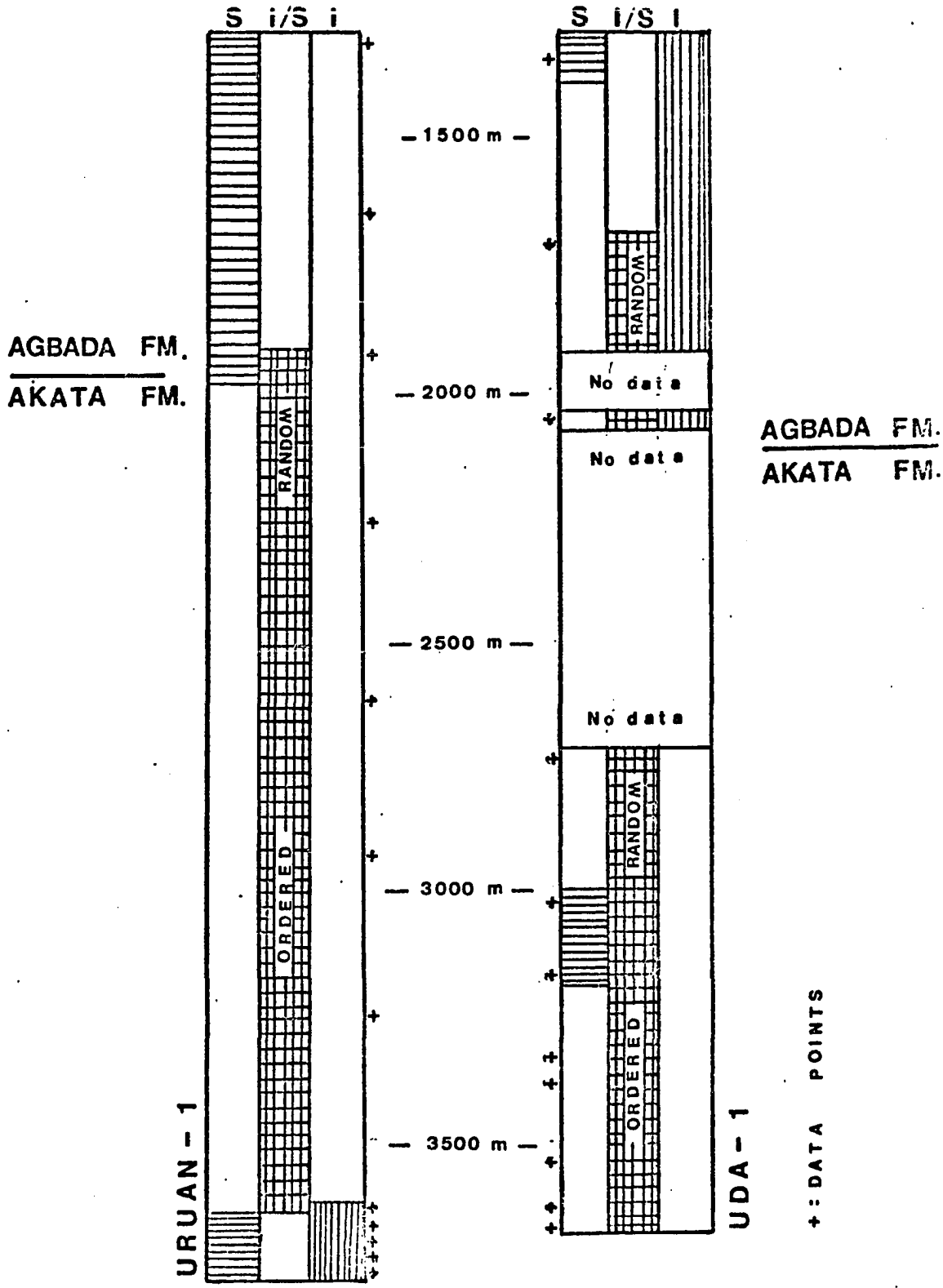

FIG. 23. Graphic representation of the vertical qualitative distribution of smectite, mixed-layer illite/smectite, and illite in wells Uruan-1 and Uda-1, Niger delta.

clay mineral suite in well Uda-1 according to the hypothesis of Perry and Hower (1970), is the distribution of the type of interstratification in the mixed-layer illite/smectite (Table 6). Although a transition from random to ordered interstratification is observed, as described by Reynolds and Hower (1970) and Reynolds (1980) (reproduced here in Table 2), as would be expected from the hypothesis of Perry and Hower (1970), the abrupt change in percentage expandables from 80% at depth 2,730 m. to 10% at depth 3,031 m. (Table 6) seems drastic and inexplicable. Furthermore, the percentage expandables from 3,031 m. increases with depth (Table 6) contrary to what should be expected. Also, the rather low percentage of expandables ($<20\%$) between depths 3,031 m. to 3,360 m. (Table 6), which have not been subjected to geothermal temperatures above 120 ^{o}C (Fig. 15) seem anomalous to the hypothesis. Perry and Hower (1970, Fig. 15 - reproduced here in Fig. 27) suggest that at about 100 ^{o}C the percentage expandable drops to 20% and remains constant till geothermal temperatures approach 200 ^{o}C, when a drop in percentage expandables should be expected (see also Weaver, 1979, Fig. 1 - reproduced here in Fig. 29).

If the hypothesis on clay mineral burial diagenesis (Perry and Hower, 1970) is correct, it would seem that between 3,031 m. and 3,688 m. a reversal in clay mineral burial diagenesis occurs. But this cannot be the case from stratigraphic considerations (Fig. 9) nor from the calculated temperature profile for well

Uda-1 (Fig. 15). The question is thus raised wheter other physical or chamical factors besides temperature are controlling the diagenetic reactions.

Figure 22 is a plot of the percentage expandables in mixed-layer illte/smectite, as a function of depth in both wells studied. In well Uda-1, there is a sharp drop in the percentage of the smectite component in the mixed-layer I/S from 80% to 10% over a relatively short stratigraphic interval. This change seems inexplicable in terms of burial diagenesis if deposition of the clayey sediments had been as uniform as the geothermal gradient is. The chemical data, discussed in detail in the next chapter, shows a general increase with depth in K_2O, in the fine-grained fraction. This indicates there was sufficient potassium available for the diagenetic reaction. A likely interpretation for this sharp drop in the percent of smectite component in the mixed-layer I/S may be a manifestation of differences in the original clay mineral suite before burial. In other words, it may be an indication of some form of stratigraphic or facies control. This plausible interpretation does not negate the possibility that diagenesis had taken place, as indeed the data indicates. But it attempts to explain the nature of the diagenetic data.

In well Uruan-1, there is a wide variation in the percent of smectite component in the mixed-layer I/S. At a depth of

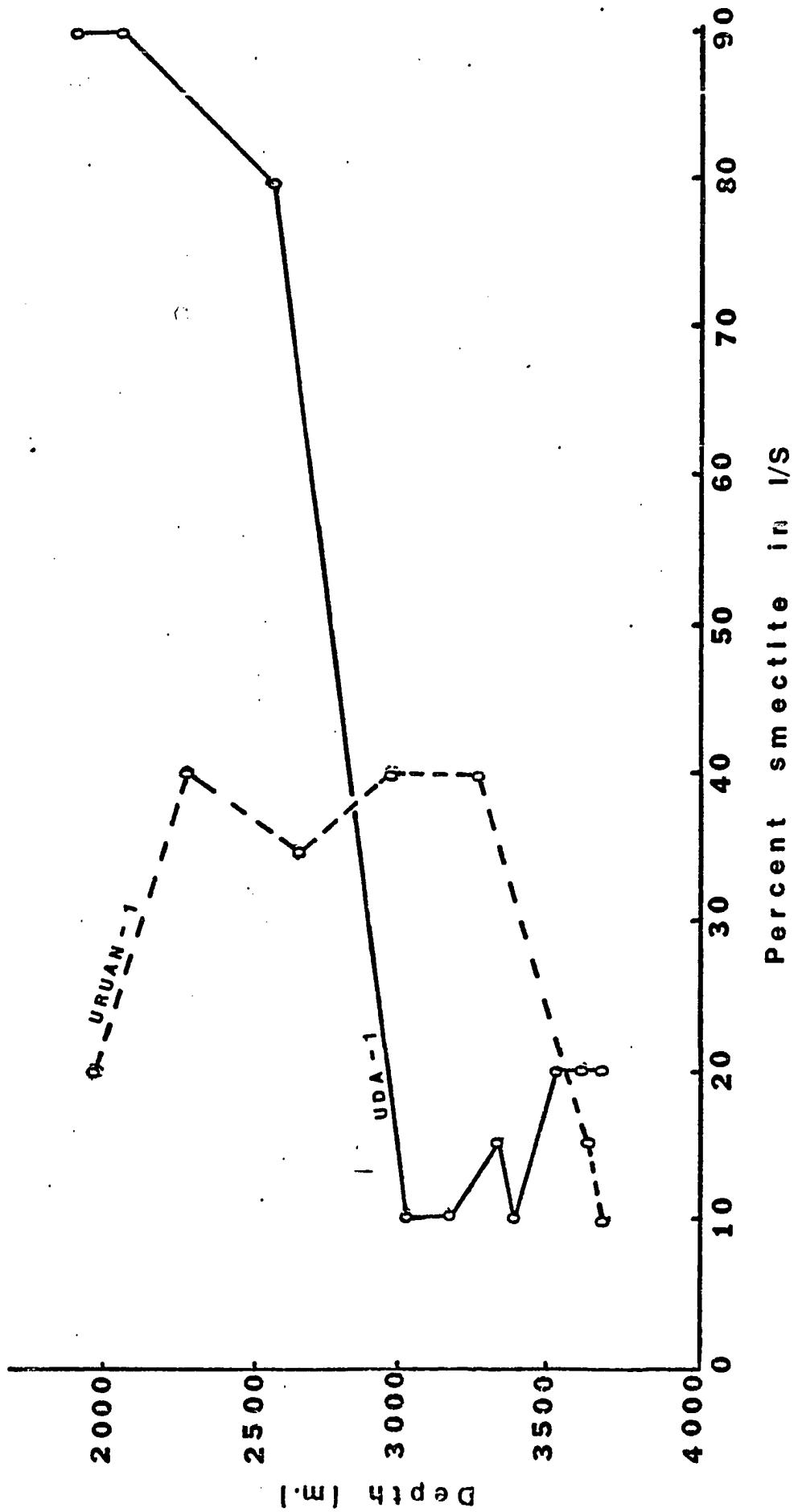

FIG. 22. Proportion of smectite layers in illite/smectite as a function of depth in wells Uruan-1 and Uda-1, in the < 0.1-um size fraction.

3,281 m., the mixed-layer I/S has 40% smectite component which reduces to 10% smectite component over a stratigraphic range of 394 m. In general, the trend in the reduction of percent smectite component in the mixed-layer I/S is within the expected range for clay mineral burial diagenesis (Perry and Hower, 1970).

The occurrence of kaolinite and chlorite in well Uruan-1 is variable and does not appear to correlate with other clays in any systematic fashion. In well Uda-1, chlorite is essentially absent. Kaolinite occurs in all samples, and appears to decrease in abundance with depth. This may be indicative of a transition from nonmarine to marine facies (Brown et al., 1977, p. 181), in which case the occurrence of both chlorite and kaolinite would be detrital, and their relative abundance a reflection of environmental control.

CHEMICAL DATA

Introduction.

The variation of seven major oxides (SiO_2, Al_2O_3, MgO, Fe_2O_3, CaO, Na_2O, K_2O) with depth, was investigated in the $<$0.1-um size fraction and in whole rock samples for both wells Uruan-1 and Uda-1. Chemical variations in the $<$ 0.1-um size fraction, which is 100% clay minerals, can suggest patterns in chemical rearrangements in depth related mineralogic changes. Chemical variations in the whole rock can reveal either an original variation in composition, or gains and losses during diagenesis. As Hower *et al*. (1976, p.732) have written, 'if the mineralogy of the original (whole rock) did not vary with depth and if there were no chemical gains or losses, there would, of course, be no variation of chemical composition of the (whole rock) with depth'.

Chemical data.

Tables 7 and 8 present the variation of seven major oxides in the $<$ 0.1-um size fraction, with depth, for wells Uruan-1 and Uda-1 respectively. Tables 9 and 10 present variation in the whole rock sample for Uruan-1 and Uda-1 respectively. Analyses were performed by atomic absorption spectrophotometry on un-ignited samples, and accordingly, the sum total of the concentration of the seven oxides in all four tables is less than 100%. The difference is assumed to represent total water.

	Depth (m.)											
	1,312	1,640	1,969	2,297	2,625	2,953	3,281	3,642	3,675	3,707	3,740	3,773
Concentration (%)												
SiO_2	67.13	66.27	63.20	65.41	63.47	64.09	63.63	62.67	62.58	62.77	62.94	62.16
Al_2O_3	14.15	13,01	15.85	14.15	13.80	14.15	13.80	12.80	14.50	13.80	14.50	15.18
Fe_2O_3*	5.30	4.60	7.30	2.60	4.90	4.00	3.65	3.30	2.50	3.00	3.00	2.00
MgO	0.78	1.32	1.74	0.96	1.28	2.10	1.50	0.78	0.60	0.84	1.80	1.78
CaO	1.20	0.80	0.70	0.90	1.00	1.10	1.08	0.82	1.22	1.10	1.10	1.20
Na_2O	0.88	0.90	0.42	0.38	0.18	0.56	0.40	0.40	0.48	0.30	0.10	0.10
K_2O	1.36	1.59	1.12	1.10	1.36	1.20	1.34	3.16	1.70	2.30	1.52	2.08
Total	90.80	88.49	90.33	85.50	85.99	87.20	85.40	83.93	83.58	84.11	84.96	84.50

Note: Analyses are on un-ignited samples. *Total Fe as Fe_2O_3.

TABLE 7. Major constituent chemical analyses of < 0.1 μm size fraction from well Uruan-1.

	Depth (m.)											
	1,719	1,870	2,730	2,854	3,018	3,031	3,189	3,340	3,360	3,530	3,661	3,688
Concentration (%)												
SiO_2	69.09	68.92	60.78	66.25	60.13	65.17	61.03	60.09	60.42	60.29	60.02	60.06
Al_2O_3	12.12	14.15	14.80	16.54	15.50	12.48	13.80	14.15	15.50	15.50	14.50	15.18
Fe_2O_3*	3.00	3.65	8.60	1.40	0.60	0.60	4.30	1.25	1.25	0.60	1.40	4.00
MgO	1.22	0.32	0.98	1.90	0.40	0.84	1.22	0.34	0.30	0.40	0.98	0.80
CaO	1.30	1.42	1.60	1.50	1.40	1.00	1.38	2.00	1.20	1.20	1.32	1.18
Na_2O	0.92	1.20	1.52	1.35	2.10	1.48	1.72	1.90	1.35	0.88	1.68	0.88
K_2O	0.82	1.15	2.68	0.98	3.70	1.62	5.00	2.15	3.70	3.80	3.36	4.50
Total	88.47	90.81	90.96	89.92	83.83	83.19	88.45	81.88	83.72	82.67	83.26	86.60

Note: Analyses are on un-ignited samples. *Total Fe as Fe_2O_3.

TABLE 8. Major constituent chemical analyses of $\prec$ 0.1 μm size fraction from well Uda-1.

	Depth (m.)											
	1,312	1,640	1,969	2,297	2,625	2,953	3,281	3,642	3,675	3,707	3,740	3,773
Concentration (%)												
SiO_2	64.37	66.52	65.48	65.97	66.07	65.92	66.49	67.08	65.03	67.29	67.14	67.65
Al_2O_3	15.18	14.80	16.54	14.15	15.50	17.58	15.18	14.80	15.50	16.54	17.58	15.85
Fe_2O_3*	7.15	1.40	5.00	5.00	2.50	1.25	5.00	5.50	8.25	4.60	4.60	2.25
MgO	1.28	0.96	0.84	0.62	0.70	0.80	2.00	2.18	1.20	0.64	0.96	1.22
CaO	1.22	1.20	1.40	1.10	1.80	2.12	1.52	1.22	1.12	1.12	1.34	1.22
Na_2O	0.28	0.30	0.22	0.38	0.38	0.40	0.80	1.32	2.18	2.42	2.10	1.88
K_2O	1.36	1.20	1.50	1.98	2.15	2.66	3.24	3.90	3.80	3.68	4.50	5.00
Total	90.84	86.38	90.98	89.20	89.10	90.73	94.23	96.00	97.08	96.29	98.22	95.07

Note: Analyses are on un-ignited samples. *Total Fe as Fe_2O_3.

TABLE 9. Major constituent chemical analyses of whole rock samples from well Uruan-1.

	Depth (m.)							
	1,719	1,870	2,854	3,018	3,189	3,340	3,530	3,661
Concentration (%)								
SiO_2	55.63	60.72	60.67	61.35	63.13	61.11	62.86	62.84
Al_2O_3	16.20	14.50	16.90	18.94	15.50	16.20	16.54	18.20
Fe_2O_3*	1.25	3.30	4.30	6.00	8.25	10.00	3.30	2.25
MgO	0.18	0.60	0.78	0.38	0.72	0.84	0.90	0.70
CaO	0.82	1.20	1.18	1.22	1.56	1.28	1.20	1.02
Na_2O	1.34	1.36	0.88	0.78	0.70	0.68	1.08	0.94
K_2O	4.20	3.92	3.92	1.82	3.28	2.64	3.22	3.18
Total	79.62	85.60	88.63	90.49	93.14	92.75	89.10	88.13

Note: Analyses are on un-ignited samples. *Total Fe as Fe_2O_3.

TABLE 10. Major constituent chemical analyses of whole rock samples from well Uda-1.

Each oxide's variation with depth in Tables 7 and 8 have been plotted in Figures 24 and 25 (for well Uruan-1). Similar plots in Figures 25 and 26 are for well Uda-1, and are plotted with data from Tables 8 and 10.

Depth related chemical variation in well Uruan-1

SiO_2 (Fig. 24) decreases with depth in the < 0.1-um size fraction while there is a slight increase in the whole rock sample. The variation in Al_2O_3 (Fig. 24) with depth appears to be mirrowed in both the < 0.1-um size and whole rock sample. There is a general slight increase in Al_2O_3 concentration. The plot of Fe_2O_3 (Fig. 24) do not suggest any depth related variation, although in both the < 0.1-um size fraction and in the whole rock sample, there is a net decrease in concentration at total depth. MgO plot (Fig. 24) does not show a net increase in the whole rock sample, but the < 0.1-um size fraction exhibits a net increase at total depth. CaO plot (Fig. 24) does not suggest any variation with depth, although there is a large increase in the whole rock sample at a depth approximately 3,000 m. Na_2O increases with depth in the whole rock sample (Fig. 24) while its concentration in the < 0.1-um size fraction decreases. K_2O increases with depth in the whole rock sample, but its concentration in the < 0.1-um size fraction is relatively constant (Fig. 25).

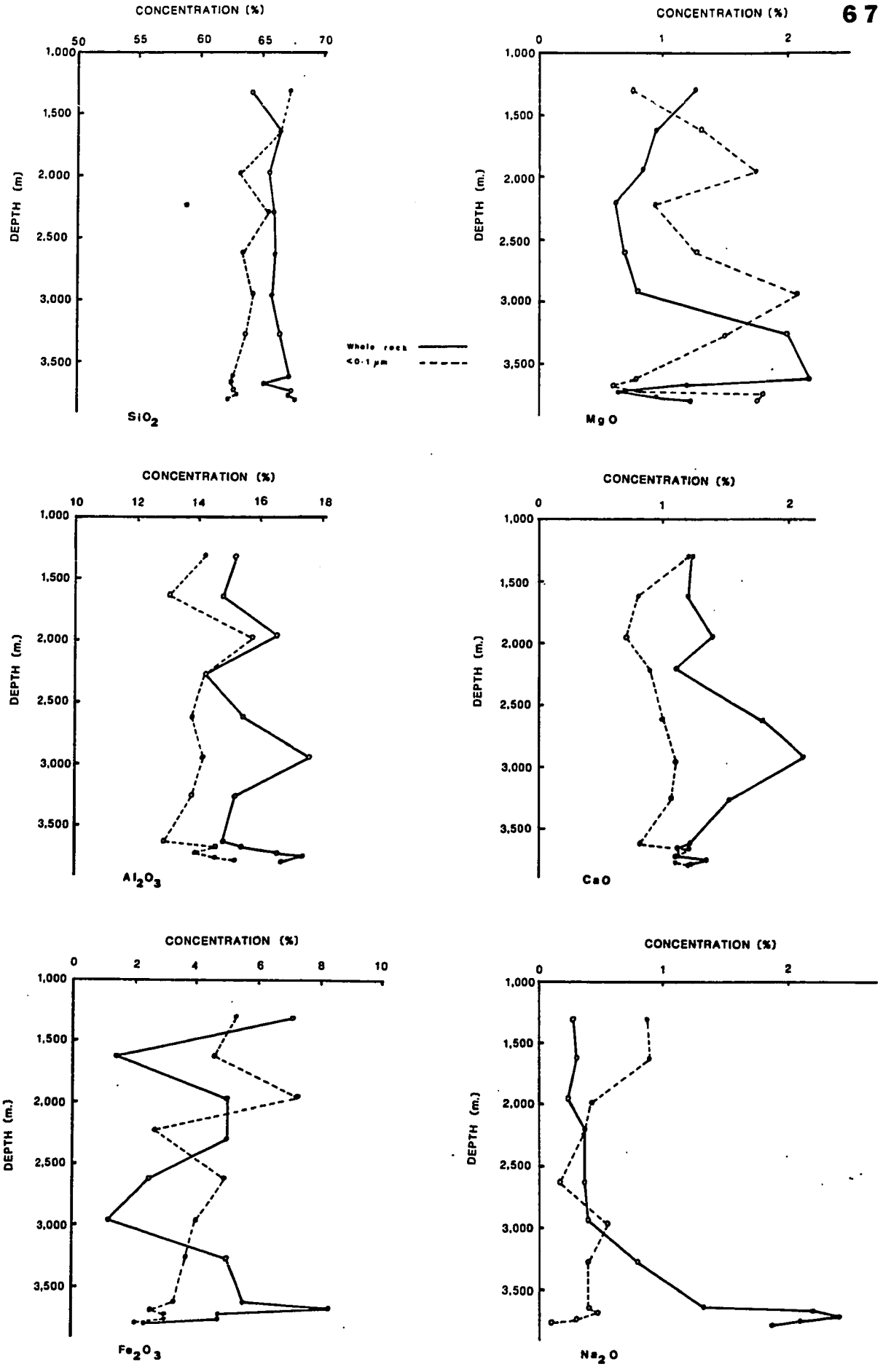

Fig. 24. Depth related variation of oxides of major elements in well Uruan-1.

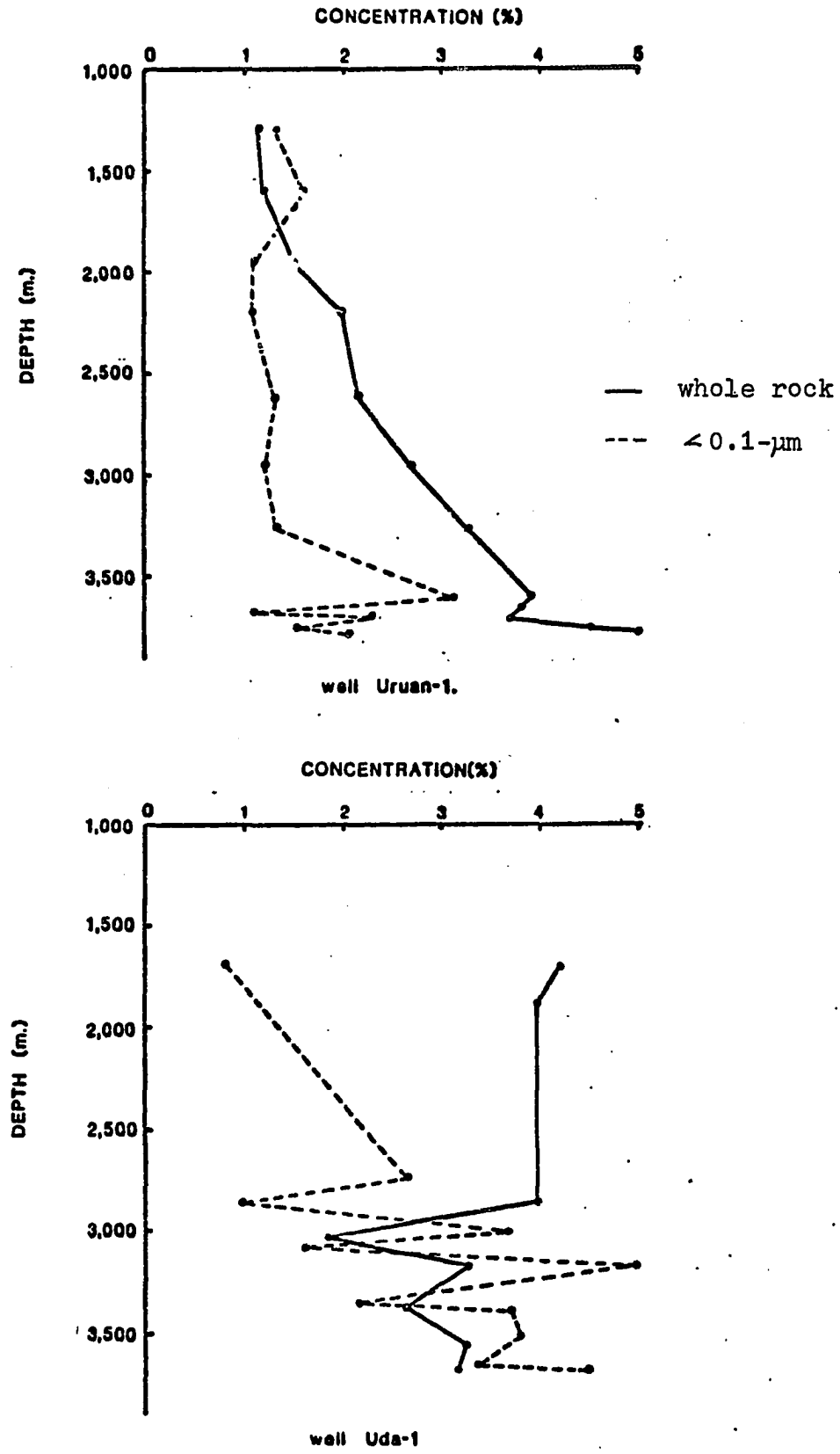

Fig. 25. Depth related variation of K_2O in wells Uruan-1 and Uda-1.

Depth related chemical variations in well Uda-1.

SiO_2 increases with depth in the whole rock sample, but decreases with depth in the $<$0.1-um size fraction (Fig. 26). Just as in well Uruan-1, Al_2O_3 appears to be mirrored in both the $<$ 0.1-um size fraction and in the whole rock sample. In both size categories, there is a net increase in concentration with depth. The variation of Fe_2O_3 with depth is unsystematic (Fig. 26) and does not suggest any trends. There however, appears to be no net increase in concentration in either the $<$ 0.1-um size fraction or in the whole rock sample. The MgO plot (Fig. 26) suggest a net increase in the whole rock sample and a net decrease in concentration in the $<$ 0.1-um size fraction with depth. The CaO plot (Fig. 26) shows no net increase in concentration in either of the two size categories. The concentration of Na_2O in the whole rock sample decreases with depth (Fig. 26). Although the Na_2O concentration in the $<$ 0.1-um size fraction does not show any net increase, there are significant increases between depths 3,000 to 3,500 m. The K_2O plot (Fig. 25) suggests a net increase in concentration in the $<$ 0.1-um size fraction, and a slight net decrease in the whole rock sample.

Discussion.

K_2O

The measured K_2O content of the whole rock samples increases with depth in well Uruan-1. Either potassium has migrated

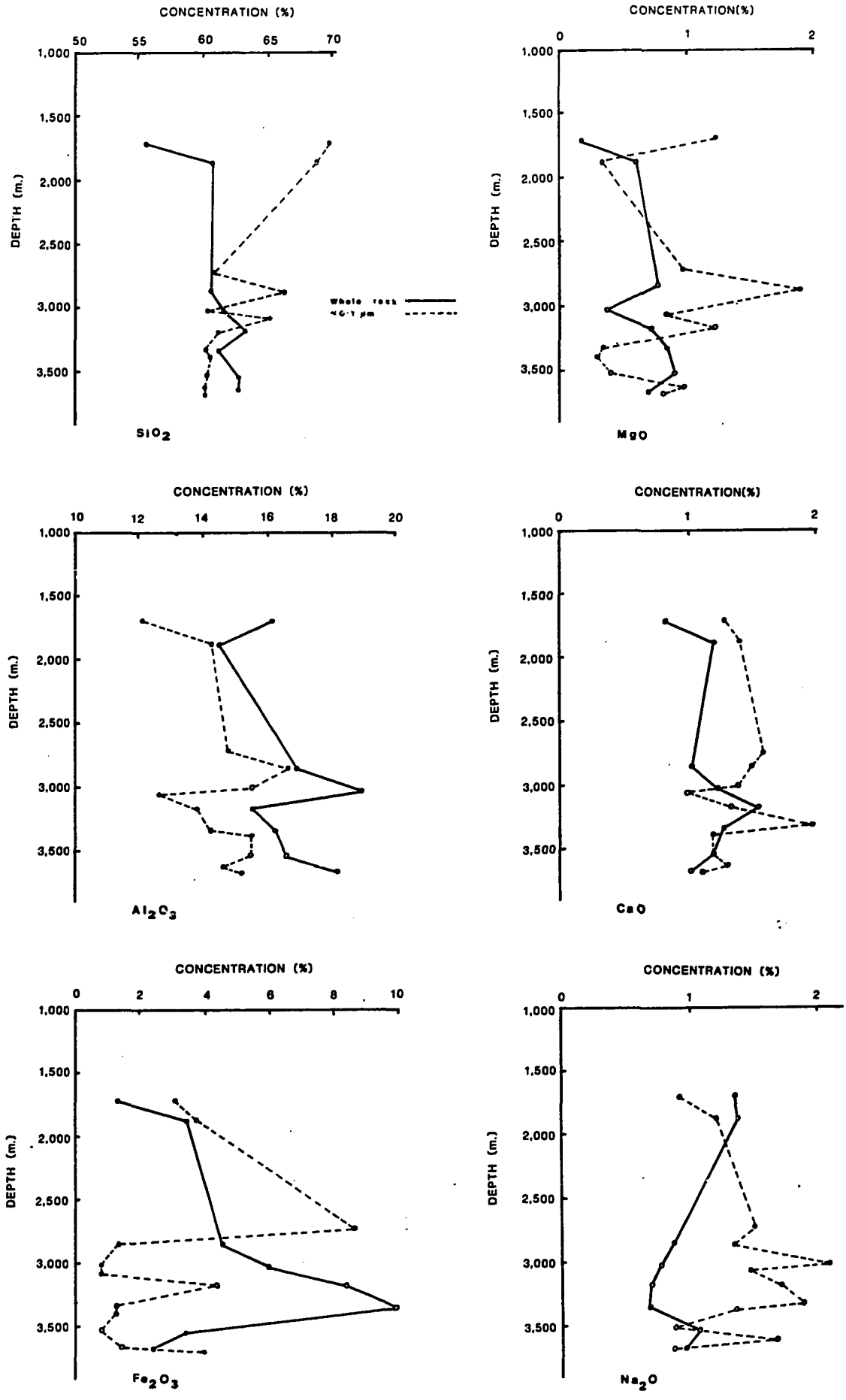

Fig. 26. Depth related variation of oxides of major elements in well Uda-1.

into the system from below during burial or the regular increase in K_2O indicates a systematic change in the originally deposited detrital minerals. The mineralogic data however shows an increasing abundance of illite, which corresponds to the increase in K_2O indicated by the chemical data, and would thus favor a sedimentological explanation for the K_2O variation. In comparison, the K_2O content of the whole rock samples in well Uda-1 shows a slight decrease with depth. Correspondingly, the illite content reduces to zero percent with depth (Table 5). The K_2O content in the $<$ 0.1-um size fraction in well Uda-1 shows a general increase with depth. Mixed-layer illite/smectite also increases with depth, and the percentage of illite component in the mixed-layer illite/smectite also increases with depth (Table 6). This increase seems to correlate with the increase in K_2O in the $<$ 0.1-um size fraction. This may be explained by a reallocation of potassium within the sediment column.

Al_2O_3

The Al_2O_3 content in both the whole rock and $<$ 0.1-um size fractions seems to be related in their variation with depth in well Uruan-1. Some slight overall increase is indicated with increasing depth of burial. This trend is also predicted by the Perry and Hower's (1970) hypothesis. In well Uda-1, Al_2O_3 increases with depth in both the whole rock and $<$ 0.1-um size fraction. This observstion seems to be reflected in the mineralogic data (Table 5) which shows a relative increase in

the abundance of mixed-layer illite/smectite. Hower et al. (1976, p. 733) suggest that 'the chemical changes in the illite/smectite generally fit the reaction

$$\text{smectite} + Al^{3+} + K^{+} = \text{illite} + Si^{4+}$$

which predicts a gain of one aluminium atom and a loss of one silicon atom for a gain of one atom of potassium'. The lack of a significnt increase in Al_2O_3 with depth in well Uruan-1 may well be a reflection of the absence of mixed-layer illite/smectite at depths below 3,707 m. (Table 3).

Na_2O

Na_2O in the whole rock increases with depth in well Uruan-1 but decreases with depth in well Uda-1. Its depth related variation in both wells revert in the < 0.1-um size fraction, increasing with depth in well Uda-1 and decreases with depth in well Uruan-1. Weaver and Beck (1971, p.48) suggest that 'after a certain depth of burial (temperature higher than 100 °C ?) little exchangeable and interstitial Na is lost from the system and with increasing temperature becomes incorporated in the solid phase ...' Perhaps this explains why deeper buried samples in well Uruan-1 are more sodic than shallower samples. Why the reverse situation is observed in well Uda-1 seems inexplicable. In a similar study on the U.S. Gulf Coast (Hower et al., 1976, Tables 6 and 7), the depth related distribution of Na_2O in both the < 0.1-um size fraction and whole rock appear similar to the observations made in well Uda-1. A comparison of the depth related distribution of Na_2O and K_2O for both size

categories in both wells Uruan-1 and Uda-1 seem to match. Hower and Mowatt (1966) have made plots which show potassium and sodium increases as the proportion of the 10 Å layers increase and as total layer charge increases. In well Uruan-1, the proportions of illite increase with depth while it decreses with depth in well Uda-1.

MgO

MgO content in the two size categories investigated, $<$ 0.1-um size fraction and whole rock, show a slight general increase with depth in both wells. In well Uruan-1, this increase seems justifiable with the relative increase in chlorite with depth (Table 3). In well Uda-1 however, the general increase in MgO with depth seem anomalous as chlorite occurs only in trace amounts. It seems probable that MgO is externally introduced into the system without any significant incorporation in the mixed-layer clay minerals.

Fe_2O_3

Total iron variation with depth in both wells Uruan-1 and Uda-1, and for both size categories fluctuates widely. Weaver and Beck (1971, p. 52) suggest that a variation in Fe_2O_3 content may be related to variations in depositional environment. For instance, they that a change from a neritic to a bathyal environment may account for an increase in total iron. Alternatively, they suggested (p. 53) that iron can be

introduced into a system from deeper in the section. Whatever may be the cause for the haphazard variation of Fe_2O_3 in both wells, it does not seem to be reflected in the clay mineralogy. The variation of Fe_2O_3 might possibly be reflected in carbonates or sulfides.

SiO_2

SiO_2 in the <0.1-um size fraction for both wells Uruan-1 and Uda-1 show a slight decrease with depth, while there is a slight increase with depth in the whole rock. The decrease with depth in the <0.1-um size fraction might be expected in the transformation of smectite to illite which results in a loss of Si^{4+} (Hower et al., 1976, p. 733). There however, seems to be no diagenetic explanation for the increase in SiO_2 with depth in the whole rock for both wells. Although the sand/shale ratio increases at depth in well Uruan-1, the reverse is the case in well Uda-1. Thus the relative abundance of quartz in both wells, is not reflected in the SiO_2 variation with depth for the Whole rock.

CaO

CaO variation with depth most probably is related to the calcite content for which no data was obtained because only the <0.1-um size fraction, essentially 100% clay minerals, was X-ray powder diffracted. Theoretically, we should expect to see a reduction in CaO as calcite dissolution is a result of burial

metamorphism (Hower et al., 1976, p. 733). However, the CaO plot for both wells between depths 1,500 m. to 3,500 m. (Fig.24 and 26), show no net increase nor net decrease for both size categories investigated.

REVIEW

of clay mineral burial diagenesis

The observation of mineralogical and chemical changes during clay mineral burial diagenesis has been documented by several investigators. Burst's (1959) observation that shales in the U.S. Tertiary Gulf Coast, that have undergone deep burial show a loss of absorbed water by smectite which, consequently, is converted to illite, was the first published study on clay mineral burial diagenesis. Subsequent to Burst's publication, several other investigators have reported the non-persistence of smectite in deeply buried shales, as well as other mineralogic changes. As the mineralogy changes with depth of burial, one can also expect the concentration of the major elements to also vary. This chapter is a review of the prevailing ideas on clay mineral burial diagenesis from 1959 - 1982. The published observations on the two major changes are reviewed (mineralogical and chemical) separately.

MINERALOGICAL CHANGES, Observation of

Burst, 1959, on the U.S. Gulf Coast.

> Smectite is less evident below 984 m., and is not found in an unmixed state below 2953 m. - 3281 m. No smectite occurs below 4593 m. Illite is interpreted to have formed from diagenetic conversion of smectite.

Mixed-layer illite/smectite is common between 984 m. - 4593 m. Chlorite is present at all stratigraphic levels, but appears to be more dominant at depth. Remarks. 'Well-developed expandable lattices that originate in bentonic volcanics seem to retain their swelling capabilities after greater burial depth, and for a greater span of geological time than do the so-called degraded three-layer mica lattices...' p.328. Also, the specific location of an expanded clay in any particular stratigraphic sequence is important in considering smectite - illite transition. 'In order for an expanded lattice to collapse, a path of egress must be provided for the interlayer water which will be discharged. Presumably, the absence of porosity in a section will retard the escape of this water and limit the progress of diagenesis'.... p.328.

Weaver, 1967, on North American clays.

With age and thus some function of depth or temperature, chlorite increases. Smectite decreases, illite increases and kaolinite decreases.

Burst, 1969, on the U.S.Gulf Coast.

He concluded that the systematic elimination of swelling clay is a valid reflection of diagenetic development in that it is unidirectional, with the alteration

being consistently from swelling to non-swelling lattices with depth. He also suggested that the shallowest depths at which fully swelling smectite is no longer in evidence can be contoured as a level of uniform diagenesis, which may have possibilities as a subsurface drilling marker. Although sediments represented by the 17 Å measurements could be from many different facies, which contain different amounts of smectite, the measurement indicates the swelling capability of the smectite component regardless of its concentration

Perry and Hower, 1970, on the U.S. Gulf Coast.

Discrete illite phases are ubiquitous and judged to be detrital. The discrete illite content of the whole rock decreases with depth. Mixed-layer illite/smectite is the dominant mineral, and undergoes a monotonic decrease in expandability from about 80% to a limit of 20% smectite layers, with increasing depth. Interstratification changes from random to ordered at about 35% expanded layers (Fig. 27). Discrete kaolinite phases are ubiquitous and judged to be detrital. The discrete kaolinite content of the whole rock shows no systematic variation. Chlorite occurrence although appreciable, is localized and stratigraphically seems to be restricted only to samples from shallow water

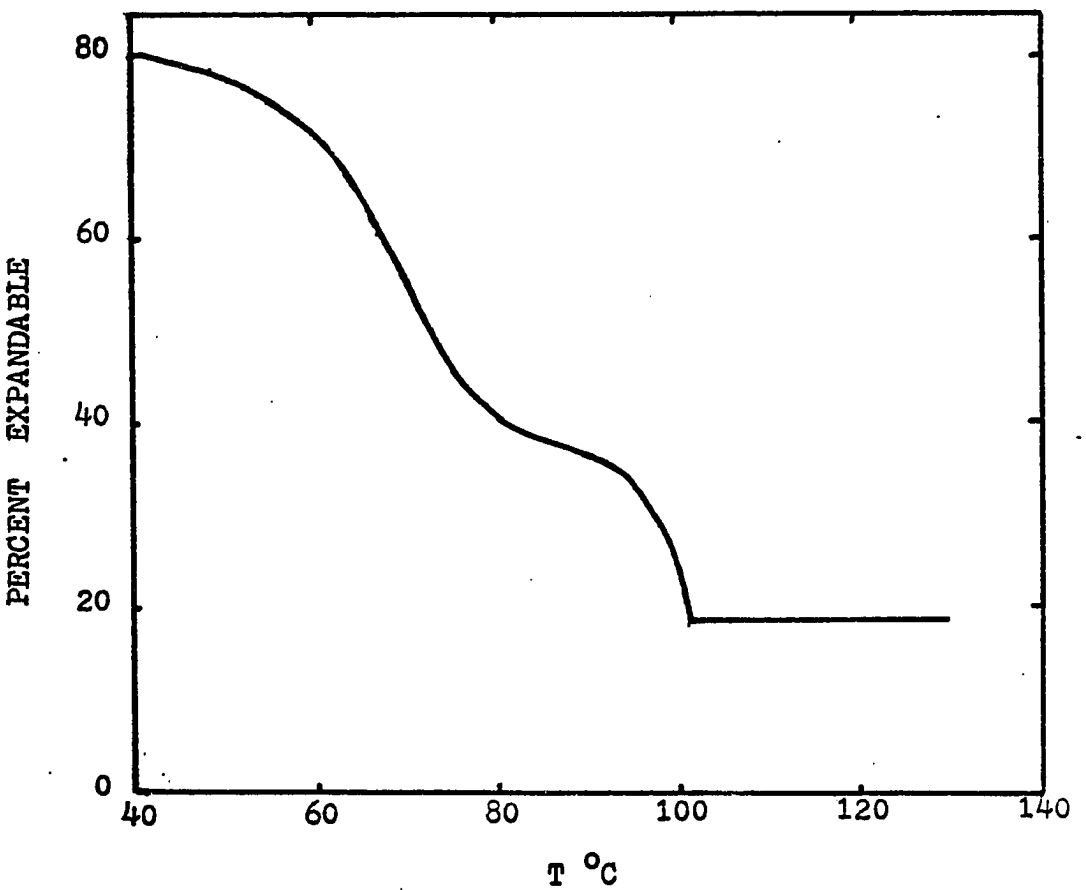

FIG. 27. Relationship between expandability and temperature for illite/smectite from a well in the Gulf Coast (After Perry and Hower, 1970, Fig. 15)

facies. The chlorite content was judged to be detrital.

Remarks. 'The rate of decrease in expandability is proportional to the geothermal gradient, rather than depth of burial. Where the geothermal gradient is highest, the sequence consists of a decrease in expandability from a randomly interstratified illite/smectite to about 35% smectite layers. Allevardite-like ordering of the interlayering, and a reduction in expandability to about 20% expandable layers over a short depth interval is observed, and this phase persists to maximum depth. Where the geothermal gradient is low, the deepest wells penetrate only the upper part of this sequence'... p.175.

van Moort, 1971, on Mesozoic shales of New Guinea and on Tertiary shales from Louisiana.

Changes in the Loisiana shales with increasing depth include a decrease in the rate of interstratified smectite/illite. Chlorite increases while kaolinite decreases.

Hiltabrand et al., 1973, on simulated clay diagenesis.

From simulated diagenetic reactions, they found that illite formed at 100 and 200 ^{o}C. Kaolinite and mixed-layer illite/smectite were destroyed or decreased in

relative amounts. They observed the persistence of smectite at 100 and 200 °C, but noticed it underwent some volumetric changes. They concluded, from a comparison of their experimental results with field samples, that the primary factor which determines the mineralogy of shales is diagenetic rather than depositional environmental.

Hower et. al., 1976, on the Tertiary U.S. Gulf Coast. They observed 'major mineralogical changes with depth over the interval 2,000 to 3,700 m., after which no significant changes are detectable. The most abundant mineral, illite/smectite, undergoes a conversion from less than 20% to about 80% illite layer over this depth interval, after which the proportion of illite layers remains constant. Chlorite appears to increase in amount'... p.725.

Brown et al., on Middle Pennsylvanian deltaic - interdeltaic clays from south-central Iowa and north-central Missouri. These authors investigated the variation of clay mineralogy vertically and laterally within various paralic clay and shale facies. They pointed out that a principal environmental variation within a deltaic system is 'the change from normal marine salinities in deltaic marine environments to brackish

- and fresh - water conditions in marshy delta plains, in upper interdistributary bays, and within flanking interdeltaic embayments'. They noted that changes from marine to nonmarine facies coincide with a decrease in illite, and an increase in kaolin, mixed-layer clays, and in the percentage of expandable layers in the mixed-layer clays. They therefore suggested that clay mineral distribution within the interdeltaic embayments may be best interpreted in terms of a depositional system in which each of the various cyclic facies is related to contemporaneous delta building and abandonement. Brown et al. (op. cit.) concluded that although the use of clay minerals alone in identifying various depositional environments should be unwarranted, subtle - to - moderate shifts in percentages within clay mineral suites however, when related to stratigraphy and depositional facies, can be used to infer paleoenvironments.

Foscolos and Powell, 1978, on Late Triassic - Late Cretaceous shales from north-west Canada.

'Upon burial of the sediments, the concentration of expandable 2:1 layer silicate, kaolinite and amorphous inorganic material decreases whereas illite increases in concentration in the clay fraction'... p.261. However, they found the absolute concentration of illite in the rock decreases with depth. They interpreted the

observed mineralogic trends within the clay fraction as due internal readjustment under the prevailing physicochemical conditions.

Srodon, 1978, on the Carboniferous of the Upper Silesian Coal Basin, Poland.

He concluded that there is a decrease of about 10% in the illite content in mixed-layer illite/smectite from pyroclastics, as compared with 'normal shales', both in thin beds and in the outer parts of thick beds. He also noted that the illite content decreases more, even down to pure smectite, towards the centres of thick beds. He contends that this kind of variation within a bed is a general phenomenon, which has been recognized in the Cretaceous of Montana and in the Ordovician of Sweden. Srodon says John Hower explains it by the deficiency of K^+ within bentonite beds. This therefore 'implies that, in nature, the process supplying K^+ is an independent variable, controlling, along with temperature, the rate of transformation of smectite toward illite....and obviously depend on the nature of the starting material'... p.258. Srodon emphasized the need of recognizing the triple control (temperature, K^+ supply, starting material) of clay burial diagenesis in more detail before the illite/smectite ratio of mixed-layer I/S can be used for the

estimation of maximum burial temperatures.

Sudo, 1978, on a review of studies on clay minerals in sediments.

Remarks. Sudo remarked that 'diagenetic patterns of sedimentary rocks are usually diverse owing to different efficiencies of the factors governing diagenesis itself'. He further stated that changes in properties of mixed-layer illite/smectite minerals with increasing depth of burial may serve to evaluate the degree of diagenesis. He reported the lowest limit of the disappearance of discrete smectite, which corresponds to the inception of the occurrence of mixed-layer mineralsto be the level of 1,000 - 3,000 m., and 80 - 100 ^{o}C. He also reported the lowest limit of the occurrence of mixed-layer minerals, which corresponds to the inception of non-mixed-layer illite, to be 4,000 - 5,000 m.

Almon and Davies, 1979, on Lower Cretaceous Muddy Sandstone, Powder River Basin of Montana and Wyoming.

They recognized clay diagenetic zones which they equated to specific equivalent sedimentological units within a depositional basin. They also reported that the diagenetic clay mineral assemblages are time controlled, matched by a change in the composition of detrital components.

Boles and Franks, 1979, on the Tertiary U.S. Gulf Coast.

They analysed mineralogic changes in sandstones and shales from depths of 975 - 4,650 m. (temperature range 55 - 210 °C) and observed no consistent trend in depositional environments, with increasing depth. They therefore interpreted the mineralogic changes as being due to diagenesis. The mineral distribution patterns they observed included a disappearance of discrete smectite at temperatures greater than 70 °C; gradation of mixed-layer illite/smectite over the entire temperature range; disappearance of kaolinite from 150 - 200 °C, accompanied by an increase in chlorite.

Davies et al., 1979, on Tertiary - Holocene volcaniclastics in southern Guatemala.

They recognised three successive episodes of diagenesis, which they suggested may not be dependent on depth of burial or temperature. They suggested that the major diagenetic control was the chemistry of the groundwater, and that boundaries between different diagenetic assemblages in the rocks they studied are therefore probably determined more by groundwater chemistry than by temperature or pressure.

Hoffman and Hower, 1979, on Mesozoic shales from Montana.

They suggested that the proportion of illite layers

in the illite/smectite mixed-layer is the most sensitive indicator of metamorphic grade in shales. The mixed-layer illite/smectite exhibit a sequence of interstratification, and proceeds to a short range ordering, and then to a long range ordering of the illite and smectite layers. Hoffman and Hower concluded that mineralogic changes in clay suites were a function of increasing metamorphic grade caused by progressive burial metamorphism (Fig. 28). At low temperatures, they suggested, clay mineral assemblages are also dependent on reaction time, but the mineral assemblages that form at higher temperatures depend on the detrital mineralogy.

Rhoton et al., 1979, on preferential clay mineral erosion from watersheds in the Maumee River Basin, northwestern Ohio. These authors showed that illite and expandable clays are selectively transported from soil surfaces, a phenomenon which they suggested can explain mineralogical differences between sediment and soil clays.

Weaver, 1979, on geothermal alteration of clay minerals and shales. He concluded that clay mineral changes which occur in shales during burial are related to temperature (Fig. 29). However, Weaver noted that most

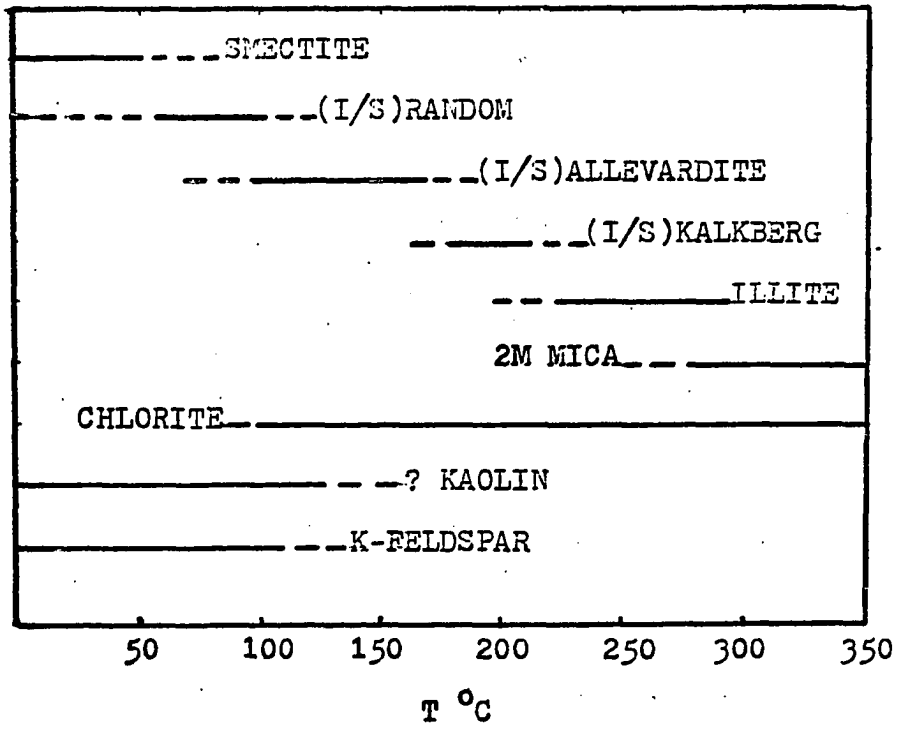

FIG. 28. Mineral diagenetic alteration sequence in shales by Hoffman and Hower (Fig. 2 adapted).

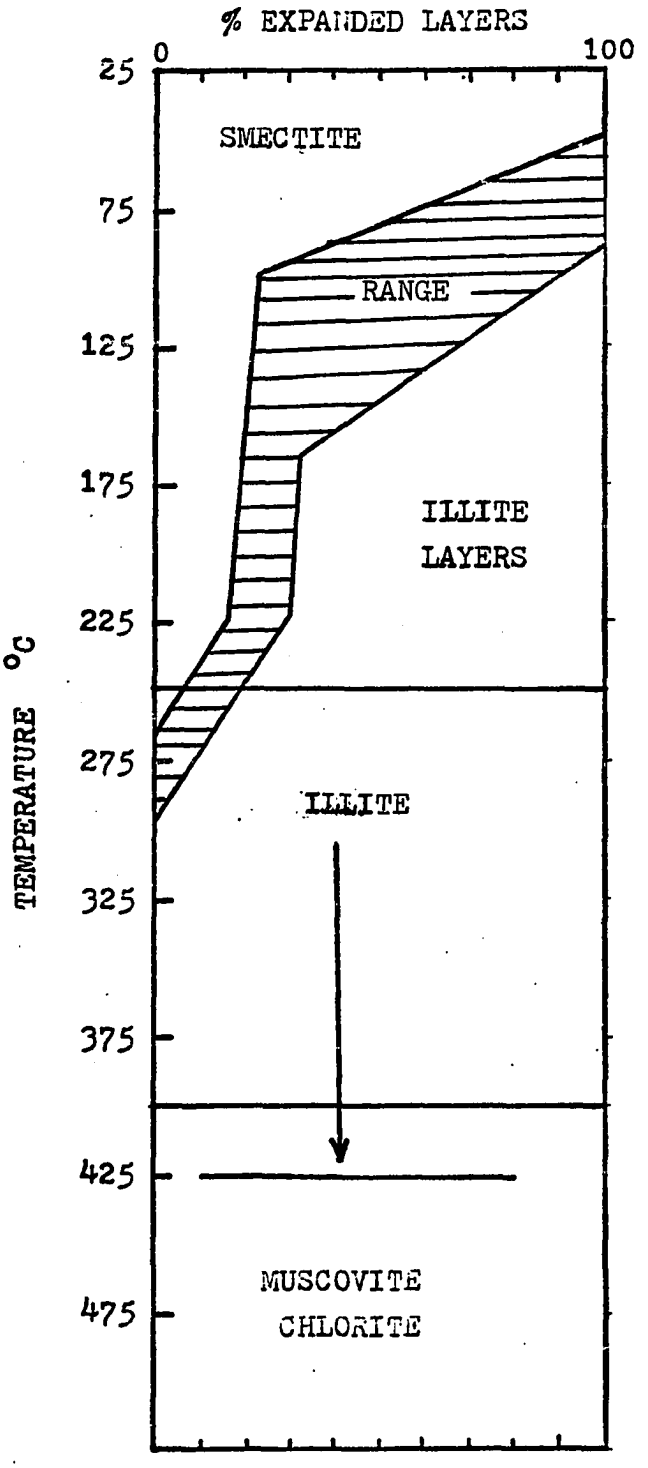

FIG. 29. Relation of diagenetic-metamorphic changes in clay minerals showing the temperature interval over which smectite is converted to illite. The area with the horizontal lines indicates the range in the proportion of illite layers that can form at a given temperature (After Weaver, 1979, Fig. 1).

mineral changes are related to wide temperature ranges, and explained this to be due to variable chemical and mineral compositions which do influence the transformation temperature.

Boles, 1981, on the Tertiary U.S. Gulf Coast.

He noted that smectite varies in composition from layer to layer, and therefore inferred the reactivity of each layer to differ. He thus suggested that 'the more aluminous smectite layers (i.e. those that chemically most closely resemble illite) react first to form illite, whereas the more iron and magnesium enriched smectite components react more sluggishly'.... p.158.

Huff and Turkmenoglu, 1981, on Middle Ordovician K-bentonites along the Cincinnati arch.

They reported the occurrence of interstratified illite/smectite (approx. 20% expandables) with rectorite-type ordering. They found the mixed-layer illite/smectite to be structurally similar to illite/smectite formed at temperatures exceeding 100 ^{o}C during burial diagenesis, but noted that stratigraphic evidence and conodont color alteration index of less than 1.5 suggest the clays have not been subjected to temperatures greater than 80 ^{o}C.

Nadeau and Reynolds, 1981, on Cretaceous Mancos Shale in the southern Rocky Mountain and Colorado Plateau.
They observed that the major clay mineral was mixed-layer illite/smectite, with 20 - 60% illite layers. They concluded that contact metamorphism of the shale by Tertiary igneous intrusions produced a regional distribution of ordered vs. random interstratification in the illite/smectite, and that this distribution can be likened to the concept of burial diagenesis in which smectite interlayers are progressively converted to illite, subsequently resulting in ordered interstratification.

Rettke, 1981, on Cretaceous shales and bentonites of the Dakota Group, northern Denver Basin.
He recognized burial diagenetic characteristics, as described by Perry and Hower (1970), but interpreted the occurrence of ordered illite/smectite from low-temperature wells, and much of the kaolinite and discrete illite from all wells, as detrital. He observed fluctuating expandabilities within individual cores, and a lack of samples containing both highly-expandable illite/smectite and high proportions of other clay minerals, and attributed this to 'episodic but frequent admixture of highly-expandable illite/smectite with detrital materials'... p.541.

Rettke does not attribute this to differential diagenesis and/or differential sedimentation rates, but he rather suggested that they are attributed to provenance differences which gave lower-expandable illite/smectite a 'head start' on diagenetic trends in sand-associated shales.

Rhoton and Smeck, 1981, on equilibration of clays in natural and simulated bottom-sediment environments.
They demonstrated that the mineralogical differences between soils in a watershed and sediments in a drainage system cannot be attributed to mineralogical transformation during residence in the drainage system.

Chang and MacKenzie, 1982, on mineral reaction pathways and mass transfer in sandstone-shale sequences, Brazil.
In studies on burial diagenesis of passive margin sandstone-shale sequences in offshore Brazil, they found the initial mineral composition of these sediments to be a major control on the diagenetic products. They also concluded that the burial pathway of Brazilian sandstone diagenesis is nearly isochemical.

Hurst and Irwin, 1982, on geological modelling of clay diagenesis in sandstones.

Using North Sea sandstones as a case study, they found mixed-layer illite/smectites which they did not attribute to burial temperatures since the maximum burial temperature reached by the samples was less than 60 ^{o}C (from organic maturation data), whereas the illite/smectite compositions suggested a maximum temperature of 95 - 100 ^{o}C by analogy with data of Hoffman and Hower (1979). They concluded that the composition of illitic clays in sandstones is controlled by the pore-water composition from which they (illitic clays) precipated and is probably independent of temperature. Hurst and Irwin (op. cit.) also suggested that because of the relatively high permeability of sandstones, phases forming in sandstones are controlled by the solution composition while in shales, the solution composition is controlled largely by the chemistry of solids.

Lambert-Aikhionbare and Shaw, 1982, on the significance of clays in the petroleum geology of the Niger delta.

They reported the occurrence of largely detrital clays in the Akata and Agbada shales, with only minimal alteration attributable to the effects of burial diagenesis. They also observed the preservation of smectite in

the Akata Formation at depths of about 3,937 m. and burial temperatures of about 120 °C. In other samples of the Akata shales occurring at shallower depths (burial temperatures approx. 105 °C) they observed the presence of mixed-layer illite/smectite, but discrete smectite was absent.

CHEMICAL CHANGES, Observations of

Clay minerals owe their origin almost entirely to weathering or diagenesis, and are therefore formed during the sedimentary cycle. They are layered silicates which have incorporated various cations into their structure. These cations are the principal factor that can be used to distinguish one clay mineral from another. One may therefore intuitively think that clay mineral diagenesis must involve a loss or gain of cations. In reality, this happens to be the case. For instance, due to the hydration of some cations, variable quantities of water can accumulate in the interlayer positions of smectite. As a result, their structure can expand to variable thicknesses depending on which exchangeable cations are present. This property of expandability is the most important creiterion for distinguihing smectite, when treated with ion-solvating liquids like ethylene glycol, from other clays. The property of expandability can be quantitatively measured by X-ray diffraction (Reynolds and Hower, 1970; Rey-

nolds, 1980; Srodon, 1980, 1981). Also, variations in the quantitative amounts of cations present in the 'daughter' products, as compared to those present in the 'parent' material can be systematically documented through a vertical lithologic section by X-ray spectrophotometric analysis (Hower et al., 1976), and by atomic absorption spectrophotometry (this study). Results from such studies provide the observed chemical evidence for clay mineral diagenesis. Similar results have been simulated in laboratory experiments (e.g. Hiltabrand et al., 1973; Eberl, 1978, 1980; Eberl and Hower, 1976, 1977, and by many others), and these results generally corroborate the observed natural chemical changes that occur during burial diagenesis.

We now feel fairly certain, from a chemical standpoint, that clay mineral burial diagenesis is a later phenomenon. For instance, Maynard (1975, p.1028), who investigated the possibility of detrital kaolinite phases reacting appreciably with sea water, indicated a two stage reaction consisting of an initial rapid sorption of H_4SiO_4 and a second, slower uptake that follows parabolic kinetics. His calculated rate constant for the second reaction was 4×10^{-13} moles/cm^2. sec$^{1/2}$, and concluded that this rate was too slow for the oceans to equilibrate with clay detrital phases. Eberl and Hower (1976, p.1326) have also shown from kinetic studies that even if the alteration reaction of clays is favored thermodynamically, we should not expect to see any alteration because the reaction rates are too

slow. They simulated an activation energy of 19.6 $\pm$ 3.5 kcal/ mole for the conversion of synthetic beidellite to mixed-layer illite/smectite. Activation energies of this magnitude would suggest that the rate - limiting step for silica removal would be through a hydrated expanded interlayer space. Any H_4SiO_4 in the system is probably absorbed in the formation of illite (Maynard, 1975, p.1028, Eq. 2).

There is a plethora of papers dealing, in one form or the other, with the chemical rearrangement of major elements during clay mineral diagenesis, either in a natural system or in simulated laboratory experiments. It is impossible to exhaustively review all the available literature on this subject in this dissertation, without distracting a bit too far from the objective of this study. I therefore present below, a review of a sample of the available literature that I think are pertinent to a better interpretation of my investigation on the eastern Niger delta.

Powers, 1957, on the adjustment of land derived clays to the marine environment.

This author noted on p. 369, that the nature of of mixed-layer clays (in depth related diagenesis) depend largely on the source material. He suggested an equivalence level of a few hundred meters at which there appears to be no preferential absorption of

Mg^{2+} over K^{+} or vice versa. Below the equivalence level, Powers thinks one of two possibilities may be likely:

(i) 'Mg^{2+} (and iron) may move into the octahedral layer of the lattice and replace Al^{3+} which moves into the tetrahedral layer. The former sites of Mg^{2+} (and iron) would be replaced by K^{+}. Thus little or no Mg^{2+} would be lost from clays as their depth of burial increases. On the other hand, Powers suggested that the amount of K^{+} should show a slight overall increase and Al^{3+} should show a slight increase relative to Si^{4+}.

(ii)'The other possibility of change with depth involves a slow but persistent replacement of Mg^{2+} by K^{+}. This reaction would occur at a shallower depth than in the above possibility, and would be related to a statistical loss of Mg^{2+} from the system. Once K^{+} is adsorbed onto the clay surface, it would be more difficult to replace than Mg^{2+}, because of its lower ionic potential'

Hower and Mowatt, 1966, on the mineralogy of illites and mixed-layer illite/smectites. They suggested that the excess H_2O in illites is present as neutral H_2O trapped in non-expandable layers. These water mole-

cules, they inferred, may be resent either in the interlayer structural positions not occupied by K^+ and/or as lenses of water. They also mentioned the possibility that 'high charge smectites formed originally in a potassium deficient environment (such as in acid hydrothermal alteration associated with ore deposition) would convert to highly expandable mixed-layer illite/smectites when introduced into a K-rich environment (the ocean for example)' Hower and Mowatt believed that smectite layers do not collapse to 10 Å unless an optimum charge is available to fix sufficient potassium. Therefore, they suggested, there would appear to be no evidence for the collapse of smectite layers with increasing depth of burial unless burial depth involves, among other factors (i.e. geothermal gradient), compositional changes as well.

Burst, 1969, on the Tertiary U.S. Gulf Coast.

He postulated that clay compaction, as a result of interlayer water discharge, is an essentially temperature-dependent phase change in which a silicate lattice hydrate (smectite), begins to dehydrate at a critical temperature in the 93 - 110 ^{o}C range, regardless of burial depth. Within the geologic framework of normal sediments, he therefore proposed

temperature to be a more effective dehydration agent than either pressure (depth of burial) or age. He described the phase transition by the equation:

$$S(H_2O)x = I + XH_2O + Hr$$

where S = a hydrated clay lattice

$(H_2O)x$ = the water held within the hydrated lattice

I = a dehydrated lattice

XH_2O = capillary (pore) water

Hr = the heat of reaction (H is negative, consequently the reaction is endothermic).

Ross and Kodama, 1970, on the differential release of potassium from interstratified mica clay minerals as related to probable differences in their mica layer components. From experimental studies, they noted the rate of potassium release to be lower when the calculated Si/Al^{IV} ratio of the mica component layers resembled muscovite, and higher when this ratio was intermediate between muscovite and pyrophyllite. This, they suggested, supported the hypothesis that the composition and structure of the mica component layers may vary in different interstratified minerals of similar total composition.

Perry and Hower, 1970, on the Tertiary U.S. Gulf Coast.

Their whole rock chemical analyses show no systematic variation with depth except for a decrease in calcium and magnesium which they attribute to the solution of carbonate. They found potassium to increase progressively with depth in the clay-size fraction and suggested this to indicate a redistribution of potassium within the rock. They also noted that 'detrital illite seems to break down with increasing depth, thereby supplying potassium for interlayer fixation in illite/smectite as the proportion of illite layers increases'... p.80.

Perry and Hower, 1972, on the Tertiary U.S. Gulf Coast.

In this paper, the authors observed random fluctuations in K_2O with depth which they thought was caused by varying the relative amounts of illite - smectite and kaolinite. They nevertheless insisted that there appeared to be an obvious trend with depth. They noted that an increase in K_2O with depth continued until the maximum proportion of illite layers had formed (at about 3,445 m.), below which the K_2O content varied with the absolute amount of illite - smectite in the rock. They interpreted the potassium gain in the clay-size fraction to mean that the illite - smectite undergoes a change in interlayer

charge, caused by ionic substitution within the octahedral and tetrahedral positions of the layer structure, thus giving rise to potassium fixation and dehydration of the smectitelayers. They concluded that because the whole-rock potassium content does not change significantly with increasing depth, the potassium fixed by the mixed-layer illite/smectite must be gained by the reaction with other potassium-bearing minerals in the sediment. They suggested that the main mineral that supplies this potassium is detrital illite, which decreased in abundance with increasing potassium fixation by the diagenetic phase. They also suggested that the potassium released by the breakdown of detrital illite pass into solution only to be extracted by the formation of illite layers in the mixed-layer illite/smectite. Because of this, they added, it is not necessary to appeal either to an extraordinarily high concentration of potassium in the pore water, or flow - through of water derived from an outside source. Perry and Hower (1972, p.2020) concluded that smectite dehydration requires compositional changes in the illite/smectite, to allow for interlayer potassium fixation and layer collapse. They added that besides temperature and pressure, other factors such as pore water composition, can inhibit or even negate the reaction, although reac-

tion rates appear to vary mainly with geothermal gradient.

Hiltabrand et al., 1973, on simulated diagenetic reactions. They found Na^{+}, K^{+} and Ca^{2+} concentrations increased as diagenesis progressed, but Mg^{2+} concentration decreased. Soluble SiO_2 concentration was stabilized near the saturation value for quartz.

Weaver and Pollard, 1973, on the chemistry of clay minerals. On page 113, these authors write that 'mixed-layer clays (illite/smectite) form by the alteration of pre-existing micas and illites, by hydrothermal action, by the alteration of volcanic glass, and by diagenetic alteration of smectite. During continental weathering, K is leached from micas and illites, and mixed-layer clays are formed. When these clays are carried to the sea, they may adsorb K and revert partially or entirely to illite. If they remain in a continental environment where K may not be available, the expanded layers can persist until K becomes available. Expanded layers formed inthis manner have a higher layer charge than those formed in a marine environment'. On page 114, they added that 'many weathered micas and illites are completely leached of K and have the swelling characteristics of a

smectite. This material is usually leached to such an extent that the layer charge of some of the layers is sufficiently lowered so that they will no longer contract to 10 Å. When these clays are exposed to sea water or K from any source, only a portion of their layers will contract and a mixed-layer clay is formed'.

Eberl and Hower, 1976, on the kinetics of illite formation.

In simulated diagenetic reactions, in which they incorporated no external source of Al, they found Al became incorporated in tetrahedral layers in the mixed-layer illite/smectite structure. This, they assumed, was derived from the breakdown of other smectite layers, and produced kaolinite and illite at the expense of smectite. This appears to contradict the observation by Hower et al. (1976) that kaolinite does not increase with depth as does illite in Gulf Coast shales. However, their simulated reactions were conducted in the absence of Na^{+}, and all were conducted in the absence of Ca^{2+} and Mg^{2+}, ions which Roberson and Lahann (1981) considered should be expected to impede the conversion.

Hower et al., 1976, on the Tertiary U.S. Gulf Coast.

They observed that 'variations in the bulk chemical composition of shale with depth show only a minor

changes, except for a marked decrease in CaO. In contrast, the < 0.1-um size fraction shows a large increase in K_2O and Al_2O_3 and a decrease in SiO_2' ... p.725. They postulated that potassium and aluminium is derived from the decomposition of potassium feldspar (and possibly mica), and that the excess silicon probably forms quartz. They interpreted all the major mineralogical and chemical changes as due to the response of the shale to burial diagenesis, and concluded that the shale acted as a closed system for all components except H_2O, CaO, Na_2O and Co_2.

Eberl and Hower, 1977, on the hydrothermal transformation of sodium and potassium smectite into mixed-layer clay. They concluded that 'when smectite is transformed by heat and pressure into a mixed-layer clay, the course of the reaction is influenced by the chemistry of the interlayers'. They believed that 'interlayer cations influence both the rate of substitution in the 2:1 layers, and the amount of substitution that must be accomplished to form a mica-like layer'... p.227. They noted that interlayer potassium gives rise to an illite/smectite series, which also forms in nature during burial diagenesis. It is worth noting that in their simulated reactions

the starting smectites initially had the same alluminosilicate composition, a situation which would hardly exist in a deltaic environment with a history of delta switching.

Boles and Franks, 1979, on the Tertiary U.S. Gulf Coast. They gave a possible explanation for kaolinite not forming diagenetically in natural systems, by suggesting that illite formation proceeds in a 'constant Al' system, and that excess octahedral ions and silica are released to solution and ultimately precipitated as authigenic cements.

Eberl, 1980, on alkali cation selectivity and fixation by clay minerals. From simulated diagenetic reactions, Eberl suggested why potassium is almost always preferentially fixed during the transformation of smectite to illite. He showed that with increasing layer charge, potassium is the first cation to dehydrate. He linked cation dehydration to cation selectivity when he suggested (p. 170) that 'cation selectivity and cation fixation in clay both result from an interplay of two competing forces:

(i) the force of attraction of a cation for its hydration shell and,

(ii) the force of attraction of the cation for clay

surfaces.

Selectivity arises because these forces differ for different cations. Fixation occurs when the second force exceeds the first. Fixation must be considered in a description of selectivity because selectivity increases dramatically for cations that dehydrate'.

April, 1981, on trioctahedral smectite and interstratified chlorite/smectite (corrensite) in Jurassic strata of the Connecticut valley. April found an interesting situation in the Connecticut valley in which mixed-layer chlorite/smectite (corrensite) stratigraphically overly discrete smectite. This appears to be an analogous situation I have found in well Uruan-1, in the eastern Niger delta, in which discrete smectite is stratigraphically overlain by mixed-layer illite smectite. April suggested two possible interpretations for the restricted occurrence of mixed-layer chlorite/smectite:

(i) 'the requisite aqueous chemistry of the depositional environment was not achieved at the time of deposition of the lower strata (in which chlorite/smectite is absent), due to changes in paleoclimate.

(ii) involves the movement of Mg-rich pore water from the lower strata into the overlying strata

during burial. This influx of magnesium would favor the aggradation of smectite to mixed-layer chlorite/smectite, whereas smectite would persist in the lower strata having lower magnesium concentrations.

Huff and Turkmenoglu, 1981, on the chemical characteristics and origin of Ordovician K-bentonites along the Cincinnati arch. They found that whole rock samples of Middle Ordovician K-bentonites contain approximately 8% K_2O and approximately 4% MgO, whereas the 0.1-um size fraction contains 6 - 7% K_2O and 5% MgO (p. 113). They compared these percentages with a hypothetical parent ash, and concluded that their values represent a net gain of K and Mg and a net loss of Si, Fe, Ca and Na during post-depositional alteration. They suggested that the 'relatively high contents of K and Mg probably reflect both seawater and parent material composition at the time of formation'.

Milliken et al., 1981, on the history of burial diagenesis determined from isotopic geochemistry, Frio Formation, Brazoria County, Texas. These authors recognized three progressive diagenetic zones in the Tertiary sediments in Brazoria County (Fig. 30). Zone 1 has passive diagenesis as it mainly involves

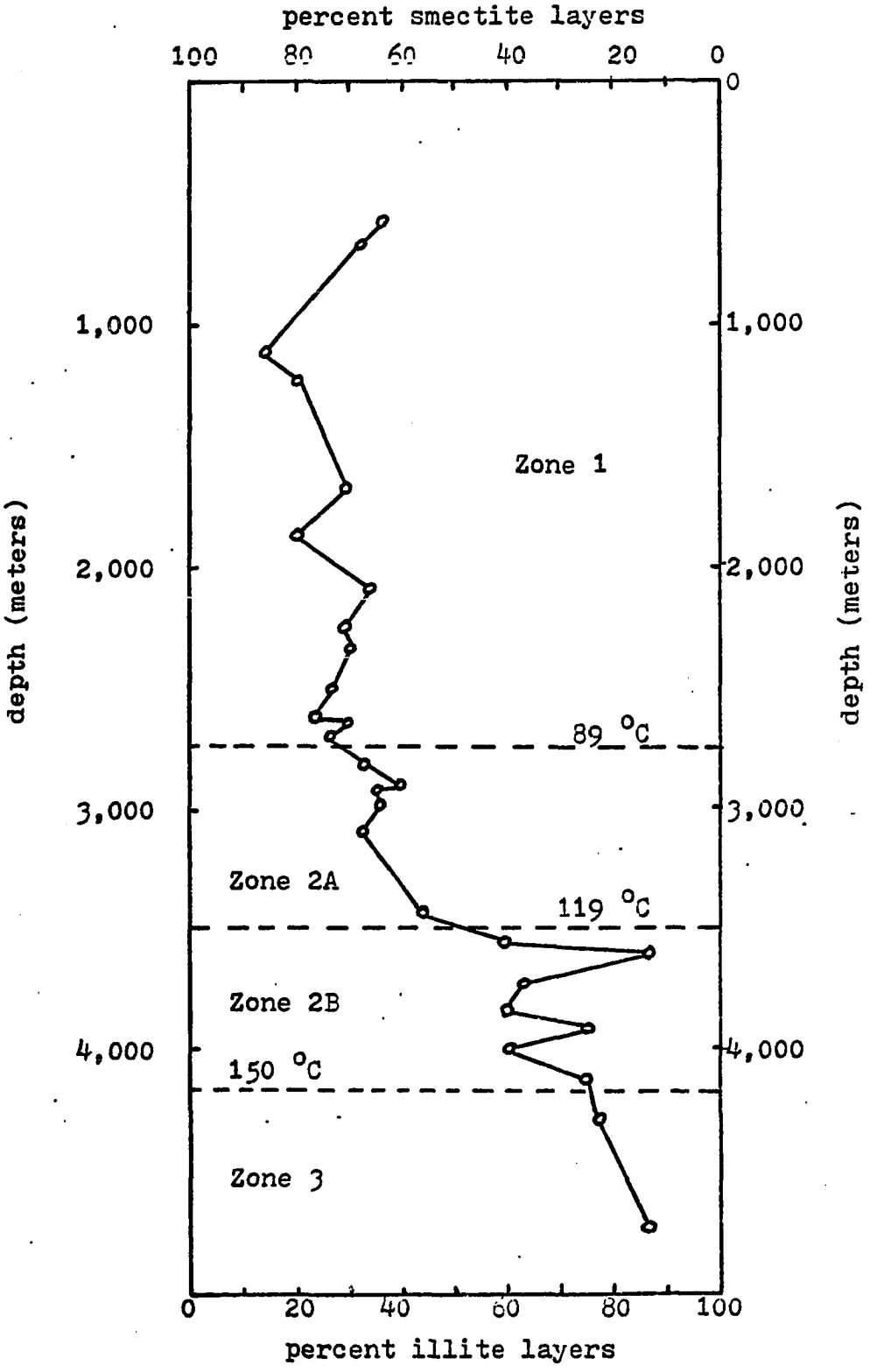

FIG. 30. Progression of smectite-illite transition with depth in Brazoria County, Texas (After Milliken et al., 1981, Fig. 12).

precipitation of authigenic minerals within intergranular pores. Diagenesis in zone 2 is active because reaction of aqueous solutions with metastable detrital components. The top of this zone is placed at the depth at which illite/smectite transition begins. Within zone 3, the illite/smectite transition is nearly complete, and with increasing temperature, this zone eventually grades into metamorphism. Milliken et al. (1981) also noted that 'the depth distribution of the various reactions gives an insight into material - transport problems in diagenesis.' Table 11 is a summary of some of the pathways of material transfer that they deduced.

Nadeau and Reynolds, 1981, on the Mancos Shale (Cretaceous) in the southern Rocky Mountains and the Colorado Plateau. These authors noted that chemical variations within shales affected the clay conversion reactions in the Mancos Shale during the early stages of transformation. In extreme cases, they noted, shales from a single outcrop may contain clays that range from pure smectite to ordered illite/smectite containing more than 50% illite layers. They therefore caution that the use of mixed-layer illite/smectite compositions to infer thermal regimes, may

Chemical Components	Mjor Sources	Major Sinks
Ca^{++}	Albitization, smectite/illite transition (zone 2); carbonates in shales (zones 1,2,3)	Authigenic carbonates
Mg^{++}	Smectite/illite transition	Authigenic carbonates
K^{+}	Albitization and leaching of K-feldspar	Smectite/illite transition
H^{+}	Hydrocarbon generation; mineral precipitation	Leaching
SiO_2	Smectite/illite transition; feldspar leaching	Albitization (zone 2); quartz cementation (zone 1)
Al_2O_3	Albitization?, feldspar leaching?	Kaolinite
$CO_3^{=}$	Hydrocarbon maturation (zone 2); carbonates in shales (zones 1,2,3)	Authigenic carbonates

TABLE 11. Pathways of material transfer for Frio Sandstones, Brazoria County, Texas (After Milliken et al., 1981, Table 5).

be misleading unless allowance is made for local chemical controls (p. 249).

Roberson and Lahann, 1981, on smectite to illite conversion rates. In simulated diagenetic reactions, they formed mixed-layer illite/smectite by subjecting smectite to hydrothermal temperature at 270 ^{o}C and 350 ^{o}C. They found that the reaction rate and the rate of ordering of the mixed-layer I/S for the reaction:

smectite + K^{+} = mixed-layer I/S + SiO_2

was inhibited by the addition of Na^{+}, Ca^{2+} and Mg^{2+}. They also found that the reaction required an activation energy of 30 kcal/mole, and appeared to proceed by solid state transformation, as suggested by:

(i) 'rapid dissolution of large amounts of silica, probably creating an Al-enriched residue'

(ii) 'similarity of particle size and morphology of the mixed-layer products to those of the original smectite, implying no extensive dissolution of Al^{3+} '... p.129.

Roberson and Lahann (op. cit., p. 134) also suggested that in the natural system, additional chemical changes, apart from the behaviour of Al, may take place within the octahedral layer, depending on the chemistry of the starting material and the chemistry

of the reacting solution. They also suggested the possibility that in nature illite might form by either solid-state reorganization or by dissolution-reprecipitation, and also the possibility that Al^{3+} as well as K^{+}, could be supplied by the breakdown of detrital K-feldspar (c.f. Hower et al., 1976).

Chang and Mackenzie, 1982, on mineral reaction pathways and mass transfer in sandstone-shale sequences, Brazil. Their material balance calculations indicated that sandstones lost less than 2% K^{+}, which they considered probably entered interstratified shales. At the same time, the sandstones gained less than 3% H_2O, H^{+} and CO_2 during burial diagenesis. They therefore concluded that the burial pathway of Brazilian offshore sandstone diagenesis to be nearly isochemical.

DISCUSSION AND CONCLUSION

Smectite - illite transformation via a mixed-layer I/S phase has been reported to be a consequence of burial diagenesis by several investigators. Since the first published study which recognised this transformation in subsurface samples from the Tertiary Gulf Coast (Burst, 1959), a hypothesis for clay mineral burial diagenesis (suggested by Perry and Hower, 1970) now seems widely accepted in the literature. The hypothesis suggests the following chemical mechanism for the transformation:

$$\text{smectite} + Al^{3+} + K^{+} = \text{illite} + Si^{4+}$$

A typical transformation commences with smectite converting to randomly interstratified I/S, with about 80% expandables (i.e. percent smectite layers in the interstratification). There is a progressive decrease in percent expandables with increasing depth of burial, culminating in an ordered interstratified I/S phase at depths between 3,000 and 4,000 m. The interstratification is ordered at approximately 40% expandables, a value corresponding to an inferred geothermal temperature of 80 - 100 ^{o}C (Perry and Hower, 1972, p. 175, Fig. 15). Similar mineralogic changes have been observed in Mesozoic shales from Papua, New Guinea and in Tertiary shales from Louisiana (van Moort, 1971), in Late Triassic to Late Cretaceous shales from the Canadian Northwest Territories (Foscolos and Powell, 1978),

in Mesozoic shales from Montana (Hoffman and Hower, 1979), and in Tertiary sediments from the Rhinegraben, West Germany (Doebl et al., 1972; Heling, 1974, 1978). This same tranformation has also been reported in studies in which there is no significant depth of burial (Boles and Coombs, 1975; Schultz, 1978; Nadeau and Reynolds, 1981), or where no evidence exists of the sediments ever having attained the geothermal temperatures postulated by the hypothesis (Huff and Turkmenoglu, 1981; Heling 1974, 1978).

Rettke (1981) recognised a transformation of smectite to illite in Cretaceous sediments of the Denver Basin, although he observed fluctuating expandabilities at certain stratigraphic levels. He ascribed these fluctuations in expandability to 'episodic but frequent admixture of highly-expandable bentonic illite-smectite with detrital clays' ... (p. 541). April (1981) found a unique situation in the Connecticut valley in which discrete smectite was stratigraphically lower than mixed-layer smectite/chlorite (corrensite), a situation which would seem enigmatic if we extend the clay mineral burial diagenesis hypothesis to include other mixed-layer clay minerals besides illite/smectite. Lambert-Aikhionbare and Shaw (1982) reported the preservation of smectite in the Akata Formation in the Niger delta, at depths of about 3,937 m. and burial temperatures of 120 ^{o}C. This seems to contradict the prediction of Perry and Hower (1972, p. 2015) that smectite dehydration re-

action as described by their hypothesis 'should occur in all sedimentary basins in which the sediments have been subjected to the increased temperatures necessary for the diagenetic reactions'.

In this study, discrete smectite occurs in well Uruan-1 at depths in excess of 3,675 m. Calculated geothermal temperatures for these depths range between 100 - 120 ^{o}C. (Fig. 15). It is therefore puzzling that smectite could survive at these temperatures. What is even more enigmatic about this observation is the occurrence of ordered interstratified mixed-layer I/S sandwiched stratigraphically between a higher occurrence of discrete smectite and the lower occurrence first observed at 3,675 m. (Fig. 23). Also, at the approximate interval at which the mixed-layer I/S occurs, there is no occurrence of discrete smectite. These observations support the clay mineral burial diagenesis hypothesis of Perry and Hower (1970) between depths 1,300 m. to 3,675 m. in well Uruan-1. The reason for the failure of the hypothesis below 3,675 m. does not seem to be a lack of potassium, a necessary element in the diagenetic process. The chemical data of both the $<$ 0.1-um size fraction and whole rock (Fig. 25) for well Uruan-1 indicates a net gain in K_2O, with increasing depths down to the total depth of the well at 3,773 m. The average K_2O concentration also compares favorably to published values for shale cuttings from a well (Case Western Reserve University Gulf Coast 6) in Oligocene-Miocene sediment of the Gulf Coast of the United States

(Hower et al., 1976, Tables 6 and 7). The oxides of aluminium and silica, Al_2O_3 and SiO_2, increase and decrease respectively in the < 0.1-um size fraction in well Uruan-1 (Fig. 24) with increasing depth. This trend, together with the increase in K_2O with depth, supports the clay mineral diagenetic reaction postulated by Hower et al. (1976, p. 733). However, the results of this study indicate that neither temperature nor the availability of potassium is the principal factor controlling the alteration of smectite into illite during diagenesis of the Tertiary sediments below a depth of 3,675 m. in well Uruan-1. What other factors may then control smectite alteration into illite ? In the Rhinegraben of southwest Germany, Heling (1978, p. 219) noted that the inherited layer charge of smectite possibly has some bearing on illite diagenesis. He added that higher charged smectite with more tetrahedral Si substituted by Al would more readily alter to illite than lower charged smectites. In this respect, Heling concluded that the detrital smectite of the Graue Schichtenfolge of Upper Oligocene age probably differed from those of the Hydrobienschicten of Miocene age, and suggested that the former were transported from a southern source while the latter came from a northern source. Another possible explanation for the existence of smectite at 'prohibitive' depths is offered by Foscolos et al., (1982, p. 149) who suggested that the formation of calcite prevents clay authigenesis, and may be responsible for the absence of mixed-layer

clays in deeper buried sandstone unit in the Viking sandstone in Central Alberta.

In the second well studied, well Uda-1 (Fig. 23), random and ordered interstratified mixed-layer illite/smectite occurs from 1,719 m. to toal depth at 3,688 m. The percentage expandables in the mixed-layer illite/smectite decreases with depth from 90 - 80% in the randomly interstratified phase. There is a drastic drop in percentage expandables from 80% at a depth of 2,730 m. to 10% in the ordered interstratified phase observed at 3,031 m. (Table 6). Such a sharp drop in the amount of smectite layers in the mixed-layer I/S, over a relatively short stratigraphic interval, may indicate a manifestation of differences in the original clay mineral suite before burial. In other words, it may be an indication of some form of stratigraphic or facies control. Smectite occurs at 1,300 m. and between 3,000 - 3,200 m. while illite does not occur below 3,000 m. (Fig. 23). The chemical data of the < 0.1-um size fraction shows a net loss in SiO_2 and a net gain in K_2O, which again agrees with the postulated clay mineral burial diagenetic reaction of Hower et al.(1976). The distribution of kaolinite and chlorite in both well Uruan-1 and Uda-1 appear to be unrelated in any systematic way to smectite - illite transformation. They are considered to be either the products of other diagenetic reactions affecting various stratigraphic levels, or the result of primary sediment deposition. In well Uda-1

however, kaolinite decreases in relative abundance with depth (Table 5). This trend seems to be indicative of a transition from nonmarine to marine facies (Brown et al., 1977, p. 181), which supports an interpretation of a detrital origin for kaolinite.

It would appear that the pattern of clay mineral burial diagenesis observed in the eastern flank of the Niger delta can be charaterised in part, by the clay mineral burial hypothesis postulated by Perry and Hower (1970). However, the occurrence of smectite in both wells at depths considered prohibitive to smectite, demands some answers if we are to accept the clay mineral burial hypothesis of Perry and Hower (1970), as being applicable to the eastern Niger delta. Let us consider the pros and cons of the hypothesis.

(A). Is the hypothesis applicable in the interpretation of clay mineral burial diagenesis in the eastern Niger delta ?

Let us assume it is applicable. We can then suggest that:

1) The geothermal temperature and pressure was not high enough to effect a transformation of smectite to illite. Paleotemperature calculations for both wells Uruan-1 and Uda-1 (Fig. 15), indicate the contrary. Geothermal temperatures at total depth in both wells reached 120 ^{o}C. In the Rhinegraben, Heling (1978, p. 211) observed smectite - illite transformation in Tertiary sediments at

temperatures as low as 80 and 40 °C. His observation would seem to question the significance of relatively high temperature in the clay mineral diagenetic process.

2) Since potassium, according to the clay mineral burial hypothesis (Perry and Hower, 1970), is a necessary element for the diagenetic alteration of smectite to illite, we could suggest that the preservation of discrete smectite in the deeply buried shales in the two wells studied is due to insufficient availability of potassium to the clay sediments. The chemical data (Fig. 25) does not support this suggestion. The K_2O concentration in both wells Uruan-1 and Uda-1 progressively increase with depth. Also, the average K_2O concentration values for the more deeply buried samples compare favorably to published values for Tertiary sediments from the U.S. Gulf Coast (Hower et al., 1976, Table 6 and 7). Thus the question arises on how significant potassium really is, to the alteration of smectite into illite ?

(B). Is the hypothesis inapplicable in the interpretation of clay mineral burial diagenesis in the eastern Niger delta ?

There are at least two reasons for assuming that the hypothesis is unable to completely explain the data obtained for the eastern Niger delta.

1) The hypothesis fails, in part, because provenance determines the type of clay minerals deposited in a basin. Provenance would be a key factor in the type of clay minerals which ultimately undergo burial diagenesis. Work by Biscaye (1965), and others shows the influence of provenance on clay minerals of Recent marine sediments. Heling (1978) and April (1981) have also concluded that provenance was responsible for the occurrence of smectite under conditions not conducive to smectite according to the Perry and Hower (1970) clay mineral burial hypothesis. If the assumption that provenance is the key factor in the observed clay mineral data is correct, we could speculate that the smectite observed at 'prohibitive' depths in both wells, came from sources different from those of the rest of the clay mineral suite. This speculation may be warranted if the smectites in the Tertiary sediments of the eastern Niger delta are of different varieties, i.e. some having a higher, and others a lower charged interlayer. Higher charged smectite has more tetrahedral Si^{4+} substituted by Al^{3+}, and inorder to balance the charge deficiency would more readily alter to illite than would a lower charged smectite (Heling, 1978, p. 219).

2) Could the Perry and Hower (1970) clay mineral burial hypothesis be inapplicable to the eastern Niger delta clay mineral data because what really determines the ob-

served suite of clay minerals in a vertical sequence is the depositional system ? Powers (1957, p. 362) noted that environments may be defined by the clay mineral composition of the samples studied. Brown et al.(1977, p. 171 and p. 184) noted in studies on Desmoinesian cyclothems in Iowa and Missouri, a vertical clay mineral distribution similar to what was observed in well Uda-1. They observed that 'changes from marine to nonmarine facies coincide with a decrease in illite, and an increase in mixed-layer clays and in the percentage of expandable layers in the mixed-layer clay'. They added that 'the principal clay detritus entering the area was illite, which underwent various degrees of alteration in different aqueous and subaerial environments within deltaic and interdeltaic areas'. Their interpretation for the Desmoinesian cyclothem seems adoptable for the clay mineral distribution observed in well Uda-1, and thus suggests a detrital origin for the clays in this well.

Although a detrital origin is suggested for well Uda-1, the mineralogy and chemical data do seem to also suggest trends which can be characterised by the clay mineral burial diagenesis hypothesis of Perry and Hower (1970). The mineralogic and chemical data for well Uruan-1 more closely relates to trends expected from Perry and Hower's (1970) hypothesis. The enigma observed in both wells is the smectite occurring at 'prohibitive'

depths. If the hypothesis is applicable, could it be that it works in certain cases and not in others ? If so, under what conditions is it valid ? These are key questions that need to be answered for a better understanding of clay mineral burial diagenesis.

What is clear from carrying out this study is that clay mineral burial diagenesis in the eastern flank of the Niger delta is complex and probably may be difficult to characterise into a simple model based purely on mineralogic and geochemical considerations. The geology of the vertical sequence under study, undoubtedly, may impose some characteristics, which may be inexplicable by mineralogic and geochemical considerations alone, on the clay minerals. For instance, Pryor (1975) emphasized the importance of fecal pellets, a biological phenomenon, as an important source of deposited muds in shallow marine, nondeltaic environments. It would not be unreasonable to assume that the clay minerals from fecal pellets may be different, in composition, from those in sediments that have not been ingested by organisms. Thus before deep burial commences, the clay mineral composition in successive strata may have already been altered differently. It may thus not be surprising if these successive strata of reworked and unreworked clays exhibit different diagenetic trends upon burial. Another geological process that may stratigraphically differentiate clays before deep burial, is transgression and regression (Millot, 1970, p. 78). Tectonics

also influences both the nature and the order of clay deposits. Active tectonics gives rise to detrital sediments while chemical deposits are more dominant in inactive tectonic times (Millot, 1970, p. 80). Millot also noted the role of climate in regulating the nature and the succession of sedimentary deposits. Even after burial, other diagenetic reactions, like the formation of calcite, may inhibit some clay mineral burial reactions (Foscolos et al., 1982, p. 149), and thus alter clay mineral diagenetic trends in a vertical sequence from what might be theoretically expected.

In both wells Uruan-1 and Uda-1, the observed depth related mineralogic and geochemical trends could in part be characterised by the clay mineral burial diagenetic trends, as described for the U.S. Gulf Coast by several investigators. However, the trends in well Uda-1 better fit an interpretation based on facies changes. Several authors seem to share the view that stratigraphy has some control on clay mineral burial diagenesis. They include Powers (1957, p. 369) who believes that the nature of mixed-layer clays depend largely on the source material. Burst (1959, p. 340) and Brown et al.(1977, p. 171) all seem to agree that clay mineral suites can vary systematically with depositio-

nal environment. April (1981, p. 37) inferred stratigraphic control as being a possible explanation for an anomalous occurrence of discrete smectite below a strata of mixed-layer smectite/chlorite. Nadeau and Reynolds (1981, p. 257) pointed out 'the importance of determining to what extent, in addition to thermal history, observed mineral assemblages are influenced by (1) initial (detrital) mineral assemblages (2) minerals formed as a result of premetamorphic alteration (3) bulk chemical composition , e.g. isochemical reactions in closed systems as proposed by Hower et al. (1976), and (4) metasomatic processes e.g. open chemical systems as proposed by Weaver and Beck (1971)'. Rettke (1981, p. 550) noted that the stratigraphy, paleogeography, and structural setting of the Dakota Group in the northern Denver basin, were responsible fot the observed clay mineral distribution.

Economic significance of study.

On the basis of an apparent stratigraphic control on the depth distributive clay mineralogy, it is possible the clay mineral data obtained in this study can be used in recognizing stratigraphic packages. With more wells for control, an investigation

of clay mineral burial diagenesis could allow for greater precision in stratigraphic correlation, especially where fossils are absent or poorly preserved. Inferences on paleogeographic reconstruction and diagenetic history can also be made from such a mineral data. This type of information would be useful in exploratory work for fossil fuels and groundwater, especially where a correlation of clay mineral data from virgin territory to nearby proven reserves can be made. Such a correlation would be useful in cutting down on exploration expenses and time, by aiding in targeting certain strata for other conventional geological means of exploration.

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APPENDIX

ATOMIC ABSORPTION DATA

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
BHVO-1, Basalt	50.83 %	26
MAG-1, Marine mud	50.87 %	26
STM-1, Nepheline syenite	60.15 %	45
SCo-1, Cody shale	62.80 %	57
SDC-1, Mica schist	65.39 %	74
RGM-1, Rhyolite	73.15 %	85

TABLE 12. Data for calibration of standards for SiO_2.

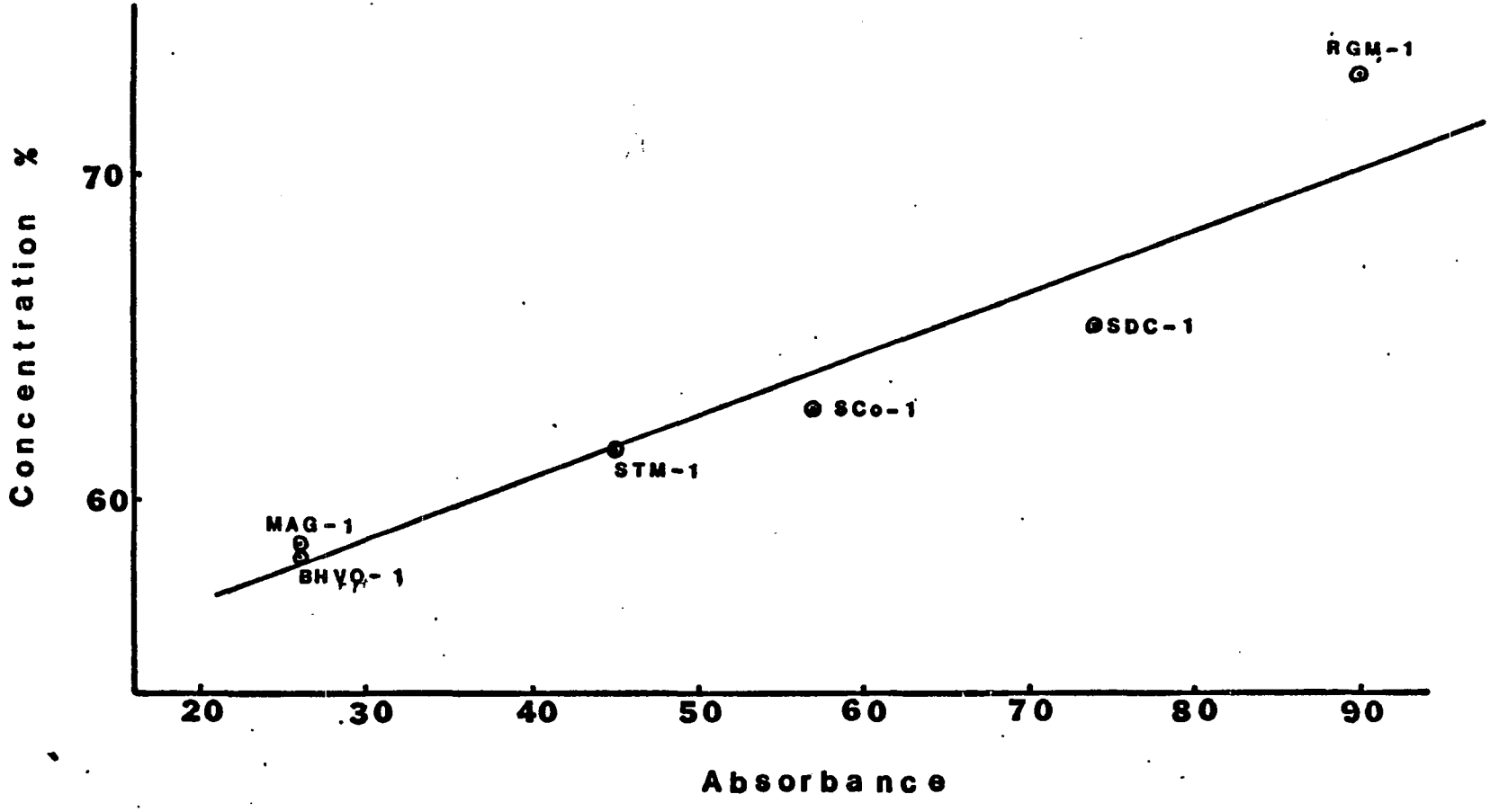

FIG. 31. Calibration curve of standards for SiO_2.

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
SCo-1, Cody shale	13.80 %	66.8
RGM-1, Rhyolite	13.88 %	67.0
BHVO-1, Basalt	13.96 %	66.6
SDC-1, Mica schist	16.68 %	68.2
MAG-1, Marine mud	16.77 %	68.4
STM-1, Nepheline syenite	18.73 %	67.8

TABLE 13. Data for calibration of standards for Al_2O_3.

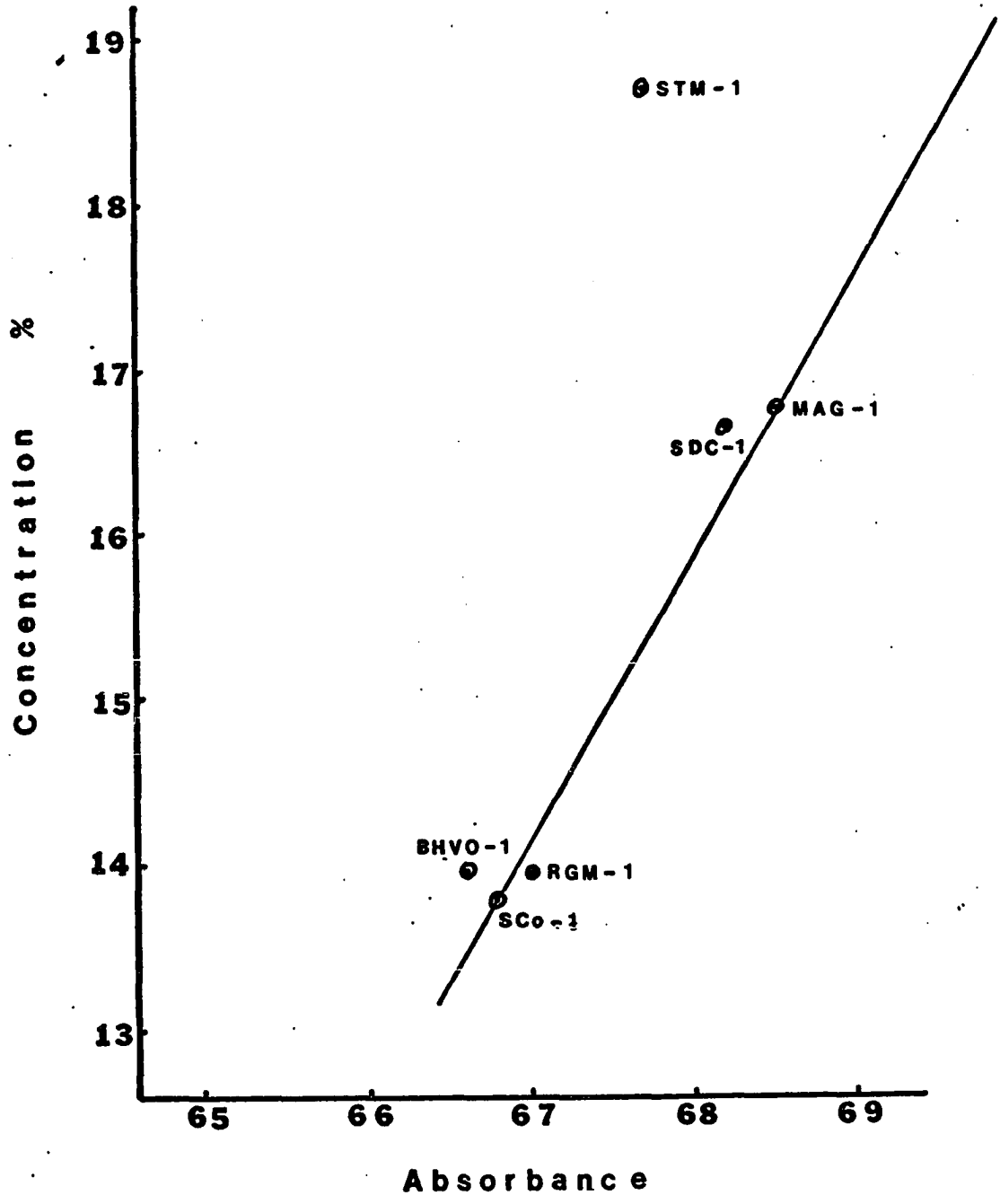

FIG. 32. Calibration curve of standards for Al_2O_3.

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
STM-1, Nepheline syenite	1.15 %	8.4
RGM-1, Rhyolite	1.24 %	10.2
MAG-1, Marine mud	1.41 %	12.4
SDC-1, Mica schist	1.47 %	13.4
SCo-1, Cody shale	2.56 %	13.4
BHVO-1, Basalt	11.47 %	20.8

TABLE 14. Data for calibration of standards for CaO.

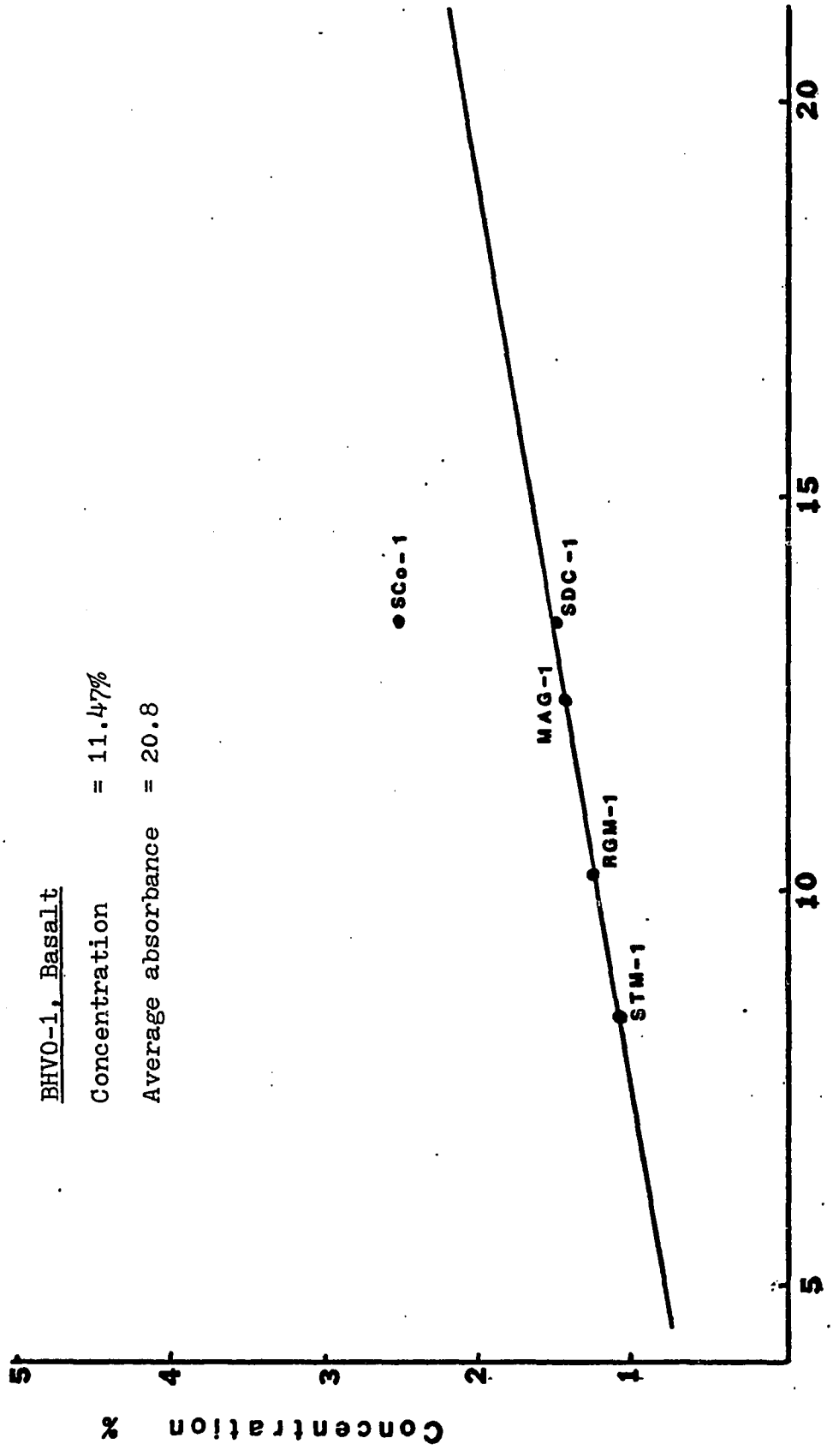

FIG. 33. Calibration curve of standards for CaO.

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
STM-1, Nepheline syenite	0.34 %	6.2
RGM-1, Rhyolite	0.39 %	8.0
SDC-1, Mica Schist	1.58 %	14.4
SCo-1, Cody shale	2.32 %	27.2
MAG-1, Marine mud	2.83 %	30.0
BHVO-1, Basalt	6.94 %	68.8

TABLE 15. Data for calibration of standards for MgO.

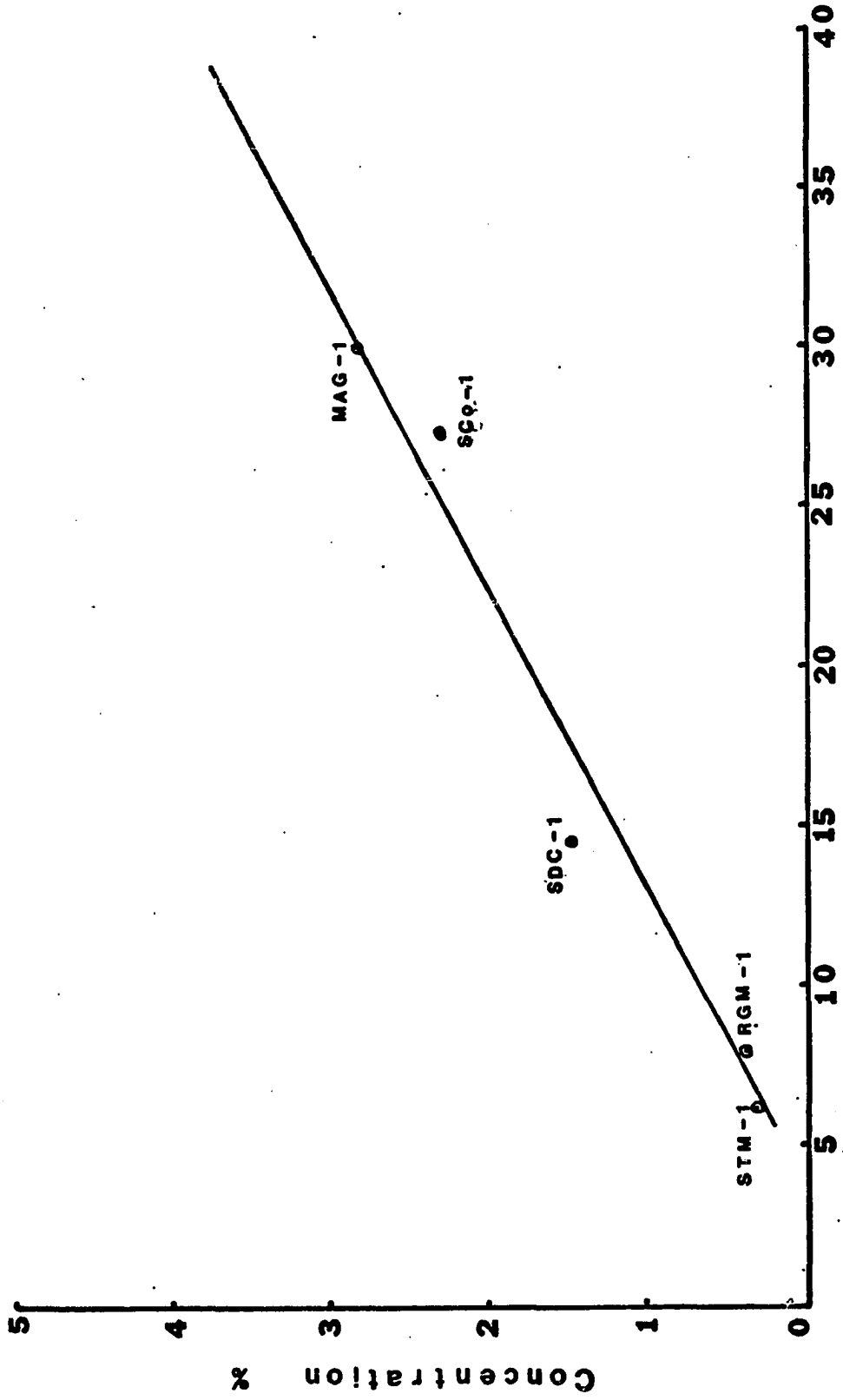

FIG. 34. Calibration curve of standards for MgO.

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
RGM-1, Rhyolite	1.95 %	4.2
SCo-1, Cody shale	5.23 %	6.0
STM-1, Nepheline syenite	5.37 %	6.2
MAG-1, Marine mud	7.09 %	7.0
SDC-1, Mica schist	7.20 %	7.6
BHVO-1, Basalt	11.91 %	10.8

TABLE 16. Data for calibration of standards for Fe_2O_3 (Total).

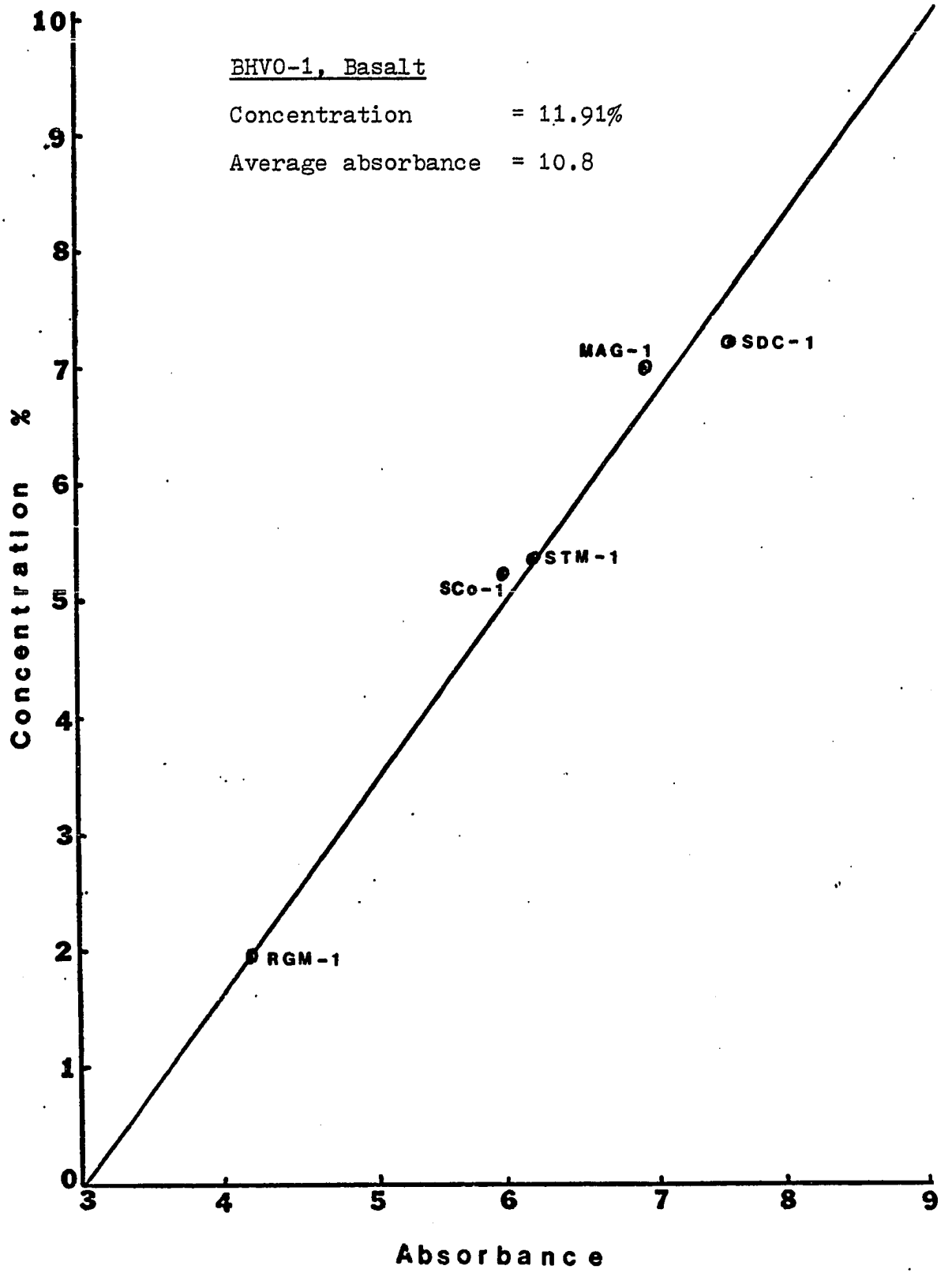

FIG. 35. Calibration curve of standards for Fe_2O_3 (Total)

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
SCo-1, Cody shale	0.78 %	7.0
SDC-1, Mica schist	1.98 %	15.8
BHVO-1, Basalt	2.35 %	18.0
MAG-1, Marine mud	3.43 %	25.6
RGM-1, Rhyolite	3.92 %	28.6
STM-1, Nepheline syenite	8.92 %	42.2

TABLE 17. Data for calibration of standards for Na_2O.

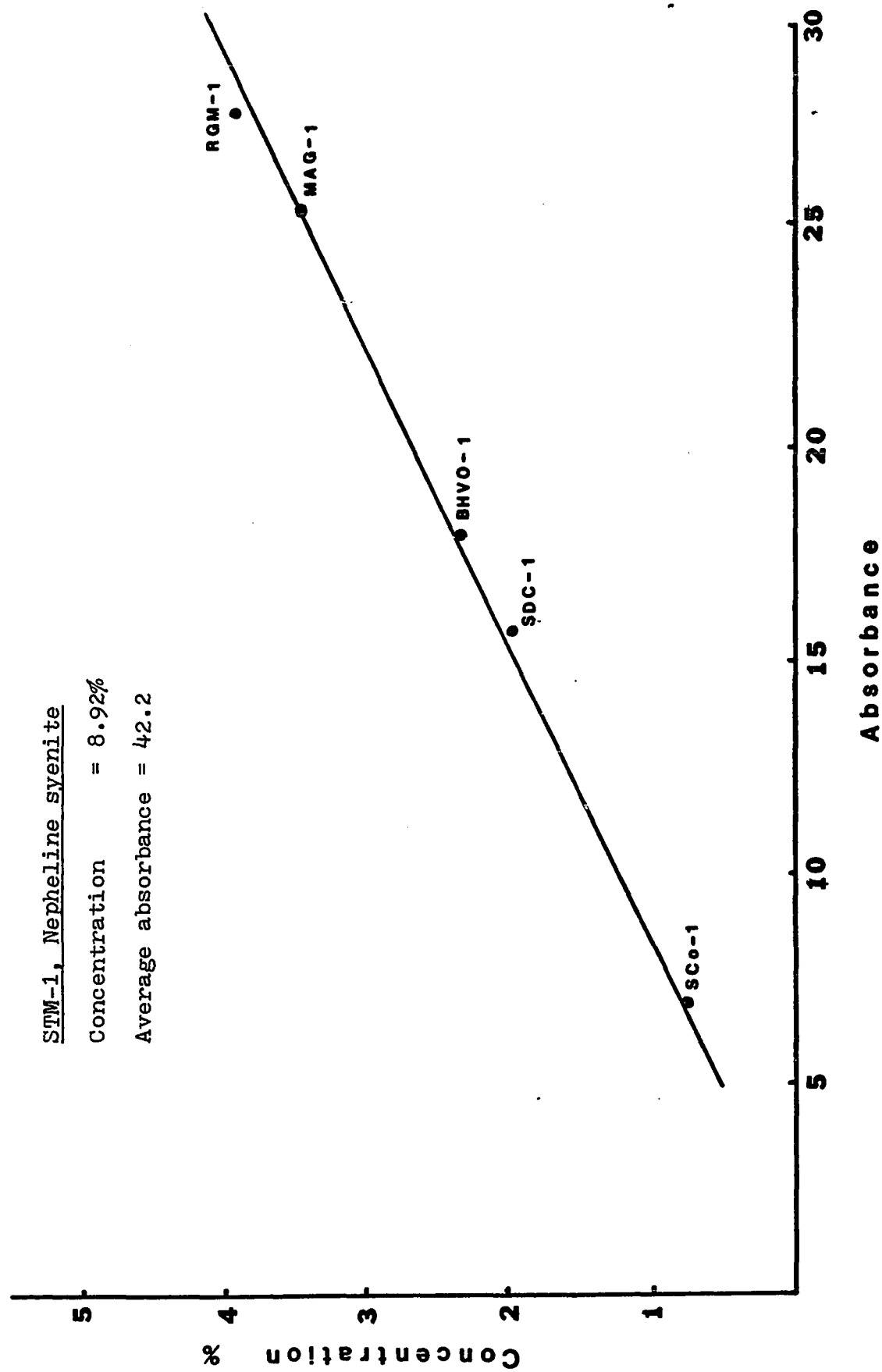

FIG. 36. Calibration curve of standards for Na_2O.

STANDARDS	USGS DETERMINED CONCENTRATION	AVERAGE ABSORBANCE (THIS STUDY)
BHVO-1, Basalt	0.52 %	6.6
SCo-1, Cody shale	2.65 %	27.0
SDC-1, Mica shale	3.26 %	35.4
MAG-1, Marine mud	3.57 %	38.4
RGM-1, Rhyolite	4.21 %	44.6
STM-1, Nepheline syenite	4.26 %	47.6

TABLE 18. Data for calibration of standards for K_2O.

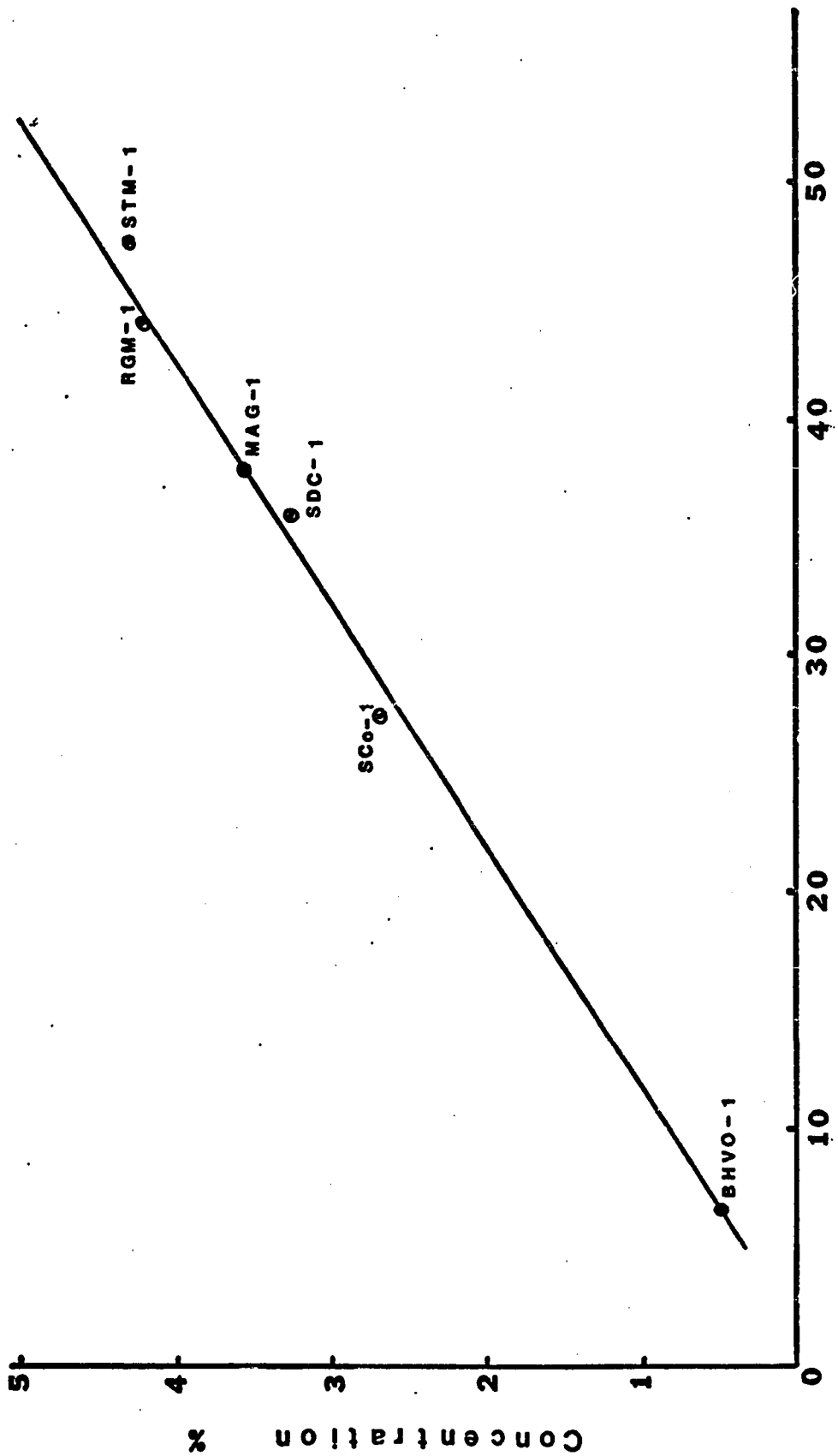

FIG. 37. Calibration curve of standards for K_2O.

TABLE 19. SiO_2 average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	74.4	67.13 %
	1,640	69.2	66.27 %
	1,969	52.8	63.20 %
	2,297	64.0	65.41 %
	2,625	53.0	63.47 %
	2,953	58.0	64.09 %
	3,281	55.0	63.63 %
	3,642	50.0	62.67 %
	3,675	49.8	62.58 %
	3,707	50.2	62.77 %
	3,740	52.2	62.94 %
	3,773	47.0	62.16 %
whole rock	1,312	58.2	64.37 %
	1,640	68.0	66.52 %
	1,969	65.6	65.48 %
	2,297	68.0	65.97 %
	2,625	68.2	66.07 %
	2,953	67.8	65.92 %
	3,281	69.8	66.49 %
	3,642	74.0	67.08 %
	3,675	62.2	65.03 %
	3,707	74.8	67.29 %
	3,740	74.0	67.14 %
	3,773	75.4	67.65 %

TABLE 20. SiO_2 average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,706	84.2	69.09 %
	1,870	83.0	68.92 %
	2,730	40.0	60.78 %
	2,854	69.0	66.25 %
	3,018	37.2	60.13 %
	3,031	63.4	65.17 %
	3,189	42.4	61.03 %
	3,340	36.8	60.09 %
	3,360	38.8	60.42 %
	3,530	38.0	60.29 %
	3,661	36.4	60.02 %
	3,688	36.6	60.06 %
whole rock	1,706	13.0	55.63 %
	1,870	39.0	60.72 %
	2,854	38.0	60.67 %
	3,018	43.2	61.35 %
	3,189	53.2	63.13 %
	3,340	43.0	61.11 %
	3,530	51.4	62.86 %
	3,661	51.2	62.84 %

TABLE 21. Al_2O_3 average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	67.0	14.15 %
	1,640	66.4	13.10 %
	1,969	68.0	15.85 %
	2,297	67.0	14.15 %
	2,625	66.8	13.80 %
	2,953	67.0	14.15 %
	3,281	66.8	13.80 %
	3,642	66.2	12.80 %
	3,675	67.2	14.50 %
	3,707	66.8	13.80 %
	3,740	67.2	14.50 %
	3,773	67.6	15.18 %
whole rock	1.312	67.6	15.18 %
	1,640	67.4	14.80 %
	1,969	68.4	16.54 %
	2,297	67.0	14.15 %
	2,625	67.8	15.50 %
	2,953	69.0	17.58 %
	3,281	67.6	15.18 %
	3,642	67.4	14.80 %
	3,675	67.8	15.50 %
	3,707	68.4	16.54 %
	3,740	69.0	17.58 %
	3,773	68.0	15.85 %

TABLE 22. Al_2O_3 average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,706	65.8	12.12 %
	1,870	67.0	14.15 %
	2,730	67.4	14.80 %
	2,854	68.4	16.54 %
	3,018	67.8	15.50 %
	3,031	66.6	12.48 %
	3,189	66.8	13.80 %
	3,340	67.0	14.15 %
	3,360	67.8	15.50 %
	3,530	67.8	15.50 %
	3,661	67.2	14.50 %
	3,688	67.6	15.18 %
whole rock	1,706	68.2	16.20 %
	1,870	67.2	14.50 %
	2,854	68.6	16.90 %
	3,018	69.8	18.94 %
	3,189	67.8	15.50 %
	3,340	68.2	16.20 %
	3,530	68.4	16.54 %
	3,661	69.4	18.20 %

TABLE 23. CaO average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	9.4	1.20 %
	1,640	4.8	0.80 %
	1,969	3.8	0.70 %
	2,297	6.2	0.90 %
	2,625	7.4	1.00 %
	2,953	8.4	1.10 %
	3,281	8.0	1.08 %
	3,642	5.4	0.82 %
	3,675	10.0	1.22 %
	3,707	8.4	1.10 %
	3,740	8.4	1.10 %
	3,773	9.8	1.22 %
whole rock	1,312	9.8	1.22 %
	1,640	9.4	1.20 %
	1,969	12.0	1.40 %
	2,297	8.2	1.10 %
	2,625	16.4	1.80 %
	2,953	20.2	2.12 %
	3,281	13.4	1.52 %
	3,642	9.8	1.22 %
	3,675	8.6	1.12 %
	3,707	8.6	1.12 %
	3,740	11.2	1.34 %
	3,773	10.0	1.22 %

TABLE 24. CaO average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,706	10.6	1.30 %
	1,870	12.4	1.42 %
	2,730	14.0	1.60 %
	2,854	13.4	1.50 %
	3,018	11.8	1.40 %
	3,031	7.4	1.00 %
	3,189	11.4	1.38 %
	3,340	18.6	2.00 %
	3,360	9.4	1.20 %
	3,530	9.6	1.20 %
	3,661	11.2	1.32 %
	3,688	9.2	1.18 %
whole rock	1,706	5.6	0.82 %
	1,870	9.6	1.20 %
	2,854	9.0	1.18 %
	3,018	10.0	1.22 %
	3,189	13.8	1.56 %
	3,340	10.4	1.28 %
	3,530	9.4	1.20 %
	3,661	7.6	1.02 %

TABLE 25. MgO average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	10.8	0.78 %
	1,640	16.0	1.32 %
	1,969	19.2	1.74 %
	2,297	12.4	0.96 %
	2,625	15.6	1.28 %
	2,953	23.2	2.10 %
	3,281	17.6	1.50 %
	3,642	10.8	0.78 %
	3,675	9.2	0.60 %
	3,707	11.6	0.84 %
	3,740	20.8	1.80 %
	3,773	19.6	1.78 %
whole rock	1,312	15.6	1.28 %
	1,640	12.4	0.96 %
	1,969	11.6	0.84 %
	2,297	9.4	0.62 %
	2,625	10.0	0.70 %
	2,953	12.0	0.80 %
	3,281	22.4	2.00 %
	3,642	24.0	2.18 %
	3,675	14.8	1.20 %
	3,707	9.6	0.64 %
	3,740	12.4	0.96 %
	3,773	15.2	1.22 %

TABLE 26. MgO average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,706	15.2	1.22 %
	1,870	6.4	0.32 %
	2,730	12.8	0.98 %
	2,854	21.6	1.90 %
	3,018	7.6	0.40 %
	3,031	11.6	0.84 %
	3,189	15.2	1.22 %
	3,340	6.6	0.34 %
	3,360	6.0	0.30 %
	3,530	7.6	0.40 %
	3,661	12.8	0.98 %
	3,688	11.2	0.80 %
whole rock	1,706	5.0	0.18 %
	1,870	9.2	0.60 %
	2,854	10.8	0.78 %
	3,018	7.2	0.38 %
	3,189	10.6	0.72 %
	3,340	11.6	0.84 %
	3,530	12.0	0.90 %
	3,661	11.2	0.70 %

TABLE 27. Fe_2O_3 (Total) average absorbance measured for samples well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	6.2	5.30 %
	1,640	5.8	4.60 %
	1,969	7.4	7.30 %
	2,297	4.6	2.60 %
	2,625	6.0	4.90 %
	2,953	5.4	4.00 %
	3,281	5.2	3.65 %
	3,642	5.0	3.30 %
	3.675	4.6	2.50 %
	3,707	4.8	3.00 %
	3,740	4.8	3.00 %
	3,773	4.2	2.00 %
whole rock	1.312	7.4	7.15 %
	1,640	4.0	1.40 %
	1,969	6.0	5.00 %
	2,297	6.0	5.00 %
	2,625	4.6	2.50 %
	2,953	3.8	1.25 %
	3,281	6.0	5.00 %
	3,642	6.4	5.50 %
	3,675	8.0	8.25 %
	3,707	5.8	4.60 %
	3,740	5.8	4.60 %
	3,773	4.4	2.25 %

TABLE 28. Fe_2O_3(Total) average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,706	4.8	3.00 %
	1,870	5.2	3.65 %
	2,730	8.2	8.60 %
	2,854	4.0	1.40 %
	3,018	3.4	0.60 %
	3,031	3.4	0.60 %
	3,189	5.6	4.30 %
	3,340	3.8	1.25 %
	3,360	3.8	1.25 %
	3,530	3.4	0.60 %
	3,661	4.0	1.40 %
	3,688	5.4	4.00 %
whole rock	1,706	3.8	1.25 %
	1,870	5.0	3.30 %
	2,854	5.6	4.30 %
	3,018	6.6	6.00 %
	3,189	8.0	8.25 %
	3,340	9.0	10.00 %
	3,530	5.0	3.30 %
	3,661	4.4	2.25 %

TABLE 29. Na_2O average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	7.6	0.88 %
	1,640	8.0	0.90 %
	1,969	4.0	0.42 %
	2,297	3.2	0.38 %
	2,625	1.2	0.18 %
	2,953	4.8	0.56 %
	3,281	3.6	0.40 %
	3,642	3.6	0.40 %
	3,675	4.4	0.48 %
	3,707	2.8	0.30 %
	3,740	0.8	0.10 %
	3,773	0.8	0.10 %
whole rock	1,312	2.4	0.28 %
	1,640	2.8	0.30 %
	1,969	2.0	0.22 %
	2,297	3.2	0.38 %
	2,625	3.2	0.38 %
	2,953	3.6	0.40 %
	3,281	7.2	0.80 %
	3,642	10.8	1.32 %
	3,675	16.8	2.18 %
	3,707	18.8	2.42 %
	3,740	16.4	2.10 %
	3,773	14.6	1.88 %

TABLE 30. Na_2O average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
<0.1-um	1,706	8.4	0.92 %
	1,870	10.2	1.20 %
	2,730	12.4	1.52 %
	2,854	11.2	1.35 %
	3,018	16.2	2.10 %
	3,031	12.0	1.48 %
	3,189	13.6	1.72 %
	3,340	15.0	1.90 %
	3,360	11.0	1.35 %
	3,530	7.6	0.88 %
	3,661	13.4	1.68 %
	3,688	7.6	0.88 %
whole rock	1,706	10.8	1.34 %
	1,870	11.2	1.36 %
	2,854	7.6	0.88 %
	3,018	7.0	0.78 %
	3,189	6.4	0.70 %
	3,340	6.0	0.68 %
	3,530	9.2	1.08 %
	3,661	8.4	0.94 %

TABLE 31. K_2O average absorbance measured for samples from well Uruan-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
< 0.1-um	1,312	15.4	1.36 %
	1,640	17.8	1.59 %
	1,969	13.0	1.12 %
	2,297	12.6	1.10 %
	2,625	15.4	1.36 %
	2,953	13.8	1.20 %
	3,281	15.2	1.34 %
	3,642	33.2	3.16 %
	3,675	18.8	1.70 %
	3,707	25.4	2.30 %
	3,740	17.4	1.56 %
	3,773	23.0	2.08 %
whole rock	1,312	15.4	1.36 %
	1,640	13.8	1.20 %
	1,969	16.8	1.50 %
	2,297	22.0	1.98 %
	2,625	23.6	2.15 %
	2,953	29.0	2.66 %
	3,281	35.0	3.24 %
	3,642	42.0	3.90 %
	3,675	40.6	3.80 %
	3,707	39.6	3.68 %
	3,740	47.6	4.50 %
	3,773	53.4	5.00 %

TABLE 32. K_2O average absorbance measured for samples from well Uda-1.

Size fraction	Depth (m.)	Average absorbance	Conc. determined from calibration curves of stands.
<0.1-um	1,706	9.8	0.82 %
	1,870	13.2	1.15 %
	2,730	29.2	2.68 %
	2,854	11.3	0.98 %
	3,018	40.0	3.70 %
	3,031	18.2	1.62 %
	3,189	54.3	5.00 %
	3,340	23.6	2.15 %
	3,360	40.0	3.70 %
	3,530	40.7	3.80 %
	3,661	36.4	3.36 %
	3,688	47.8	4.50 %
whole rock	1,706	44.6	4.20 %
	1,870	42.2	3.92 %
	2,854	42.1	3.92 %
	3,018	20.4	1.82 %
	3,189	35.4	3.28 %
	3,340	28.8	2.64 %
	3,530	35.1	3.22 %
	3,661	34.4	3.18 %