

PRESSURE-TEMPERATURE-COMPOSITION OF ILLITE/SMECTITE MIXED-LAYER MINERALS: NIGER DELTA MUDSTONES AND OTHER EXAMPLES

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Abstract—X-ray powder diffraction (XRD) studies of the clay fraction of Upper Cretaceous mudstones from a shallow (2.5 km) drill hole in the Niger delta indicate a high geothermal gradient (about 100°C/km) during diagenesis. The mineralogy of the clays is similar to that observed elsewhere and consists of interstratified illite/smectite (I/S), kaolinite, and chlorite. Detrital mica and K-feldspar are also present throughout the section. The composition-depth relationship of the I/S is different from that observed in deeply buried Gulf Coast shales. The Niger delta rocks show a linear change in composition of the I/S as a function of depth in the drill hole from 60 to 10% smectite layers. The I/S ordering is R=0 in shallower samples and progresses to R=1 in deeper samples. The I/S in the deepest samples has R=3 ordering. No R=1 I/S showing a first-order 27-Å XRD reflection was found. The Niger delta sequence differs from the Gulf Coast sequence by (1) a lack of R=1 I/S showing a 27-Å XRD reflection (which are common in Gulf Coast samples and contain 20% smectite layers), and (2) the existence of a simple, continuous linear relation between the composition of the R=1 and R=0 I/S and depth.

A comparison of composition-temperature curves for I/S formed under different diagenetic regimes shows different types of I/S ordering in which the presence of R=1 I/S showing a 27-Å reflection and R=3 I/S types changes the composition-depth (and thus, composition-temperature) relations. These changes suggest a difference in the energy necessary to form the various ordering types. Also, geothermal gradient during burial appears to be responsible for different composition-temperature gradients found for the same type of I/S ordering.

Key Words—Diagenesis, Geothermal gradient, Illite/smectite, Ordering, Smectite.

INTRODUCTION

The diagenesis of clay minerals in pelitic sediments has been amply documented in areas of low geothermal gradients (10°–25°C/km). The best known of these investigations have dealt with sediments in the Gulf Coast of the United States (Hower *et al.*, 1976; Perry and Hower, 1972; Boles and Franks, 1979; Yeh and Savin, 1977; Schmidt, 1973; Weaver and Beck, 1971; Bruce, 1984; Freed, 1981). Here, mixed-layer illite/smectite (I/S) has been shown to change continuously with burial depth. The importance of these studies lies in the fact that the basin investigated has not been uplifted and therefore the present-day geothermal gradients are thought to represent the geothermal gradients that existed at the time of deposition, i.e., the present geothermal gradients, as measured in drill holes, are assumed to be the same as those of the past. This assumption is probably not totally correct, but it provides a convenient starting point for the study of diagenetic transformations.

The present study concerns a series of drill hole cuttings of mudstones collected from a shallow (2.5 km) well in Upper Cretaceous sediments of Nigeria. The geothermal gradient in the area is relatively high (55°C/km, according to Nwachkwu, 1976). The major purpose of this study is to explain differences between clay diagenesis in the Gulf Coast and the Niger delta in

terms of variations in present and past geothermal gradients.

MATERIALS AND METHODS

All samples were kindly provided by Elf Aquitaine Company. X-ray powder diffraction (XRD) analyses were made on cutting chips of mudstones. Ground rock samples were examined as un-oriented specimens. The 2–0.4- μm fraction was obtained by centrifuge separation and sedimentation on a sizing filter. The oriented sample on the filter was transferred to a glass slide (Brusewitz, 1982). Identification of the I/S ordering type was made using the criteria of Reynolds and Hower (1970) and Reynolds (1980), using glycolated samples. The percentages of smectite layers in highly expandable, R=0 I/S was determined using glycolated samples in which the peak height of the 17-Å reflection was compared with its low-angle background intensity.

The estimate of the smectite content for R=1 and R=3 I/S samples was made using water-saturated (air dried) rather than glycolated samples. Supplementing the data of Hower (1981) with spacings generated using the methods of Reynolds (1980), a series of calculated XRD patterns were produced; determinative curves based upon these patterns are presented in Figure 1 for the R=1 and R=3 stacking types. The advantages of this method are its ease of use for certain sample types

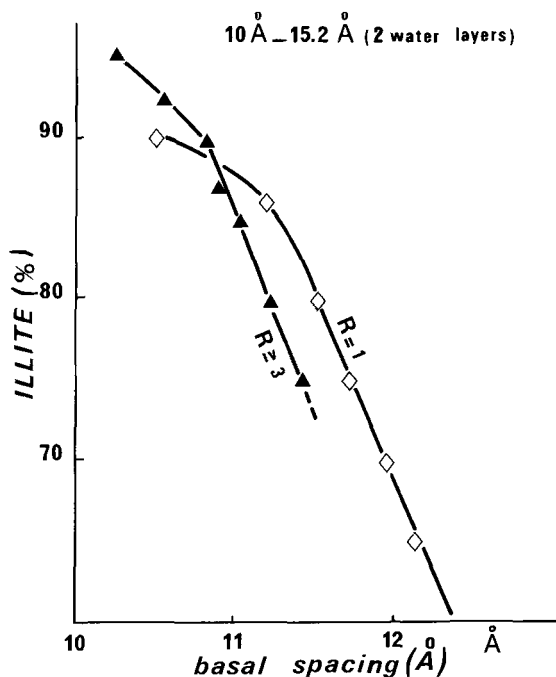


Figure 1. Theoretical determinative curves for percentage of illite using X-ray powder diffraction traces of the $R=1$ and $R=3$ stacking sequence structure in the air-dried (hydrated with two water layers) state. Symbols show points derived from calculated diffraction patterns using Reynolds (1980) program.

compared to the method proposed by Środoń (1980). Środoń's method uses peaks of low intensity near $45^\circ 2\theta$ ($\text{CuK}\alpha$ radiation), which are not observed in many specimens, and requires interpretation of the smectite layer thickness. Another method given by Reynolds and Hower (1970) uses lower order, relatively intense reflections which are, unfortunately, highly asymmetric (peak at 5 \AA , Figure 2) for the samples studied here (see Figure 2), resulting in a great imprecision in measurement. Given that the material studied here is polymineralic and that the intensities of the I/S reflections were commonly low, use of the 001 high-intensity reflection was generally required. The measurements were made on the peak having the highest intensity of those normally observed for the minerals concerned.

Hydration state is critical when using air-dried samples to determine I/S composition. The easiest way to assure a two-layer hydration at typical laboratory humidity is to saturate the clay with calcium or magnesium. In the methods used by many workers, the separation procedure includes a dispersion step using Na_2CO_3 . This procedure introduces Na into the interlayer site. Na has a notoriously variable hydration state at typical laboratory humidities. Therefore, Ca- or Mg-saturation is preferred when using the air-dried determinative method. As it turns out, smectite prefers Ca over Na, and in nature the clays in detrital, pelitic

sediments are therefore likely to be Ca-saturated. Although the methods of the present study did not involve exchange-cation saturation of the sample, no hydration problems were observed. Such will not be true, however, for sodic bentonites. The usefulness of the method in determining basal spacings for mixed-layer minerals in pelitic rocks can be seen in the regular sequence of values presented as experimental results here. XRD patterns of some samples in both the air-dried and glycolated states are presented in Figure 2.

Identification of the other minerals was made using the JCPDS reference cards. Chlorite was distinguished from kaolinite by XRD peaks at 3.57 and 3.53 \AA , respectively. The chlorites gave weak 14-\AA peaks, suggesting a high iron content and thus a chamositic composition. No attempt was made to quantify the minerals; however, if a phase is reported, it generally represented at least 10% of the sample. From a phase equilibrium standpoint, the abundance of a phase is not important if one can explain the assemblage present.

Samples studied

Twenty-two mudstone samples of drill-hole cuttings were hand picked to assure lithologic homogeneity. According to the Elf-Aquitaine geologists (personal communication), the Cretaceous strata sampled are transgressive in the lower part and regressive in the upper part. Short and Stauble (1967) indicated only a regressive sequence for the rocks. Shallow samples were taken at various depths from 0.3 km (Lower Maastriechian) to 2.5 km (Cenomanian). Outcrop in the area is late Upper Cretaceous in age. Tertiary sediments crop out to the west. For proprietary reasons, the exact location of the well cannot be divulged. A summary of the mudrock mineralogy is given in Figure 3 along with the sampling depths. Several vitrinite reflectance determinations (each an average of many measurements) were made by Elf-Aquitaine on samples collected at 1000 m (1.1%), 1250 m (1.25%), 1750 m (1.75%), and 2100 m (2.35%).

CLAY MINERALOGY

As shown in Figure 3, at a depth of about 1800 m kaolinite becomes much less abundant and the I/S changes from the $R=1$ to the $R=3$ form (Figure 3). Figure 4 shows the estimations of smectite content of the I/S as a function of depth of the drill hole. Diagenetic changes are apparent inasmuch as the smectite content of the I/S decreases continuously with depth. The original mineralogy of the mudstones has apparently been modified by exposure to a continuous geothermal gradient. An abrupt change in the relation between smectite content of the I/S and depth in the drill hole exists which can be interpreted as a change in the slope of a dx/dT function, where x = smectite content

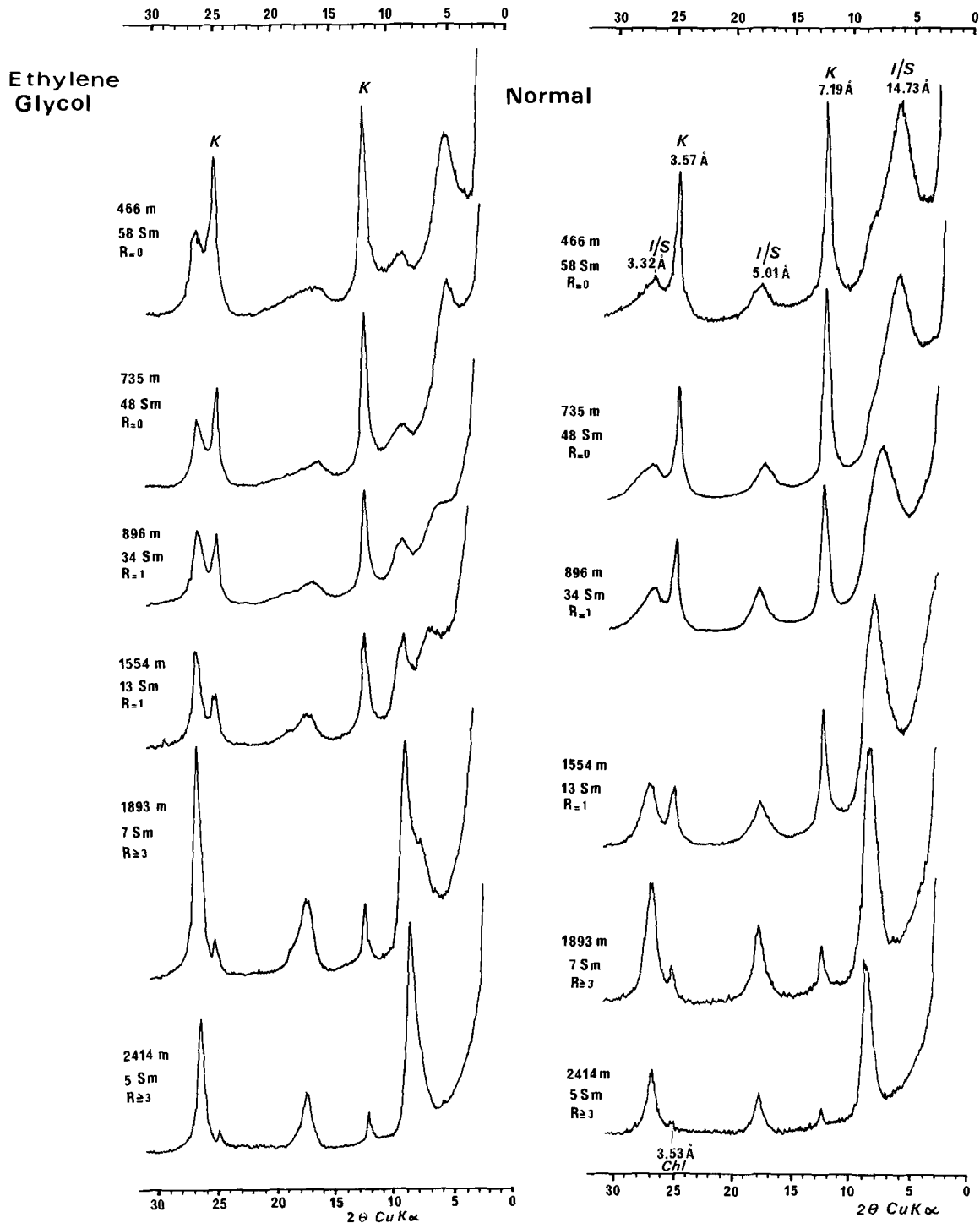


Figure 2. X-ray powder diffraction traces of typical Niger delta samples used in this study (oriented, 2–0.4- μm fractions). Depth, percentage of smectite in I/S (n Sm) and stacking type (R=n) are indicated. K = kaolinite, I/S = mixed-layer I/S, Chl = chlorite. Diagrams for the air-dried samples are on the right; those for glycolated samples on the left. $\text{CuK}\alpha$ radiation.

of I/S and T = temperature (due to burial). This change in slope of the smectite content of I/S as a function of temperature occurs when the I/S ordering changes from

R=1 to R=3. On the other hand, the change in I/S ordering (R=0 to R=1) at about 800 m depth does not affect the dx/dT relations (slope). Linear regressions

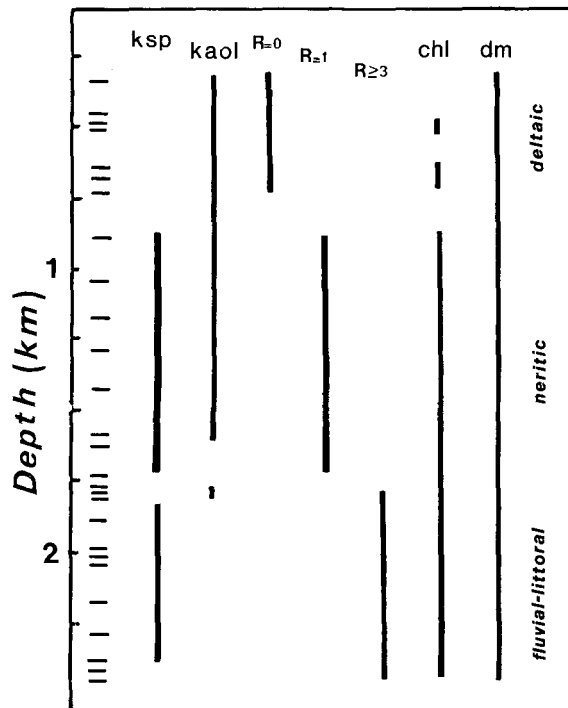


Figure 3. Graphic representation of the clay mineralogy of the Niger delta samples studied. Bars on right-hand side of the depth scale indicate position of the samples. ksp = potassium feldspar, kaol = kaolinite, $R=n = I/S$ ordering type, chl = chlorite, dm = detrital mica.

for two different groups of data points give a slope of -40% smectite per kilometer in the $R=0$, $R=1$ sequence and -10% smectite per kilometer for the $R=3$ stacking type (Figure 4).

DISCUSSION

Clay mineral assemblages as a function of depth

Visual estimates of mineral content from XRD patterns (as in Figure 2) suggest that the abundance of chlorite has not been greatly affected by the disappearance of kaolinite (Figure 3), nor was K-feldspar completely lost. The amount of detrital mica also does not seem to have changed significantly, although the use of only visual estimates of XRD peak intensities makes this statement somewhat tentative. It is evident, however, that K is abundant throughout the diagenetic sequence investigated, although most of it appears to be locked up in metastable phases. The percentage of illite layers (and hence, the K content) of the I/S increases continuously with burial depth.

In general, three mineral assemblages appear as depth increases: (1) kaolinite-I/S ($R=0$); (2) kaolinite-I/S ($R=1$)-chlorite; and (3) I/S ($R=3$)-chlorite. The increase in chlorite content, before the loss of kaolinite, suggests that Fe^{2+} could have increased in the diage-

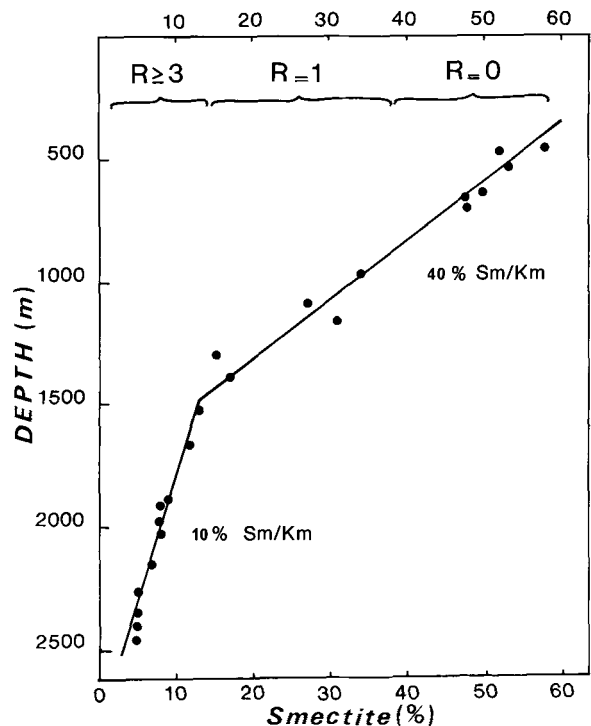


Figure 4. Relation of estimated percentage of smectite in I/S and depth in the Niger delta drill hole sequence. Sm = smectite content of I/S.

netic system, probably by the reduction of Fe^{3+} . Such a reaction makes iron oxide phases, commonly thought to be outside of the diagenetic system, important contributors to the final clay mineral assemblage (Velde, 1985a).

The increase in the illite content of the I/S could have been controlled by an increase in K availability to the neoformed assemblage, as has been suggested by Boles and Franks (1979) and Hower *et al.* (1976). Such an increase in K is possible, but it may not have been necessary. If the mudstones were, as is usually assumed, relatively impermeable, the diagenetic system would have been buffered by the composition of the rock and not by the composition of the solution. Thus, any addition of material to the diagenetic system must have been chiefly the result of the dissolution of metastable or unstable phases in the mudstone itself. Neoformed diagenetic minerals, therefore, could have changed towards a more K-rich bulk composition by the dissolution of detrital feldspar and/or mica. If so, the increase in illite layers in I/S would not have been controlled by temperature (as suggested by Figure 3), but by the absolute amount of K available in the diagenetic system. An increase in the illite content of the I/S due to an increase in K (i.e., K-metasomatism) should therefore have been accompanied by a loss of all of the Al-containing, non-alkali phases in the sys-

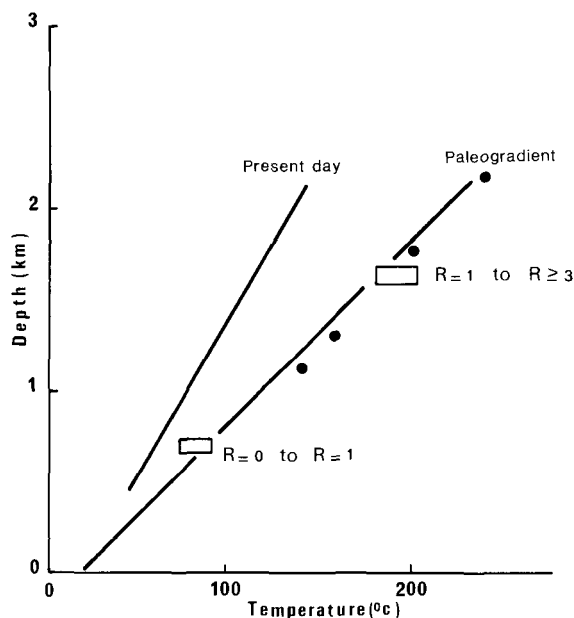


Figure 5. Estimation of paleo-geothermal gradient responsible for the diagenetic clay mineralogy observed in Niger delta samples. Rectangles show temperature intervals of the transitions from $R=0$ to $R=1$, and $R=1$ to $R=3$; dots show values deduced from vitrinite reflectance measurements. Second gradient is that of the present day.

tem, e.g., both chlorite and kaolinite. Chlorite and/or kaolinite, however, are present throughout the well. The major change in mineralogy in the Upper Cretaceous Niger delta samples is the loss of kaolinite at depth; chlorite is present throughout. The relative amount of ($\text{Fe}^{2+} + \text{Mg}$) in the active silicate system probably changed. The phase relations of these mineral assemblages were analyzed by Velde (1985b). In summary, the increase in illite content of the I/S was probably due to a variation in the temperature of diagenesis and not to a change in the amount of available K.

The loss of kaolinite may affect the change in the type of I/S stacking. Similar to the trend in the Niger delta, the data of Dunoyer de Segonzac (1969) show that in the Gulf of Gabon kaolinite is lost before the appearance of $R=3$ I/S. The same conclusion can be drawn from the information given by Weaver and Beck (1971) for a sequence from the Gulf Coast of the United States. For hydrothermal samples, Steiner (1968) found the same relation; however, Jennings and Thompson (1986) found kaolinite to persist into the illite-chlorite zone. Thus, the presence of kaolinite is not critical to the type of I/S ordering.

Thermal gradient

Velde (1985b) summarized the depth-temperature mineral relations reported for drill holes in recent and Tertiary sediments. He noted that the change from $R=0$ to $R=1$ I/S took place at about 80°C in high

geothermal gradient sequences and at $50^\circ\text{--}80^\circ\text{C}$ in deep drill holes. Because the samples examined in the present study represent a relatively shallow sequence and therefore one of high geothermal gradient, a temperature of about 80°C will be assumed (Figure 5).

The second temperature of interest concerns the transition from $R=1$ to $R=3$ I/S. Data from Steiner (1968, p. 199), McDowell and Elders (1980), Weaver and Beck (1971, implicit in written descriptions of X-ray diagrams), Jennings and Thompson (1986), and Hower (John Hower, Department of Geology, University of Illinois, Urbana, Illinois, personal communication, 1983) indicate that this change in stacking sequence of I/S is at $\sim 180^\circ\text{C}$ for both deep (6–8 km) and shallow (2 km) wells. A temperature of $\sim 180^\circ\text{C}$ is assumed here to be that of the transition from $R=1$ to $R=3$ I/S during burial metamorphism.

The vitrinite reflectance values for the Niger delta sediments can also be used to estimate the temperature gradient to which the sediments were subjected. The values of the present study can be compared with those of Teichmüller (1979) and Bacher (1982) because both concern shallow sediments in areas of high geothermal gradients (Tertiary sandstone in a graben and material from active geothermal zones, respectively) which approach the conditions of the sequence studied here. Figure 3 shows the temperature estimates derived from the clay minerals and those from the vitrinite reflectance of the organic material compared to the present geothermal gradient. A paleo-geothermal gradient of $100^\circ\text{C}/\text{km}$ was apparently responsible for the diagenetic clay minerals in the sample and for the transformation of the solid organic material. No information is available to indicate when this high thermal regime occurred. The paleo-geothermal gradient of $100^\circ\text{C}/\text{km}$ will be used for the sediments investigated here.

Comparison of I/S clay mineral sequences

The time interval between sedimentation and burial to present depth along the Gulf Coast and in the Niger delta are similar. The Gulf Coast sediments range in age from 10 to 50 m.y., whereas those investigated here span 30 m.y. Eberl and Hower (1976) pointed out the potential importance of reaction rate in the transformation of smectite to illite through a series of intermediate I/S phases. A review of the relations between mineralogy and age of the sediments in Gulf Coast drill hole sequences is given in Velde (1985b); however, the importance of the time dimension using these data cannot be estimated. The variations in I/S reported by Jennings and Thompson (1986) for an area of high geothermal gradient (Colorado River delta) occurs for 1–2-m.y. old sediments, but are similar to those of the Gulf Coast. Thus, a time of <2 m.y. is sufficient to produce clay mineral reaction in sedimentary rocks at temperatures similar to those found in Gulf Coast Ter-

tiary sediments. Weaver and Beck (1971) reported data for Mississippian age rocks which indicate that at present-day temperatures similar to those in the Colorado delta sediments, the same mineral changes occur. From these studies, it is difficult to establish the kinetics of clay transformation. Although different temperatures for the transition from R=0 to R=1 I/S were reported, the appearance of R=3 I/S at about 180°C for both old and young sediments is striking. The reaction kinetics for this phase do not therefore seem to be important, at least not over periods of about 10–30 m.y.

Figure 6 shows the relation between smectite content of I/S and temperature for Gulf Coast samples (Bruce, 1984; Freed, 1981). This relation is plotted (Figure 6, top) for the Niger delta material and for the data reported in Jennings and Thompson (1986). Three types of curves arise: (1) that for the Niger and Colorado delta samples, where the slope is interrupted only at the transition from R=1 to R=3 I/S; (2) that for samples where the slope is interrupted by the transition between R=1 and the R=1 showing a 27-Å reflection which occurs at near 20% smectite; and (3) that for samples where two distinct breaks exist in the curve, one near the R=0-to-R=1 change and another at the change from R=1 to the R=1 showing a 27-Å reflection I/S type. In this last type (the “S”-shaped curve, Figure 7), the change from about 60 to 20% smectite is commonly nearly isothermal (<20°C interval). Excluding this latter type of curve for the moment, the R=0, R=1 dx/dT curves have a different slope for shallow and deep burial types (Figure 6). The effect of geothermal gradient on I/S ordering is apparently important. In the shallow (high geothermal gradient) sequences, the apparent conversion rate is about 0.65% smectite/°C, whereas in the deep-burial sediments the rate is about 2% smectite/°C. The dx/dT relation of the R=3 and the R=1 I/S showing a 27-Å reflection also varies with the present-day geothermal gradient. The slope of the R=3 is about 0.2% smectite/°C, whereas that for the R=1 I/S showing a 27-Å reflection is almost zero. Thus, the geothermal gradient is also important in determining the composition of both the R=1 I/S showing a 27-Å reflection and the R=3 type.

Chemical controls on reactions

The third type of composition-temperature (dx/dT) relation is that of the “S”-shaped curve illustrated in Figure 7 which shows an abrupt change in smectite content over a small range of temperature (<20°C), which is almost isothermal. From the data reported by Hower *et al.* (1976), this abrupt change in smectite content could be due to a change in the effective chemical system of the reacting diagenetic phases. The details of such a mechanism were given by Velde (1985a). The entry of iron into the active diagenetic system takes place by the reduction of iron oxide phases (Fe₂O₃).

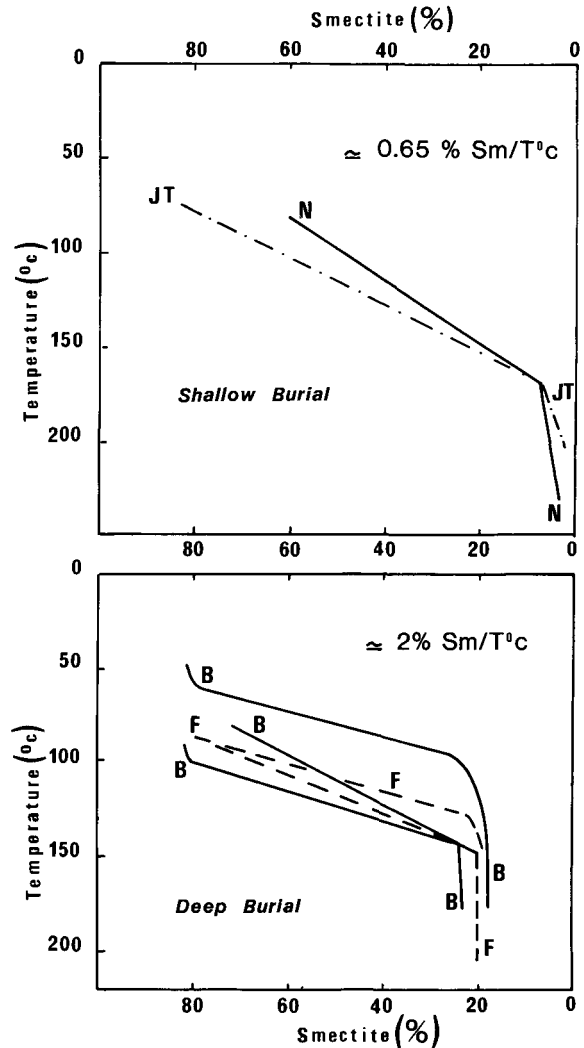


Figure 6. Diagrams showing the two types of dx/dT (composition/temperature) relations for shallow (top) series and deep (bottom) wells. Data are taken from Jennings and Thompson (1986) = J-T; the present study = N; Bruce (1984) = B; and Freed (1981) = F. dx/dT gradients of 0.65 and 2% smectite/°C found for R=0, R=1 I/S minerals. Lower values were found for R=3 I/S in shallow burial sediments and in R=1 (superlattice) I/S minerals in deep burial sediments.

The result is the transformation of kaolinite into chlorite. Because abundant chlorite is already present, the net result of such a reaction is to reduce the number of active diagenetic phases from three to two. This reaction is accomplished by an abrupt change in the smectite content of the I/S because the tie-lines for the three- and two-phase systems are not the same. At present the existence of the tie-lines is not proven, and consequently it is not instructive to go further into the analysis. It is sufficient to try to distinguish between the two types of dx/dT curves, those with a continuous slope in the R=0, R=1 range and those which show

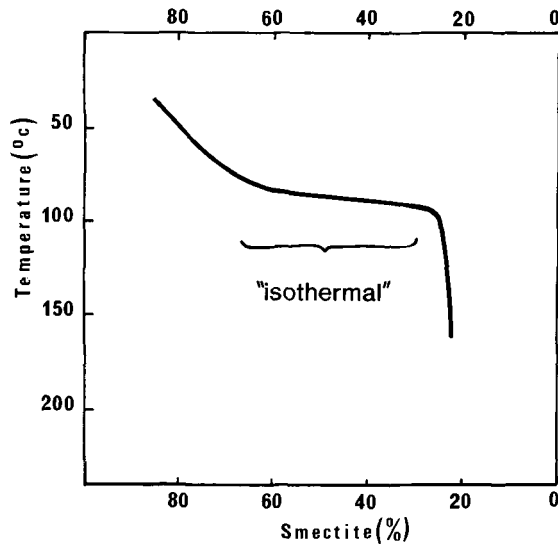


Figure 7. Composition-temperature relations for an "S"-shaped profile, Gulf of Mexico. Data from Hower *et al.* (1976). Change from 60–70% smectite to 20% smectite occurs over a short temperature interval.

two different slopes which produce the "S" curve (see Bruce, 1984, for such descriptions).

CONCLUSIONS

The data discussed here for several sequences of diagenetically transformed sediments show that the slope of the relation dx/dT for I/S is a function of geothermal gradient and I/S ordering type. The $R=3$ and $R=1$ (showing a 27-Å reflection) I/S varies the least with temperature. The $R=0$ and $R=1$ types in shallow sequences change the most with temperature. These factors can be used to identify paleo-sequences of diagenetic minerals; however, bulk chemistry can influence a diagenetic sequence, which can be identified by an abrupt change in the composition of the I/S. To interpret the conditions of diagenesis in clay mineral sequences, a series of samples from a large depth range must be analyzed to determine the type of evolution encountered. The possible influence of chemical variations in the active diagenetic system must also be considered.

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(Received 17 April 1984; accepted 5 March 1986; Ms. 1376)