Estimation of the diagenetic smectite to illite transformation in time-temperature space

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Abstract

A model is proposed to estimate the change in expandability of illite/smectite (I/S) minerals during burial diagenesis. This model uses a classical, first-order kinetic formulation. The values of activation energy and the preexponential constant are derived empirically by fitting the expandability of I/S minerals in samples from six deep wells in three sedimentary basins (U.S.A. and Japan) that had various burial rates. The series range in age at greatest depth from 4 to 150 Ma. Present thermal gradients are assumed to have pertained during the burial history of the sediments investigated, i.e., the upper three-fourths of the basin history. The derived kinetic values were tested on a seventh, older well (France, 210 Ma at greatest depth).

A one-step reaction model cannot be fitted to all of the different wells. Following mineralogical, crystallographic indications and the results of experimental studies, the I/S series was divided into two reactions: one involving the disordered $R = 0$ structure minerals (100–50% expanding layers) and the other the ordered $R = 1$ I/S (50–0% expanding layers). Reduction of expandability of the $R = 0$ minerals is assumed to determine the initiation of the second reaction. The second reaction shows progressive illitization of the ordered, $R = 1$ mineral that initially contained 50% smectite.

The first reaction was fitted with a 69.7 kJ/mol activation energy and a preexponential factor of 2.17 10^9/Ma. The second reaction has a fitted activation energy of 37.4 kJ and a preexponential factor of 1.34 10^3/Ma. These kinetic values were obtained by an optimization procedure using all of the 125 experimental points for six wells.

The derived kinetic values show that the clay reaction is very time sensitive (low activation energies and preexponential factor) and much less temperature sensitive than many previous estimates based upon laboratory experiments.

Introduction

The proportion of smectite or expanding layers in illite/smectite interstratified minerals (I/S) has been observed to decrease during burial diagenesis as well as in geothermal alteration (see Velde, 1985, for a summary). Because temperature, time, and some chemical variables can change simultaneously, it is difficult to attribute with certainty the parameters that affect the apparent smectite to illite reaction series. Depth-dependent variations in smectite content (expandability) of the I/S minerals can be significantly different in different parts of one sedimentary basin (Bruce, 1984), demonstrating that a study of sediments in a single portion of a basin can lead to conclusions that cannot be generalized. Estimations of the rate of change of expandability of I/S in specific wells or wells from one portion of the Gulf Coast basin have led to various hypotheses. For example, in the Texas and Louisiana Gulf Coast sedimentary series, Morton (1985) and Freed and Peacor (1989) observe that the smectite to illite reaction occurs over short present-day temperature intervals in different wells. This observation leads to the concept of punctuated diagenesis (Morton, 1985), i.e., one with very rapid reaction rates. Using data from similar stratigraphic sequences in the same area, Bethke and Altaner (1986) and Dutta (1986) propose very different kinetic models for the smectite to illite reaction. However, application of these models to other sequences in the same basin or in geothermal areas does not explain the relationships observed between expandability and depth (see Jennings and Thompson, 1985).

One way of investigating the kinetic aspect of the smectite to illite reaction is to compare the change in I/S composition with that of another mineral reaction in the same rocks in sedimentary series of different ages. Velde and Espitalié (1989) showed that there is definitely a kinetic factor in the smectite to illite transformation by comparing the maturity of organic matter with expandability of I/S in the same samples for series of widely different ages (early Tertiary to Paleozoic). In this study it was clearly demonstrated that clays in old shallow sedimentary series evolve more than organic materials in the same rocks. The reverse is true for young basins. One can deduce that the clay reaction is much less temperature sensitive than

organic material maturation, and the former continues to proceed at low temperatures. Another comparison was made by Velde and Iijima (1988) between I/S evolution and zeolite facies in Paleogene sediments, 5–15 Ma, in Japan. It was shown that I/S clays seem to have reached the same state of maturity at the present-day temperature in deep wells in Japan. The zeolites found in the same rocks exhibit a facies transition as a function of time. I/S clays and zeolites in the same rocks evolved at different rates. The above cited studies indicate that kinetics is important in the change of I/S composition (expandability) and that the kinetic factors of the clay reactions are different from those of zeolites and organic matter.

There are basically two approaches that can be used to estimate the kinetic parameters of a reaction observed in a geological setting. The first is to use laboratory reactions to simulate the mineral transformations. Attempts in the past (Eberl and Hower, 1976; Roberson and Lahann, 1981; Howard and Roy, 1985; Whitney and Northrop, 1989) have given widely different estimations of kinetic values for I/S transformations, suggesting that the method might be subject to some difficulty. A second approach uses natural mineral assemblages from wells in different basins with a well-known, continuous burial history (depth-age relations). This method requires some assumptions concerning geothermal gradients over the history of the basin.

We propose to test the relations of depth and I/S composition using natural mineral series in sedimentary rocks of widely varying age in order to explore the time-temperature relations of I/S clay mineral changes.

EXPERIMENTAL METHODS

XRD determinations

This study is based upon X-ray diffraction (XRD) determinations of the illite and smectite content (or expandability) in I/S mixed layer clays. This method uses comparative data, i.e., in using the same method of estimation of mineral composition from one series of data to another, one can estimate the rate of change of mineral composition. The absolute values, or the precision of the determination of mineral composition, are not as important as the relative change in composition with respect to stratigraphic position in the sequence. The error in precision of determination is more important than the absolute value.

The I/S expandability (assumed to be smectite content in this paper) was determined using two XRD methods depending upon the structural ordering of the different layer components in the I/S crystallites. For $R = 0$ (disordered) I/S types, the maximum of the first-order peak under glycollated conditions was used for compositional identification. This peak was chosen because of its very high intensity and the low intensities of higher order peaks as well as interferences by the reflections of other minerals. Calculations of X-ray diffractograms of I/S were made using the Reynolds Newmod program (see Reynolds, 1980) to establish the change in XRD peak position

and peak width as a function of the percent smectite in I/S of the diffracting layers in the oriented specimens as well as the number (n) of coherently diffracting layers in the crystallites. Estimations of the shape and position of the peaks were made on background-stripped spectra, either calculated or experimental. According to the simulated XRD spectra, the width and position of the peak are a function of both composition and number of coherently scattering layers in the grains. The basal spacings of expanding layers (smectite) are assumed to be constant at 16.9 Å under ethylene glycol saturation and 10.0 Å for mica-like layers. It is further assumed that these distances do not change in a given diagenetic sequence because the exchange cation population is expected to be similar in all specimens, given the similarity of the minerals present in each specimen. Exchange cations are assumed to be dominated by Ca or Mg divalent ions rather than Na and K, which are selected against by the normal equilibrium exchange coefficients for all dioctahedral smectites (Velde, 1985, p. 123). Figure 1 shows calculated peak position and peak width at half height as a function of smectite content and the number of coherently diffracting layers in the clay particles. Figure 2 shows a typical sequence of diagenetic samples plotted in the width-position coordinates. In all of the series of samples investigated, the effect of diagenesis (increasing temperature, T, and time, t) increases the average number of coherently diffracting layers in the crystallites as the illite (10 Å) content increases.

This method of determining smectite content by peak width position was compared with that proposed and corrected by Inoue et al. (1989), which uses the peak-saddle method of estimation. The illite content deduced using the width-position method generally differs by 10% or less from that deduced from the peak-saddle method. This is possibly due to the fact that the peak-saddle method assumes that there is a constant number of layers diffracting in the crystal aggregates, which appears not to be the case in natural diagenetic series. According to the width-position method, the number of coherently diffracting layers in the diagenetic disordered I/S minerals increases with depth in a burial sequence.

The smectite content of the $R = 1$ type ordered I/S minerals was estimated using the position of the maximum of the combined (001) peak in the air-dried state. The model calculations assumed that the average crystallites had eight layers diffracting coherently (see Velde et al., 1986, for details). The $R = 1$ minerals in the samples studied had narrow peaks of the type that indicate a rather large number of layers in the diffracting domains. An increase in the number of layers diffracting does not change the peak positions significantly. The use of a single peak (under air-dried conditions) is more reliable when I/S and illite are present in the same sample (Lanson, 1990; Lanson and Champion, 1991).

Repeated measurements of the same sample suggest that the reproducibility errors are on the order of $\pm 5\%$ smectite.
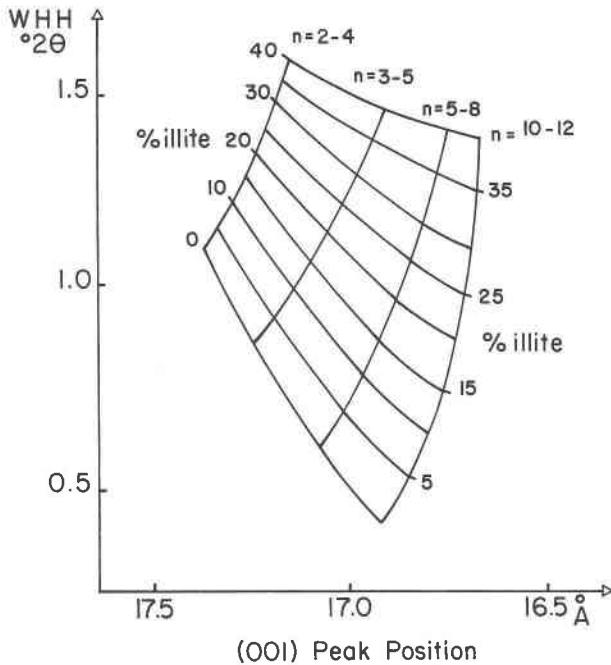
Fig. 1. Graphic representation of results of calculated XRD patterns for $R = 0$ structure minerals. Peak width of the first order band (WHH or width at half height) is plotted against peak position assuming an interlayer spacing of 10 and 16.9 Å for the illite and smectite layers. Composition (percent illite) and the number of coherently diffracting layers per particle (n) determine the peak position and width.

Samples

The suites of samples studied have been described for the most part. Information from the Texas Gulf Coast includes data from two onshore wells in Texas (Carter, Tyler County in central Gulf Coast Texas, and Peeler, Atoscosa County in south Gulf Coast Texas) published in Velde and Espitalié (1989). The age of the samples is lower Tertiary. Samples from a new well (Mustang Island near Corpus Christi, Nueces County) were added to the data base. The data for this well, which sampled Pleistocene sediments, were supplied by the Bureau of Economic Geology Repository in Austin, Texas.

We studied samples from two MITI wells in the young Niigata basin, Honshu Island, Japan (Masugata, Shimiogarshi). Also, samples were obtained from a well from the eastern edge of the very young Los Angeles basin, near Whittier (Orange County, California). The data for these wells can be found in Velde and Iijima (1988).

The well from the Paris Basin provided the oldest rocks studied. Data on this well have been published by Mathieu and Velde (1989). The well is near the center at Melun, showing almost none of the erosion known in the lower Cretaceous–upper Jurassic in the west of the basin nor the erosion in the late Cretaceous–early Tertiary that is known in the east of the basin. Thus, the well provides data on an almost complete burial sequence. However, as there were periods of erosion in the basin, there is no
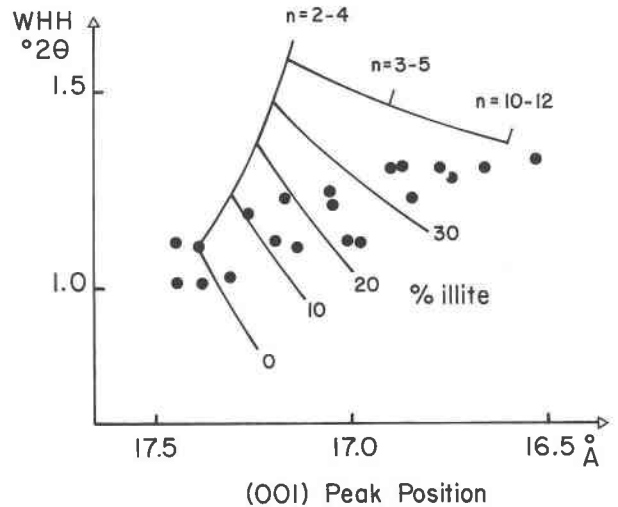

Fig. 2. Plot of the data for the California well on the coordinates of Figure 1.

guarantee that the thermal flux was constant; for this reason we consider the results from this well as a category separate from the others.

In all cases the deepest sediment analyzed came from a point at least one-fourth of the distance from the deepest part of the sedimentary basin (basement).

Figure 3 shows the burial histories of these wells plotted on age-depth coordinates. Measurements of stabilized bottom hole temperature were used to estimate linear thermal gradients for the deeper wells, and a measured geothermal gradient (Demongodin et al., 1991) was used in the shallower Paris Basin well. Figure 3 shows the rather smooth change in age with depth for the different wells. This seems to indicate that little or no erosion has occurred in the sequences of each well.

The bottom hole temperatures were measured in all cases after at least 12 h thermal stabilization time. As they are all 125 °C or higher, an error of less than 5–10 °C can be assumed (see Boles and Franks, 1979). The great depth of the wells and the relatively small error for a relatively high temperature permit reasonable estimations of average present-day thermal gradients. Figure 4 shows the estimated smectite content of the I/S mineral aggregate as a function of depth for each well. Little change is seen in the youngest well (4.5 Ma) at 5-km depth, whereas almost no smectite is left in the oldest well (210 Ma) at 2.5-km depth.

In these data sets, the wells of young and intermediate age show rapid burial, and there are almost no hiatii in the burial sequences in the sedimentary basins. These are the Japanese, Californian, and Texas Gulf Coast wells. Here we can assume rapid, continuous burial and can hope that there has been little significant change in the thermal parameters of the sedimentation sequence. However, in the oldest basin (Paris Basin) there are two known periods of erosion that, although they do not directly af-
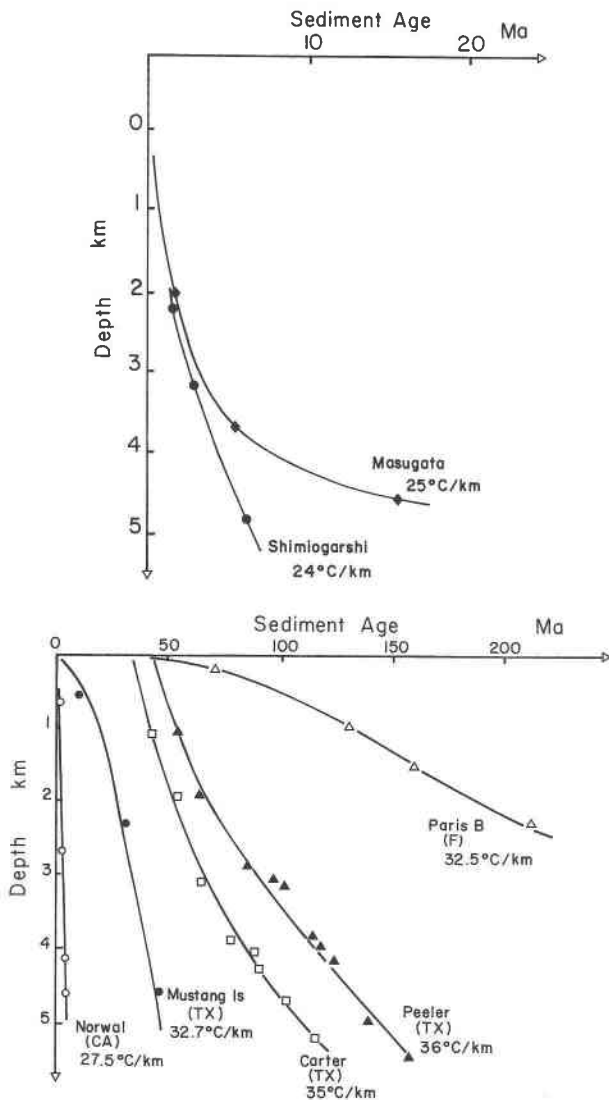
Fig. 3. Plot of depth and age of the sediments in the different wells used in the present study. Symbols on the curves indicate the points where age determinations were available. Thermal gradients are indicated as determined from bottom hole measurements.

fect the stratigraphic sequence in the well chosen, could indicate changes in thermal regime in the past.

We propose to use the six younger wells in the Japanese and American basins to establish the kinetic model because they present fewer problems with stratigraphic and geologic continuity. We will then use the derived kinetic formulation to simulate the clay evolution in the older Paris Basin as a test of the method.

In all the samples studied here, only the shale or mudstone was investigated. This insures chemical and mineralogical homogeneity of the samples. The rocks should have been a relatively closed system chemically (i.e., one where the solids dominate the chemistry of the solutions). This selection eliminates the often great changes in I/S

composition, seen over short depth intervals, that are due to changes in lithology and chemistry of the reacting system (Velde and Nicot, 1985).

ESTIMATION OF KINETIC PARAMETERS

Mineralogy of the smectite to illite transformation

The present paper attempts to develop a model for the change in average smectite content (expandable layers) of the overall I/S clay mineral assemblage as a function of depth in burial diagenesis. In this undertaking several initial conditions must be met and certain assumptions are made:

1. The smectite content of the samples used as a data base to derive the reaction model is determined by an estimation of the maximum of the peak representing the aggregate I/S, <2-μm clay mineral assemblage present in the mudstone samples. The XRD maxima given by the I/S mineral grains are treated as a whole, i.e., no attempt was made to decompose possible composite peaks due to the existence of two different mineral phases ($R = 0$ and $R = 1$) into individual population components (see Lanson and Champion, 1991). Thus all of the crystallites of both $R = 0$ and $R = 1$ structures present in the same sample that diffract in the same angular 2θ region are assimilated into a single phase. This is particularly important when $R = 0$ and $R = 1$ phases appear together in similar quantities in the 40–60% smectite region. The I/S mineral aggregate found before and after this intermediate compositional range is dominated by either the disordered, $R = 0$ smectite-rich or the ordered, $R = 1$ illite-rich mineral that can be considered single phase assemblages of crystallites in these compositional ranges. The most reliable data then come from the beginning and the end of the smectite to illite conversion series.

2. It is assumed that the same mineralogical phase is present in all examples at a concentration of 100% reactant at the inception of the reaction. This prerequisite is most likely fulfilled in the burial diagenesis examples investigated here. It should be noted that the stage of 100% smectite does not necessarily occur at the surface in a well. Data presented and commented upon by Velde and Iijima (1988) for wells in Paleocene sediments, by Jennings and Thompson (1985) for geothermal sedimentary reactions, and by Hower et al. (1976) and Freed (1982) in upper portions of Tertiary Gulf Coast wells show that the upper 1–2 km of clays in young sedimentary basins often show great variability in I/S smectite content from one stratigraphic level to another. However a 100% smectite phase most often becomes dominant at greater depths. The older the sedimentary series, the shallower the point at which 100% smectite occurs. In young basins, the upper heterogeneous zone represents the detrital, unreacted sediment material where the proportion of pure smectite is most often small and not well identified. The change from the variable composition I/S mineral assemblages to an almost pure smectite mineral in the wells occurs over a range of several hundreds of meters in older wells
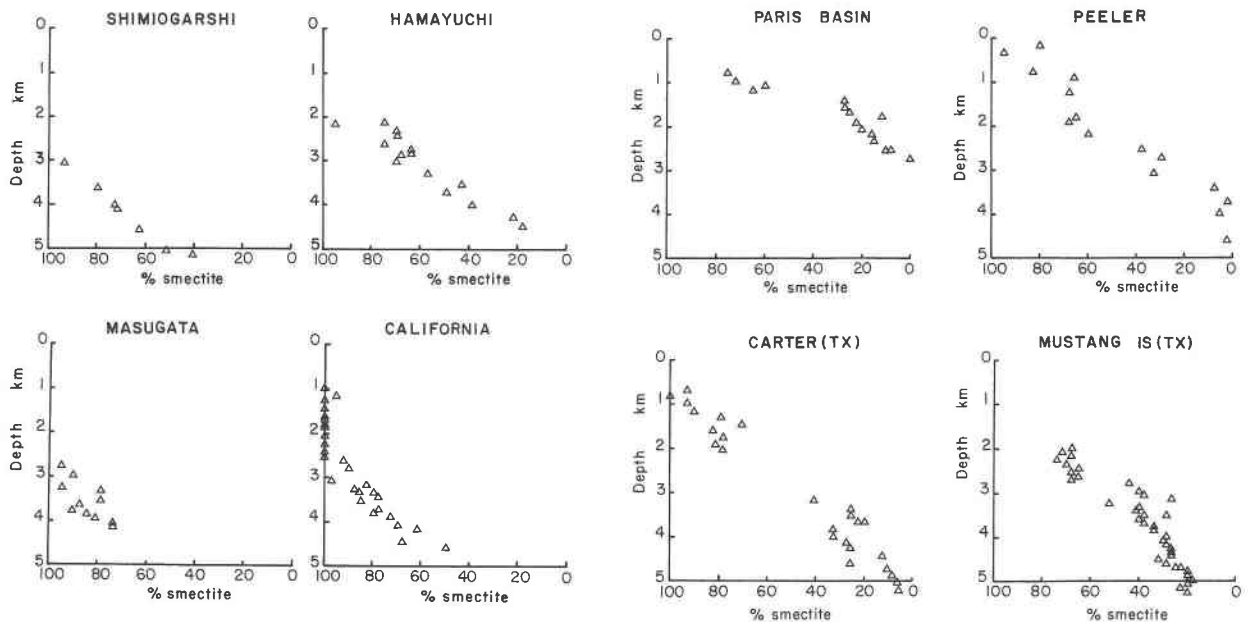
Fig. 4. Results of determinations of the smectite contents of the I/S clays in the different wells used in the present study.

to 1–2 km depth in younger wells. The 100% smectite mineral assemblage evolves at further depth in a regular manner toward the illite composition (Velde and Iijima, 1988). This indicates that there is a recrystallization at depth where initial detrital I/S minerals and other material form a pure smectite mineral, which is the starting point for the smectite to illite transformation in diagenesis.

3. In a chemical reaction, mineralogical continuity of the components during the reaction must be established. In different geological environments in shales, the chemical composition of the expandable, smectite layer in the I/S minerals appears to be almost identical in different stages of a reaction series (Velde and Brusewitz, 1982; Meunier and Velde, 1990), and hence the reaction concerning smectite should be chemically similar. However, Šrodoń and Eberl (1984) find that the composition of the illite component changes at the midpoint of the compositional series in bentonites. Thus the reaction is most likely not homogeneous concerning the two major components of the mixed-layer mineral, but it could be considered as two series of compositions.

Further, in the I/S minerals there are at least three structurally and morphologically distinct crystalline forms: flake-shaped crystals for smectite-rich forms with an $R = 0$ disordered stacking sequence (100–50% smectite), lath-shaped $R = 1$ ordered structure crystals (50 to near 0% smectite), and hexagonal shaped, illitic crystals (see Lanson and Champion, 1991, for a summary of these observations).

Therefore the I/S reaction sequence cannot be considered to be homogeneous, either chemically or structurally. In fact there are two series of I/S minerals, and hence one could expect two successive reactions.

Physical parameters

In the case of burial diagenesis, estimation of physical parameters involves a detailed knowledge of stratigraphy and estimations of paleo-temperatures. The stratigraphy of the sediments in the wells investigated shows rather smooth curves in the depth-age plots. This indicates that no significant uplift or erosion has occurred in the basin at the location studied. However, several wells are located on older than present-day sediments, indicating that there could have been some erosion in the latest stages of the sequence. Small amounts of late-stage small erosion will not greatly affect the estimations sought here.

Very simple assumptions were used for estimating the temperature history of the sediments. First, thermal conductivity variations as a function of depth were neglected. The temperature gradient is therefore assumed to be constant and its present value is deduced from thermally equilibrated bottom hole temperature measurements. Second, the variation in thickness of the sedimentary layers as a function of compaction was not taken into account. These two effects can however, be considered as second-order corrections.

Estimations of paleo-gradients pose greater problems because they could have varied over time and therefore not represent the current value. Basin evolution is currently associated with a thermal phenomenon such as in the stretching model of MacKenzie (1978). Initial stages of linear basin evolution have a higher heat flow, which diminishes in several tens of millions of years to attain a thermal equilibrium. However, from our data sets, the youngest basins show the lowest current thermal gradients (Fig. 3); the gradient shows a steady increase with the age of the basin. This observation could reflect the

great differences in sedimentation rates in the wells studied or something more fundamental in the evolution of thermal gradients in basins. In any event, according to current models one could hardly expect the young basins studied here to have had a high initial gradient and then have cooled to such low values so rapidly while the intermediate age basin (Gulf Coast), which has a similar tectonic setting, heated up in its later stages of evolution.

As a first approximation, we will then assume that the present thermal gradient was one that was maintained throughout most of the history of the sediments studied (the upper three-fourths of the basins).

Reaction kinetic formulations

The basic assumption in the present study is that the overall formulation of the complete smectite to illite reaction can be modeled using the formalism of a first-order reaction. This follows previous attempts in the same direction (Eberl and Hower, 1976; Dutta, 1986; Bethke and Altaner, 1986, among others). This is not the assumption of Pytte and Reynolds (1989), Whitney and Northrop (1989), nor Elliott et al. (1991), who use a variable higher reaction order approach to fit illite-smectite compositional change. We have chosen this method in our approach because first-order reactions have often been considered to represent adequately complex reactions in which a rate-limiting reaction step predominates in reaction advancement (Lasaga, 1981).

One-step model. Our initial approach used a simple first-order, one-step reaction to model the entire range of I/S compositional change in all the wells, even though mineralogically there are obviously two sequences of I/S minerals. This one-step formulation will give an idea of the general reaction relations for younger and older wells.

The basic equations for a one-step reaction are

$$dS/dt = -kS, \quad S = S_0 e^{-kt}$$
$$k(t) = A e^{-E/RT(t)} \tag{1}$$

and, by the identity $A = e^{\log A}$,

$$k(t) = A e^{-E/RT(t)} = e^{\log(A) - E/RT(t)} \tag{2}$$

where S is the smectite phase, $k(t)$ is the time-dependent reaction constant, t is time (Ma), T is the temperature in degrees kelvin, E is the energy of activation in kilojoules per mole, A (Ma^{-1}) is the preexponential factor (considered constant over the temperature interval studied), and R the universal gas constant. Since the age of the sedimentary layer, temperature at burial depth, and mineral composition are considered to be known, the essential variables to be determined are E and A.

The reaction progress for a point in a well can be calculated using fixed kinetic parameters. For a layer deposited at time t, S (smectite content) is given by

$$S(t) = S_0 e^{-\int_0^t k(t')dt'} = S_0 e^{-\int_0^t e^{[\log(A) - E/RT(t')]}dt'} \tag{3}$$

where S_0 is the initial smectite portion in the I/S and k is

the reaction constant that depends on t from the temperature history $T(t)$. In this expression one can see that if T does not vary greatly, E/RT and $\log A$ will have approximately the opposite effect on the value of k and thus on the value of S. Therefore an increase in one can be compensated by an increase in the other, giving approximately the same estimation of S. As a result, one could expect difficulties in estimating the effects of E and A from observed values of S in one well.

In a one-step model one must determine the value of the kinetic parameters (here E and $\log A$) that give the best fit between observed smectite content and calculated values. In order to solve this highly nonlinear problem, we used the Baysian approach developed by Tarantola and Valette (1982). This method allows one to compute iteratively the optimum values of the parameters $\log A$ and E that give best least-squares fit of the data. Moreover, it allows an estimation of the confidence domains of the parameters. An error of $\pm 5\%$ was assumed for the smectite content of the I/S minerals analyzed. When applied to each well independently, this gives valus of $\log A$ and E as shown in Figure 5. The values are highly scattered and the confidence domains do not overlap. Figure 6 shows the computed smectite content for four different wells using the derived parameters of each well. Obviously it is not possible to fit the various series of data with a single set of parameters. Younger and older wells differ markedly.

Dual reaction model. Despite the negative result using a one-step reaction model, a careful examination of Figure 6 shows that for the younger wells where the smectite content is dominated by 100–60% smectite in I/S with the disordered, $R = 0$ structure, the estimates show a high activation energy and a high $\log A$, whereas in the wells where the expandability is in the 50–0% range (dominated by the $R = 1$ ordered minerals in the older wells), estimates show lower activation energies and $\log A$ values. This suggests that there are two kinetic processes occurring in two reactions, and this view is supported by the content of the I/S minerals (Inoue et al., 1988) and also by experiments on natural minerals (Whitney and Northrop, 1989).

A new model of I/S evolution is divided into two parts with sequential reactions that determine the aggregate smectite content of the I/S clays in the sediments. In this reaction sequence we assume that once a smectite layer becomes illite in the $R = 0$ I/S mineral, this illite layer is associated with a smectite layer to form an ordered, $R = 1$ structure mineral (M). The mineral M is then gradually modified by adding illite in the second reaction, thus reducing its smectite content.

We therefore write for the two reactions:

$$\frac{dS}{dt} = -k_1 S \qquad \text{with } \log(k_1) = \log(A_1) - \frac{E_1}{RT} \tag{4}$$

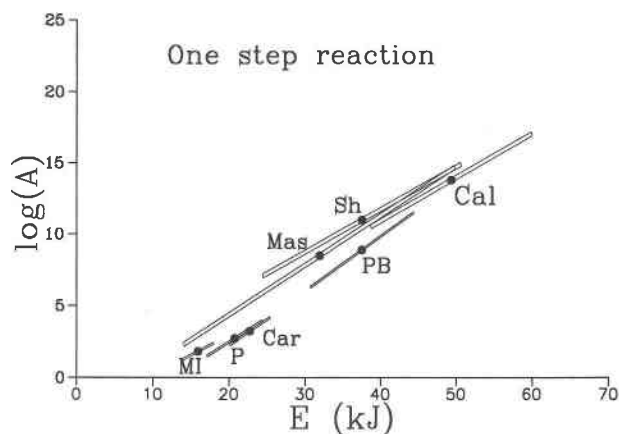$$\frac{dM}{dt} = k_1 S - k_2 M \quad \text{with } \log(k_2) = \log(A_2) - \frac{E_2}{RT} \tag{5}$$

Fig. 5. Plot of the parameters log A and E (activation energy) using a one-step model for each well. The value (dot) and confidence domain (rectangle) are shown for the wells MI = Mustang Island, Texas; P = Peeler, Texas; Mas = Masaguta, Japan; Sh = Shimiogarshi, Japan; Cal = California Los Angeles Basin; PB = Paris Basin.

where S corresponds to the smectite concentration of the disordered, $R = 0$ I/S mineral in the first reaction and M to the concentration of the ordered, $R = 1$ I/S mineral. The smectite content of this mineral is 50% or $M/2$. The k_1 and k_2 are two kinetic coefficients for each A_1, E_1 and A_2, E_2.

Starting from S_0, pure smectite, the integration of these kinetic laws gives

$$S(t) = S_0 e^{-\int_0^t k_1(t')dt'} \qquad (6)$$

$$M(t) = S_0 e^{-\int_0^t k_2(t')dt'} \cdot \int_0^t k_1(t')e^{-\int_0^{t'} [k_2(t'')-k_1(t'')]dt''} dt'. \qquad (7)$$

The overall aggregate smectite content of a sample at any time is given by $S + (M/2)$. The problem is now to define the set of four parameters ($\log A_1$, E_1, $\log A_2$, E_2) that best explains the experimental data for the six wells. As often occurs when many parameters must be determined simultaneously, this problem is very unstable and there are too few data in each well to perform a significant regression on the whole set of parameters.

Therefore, the inversion procedure was applied to the data set composed of the six younger basins (Japanese and American) using 125 data points. The result of this inversion appears robust (does not depend upon the a priori starting point). It leads to the following set of parameters:

$\log(A_1) = 21.5 \pm 0.8\,(\text{Ma}^{-1}), \quad E_1 = 69.7 \pm 2.5\,\text{kJ/mol}$

$\log(A_2) = 7.2 \pm 1.1\,(\text{Ma}^{-1}), \quad E_2 = 37.4 \pm 3.6\,\text{kJ/mol}.$

The confidence domains (Fig. 7) are quite small, showing that the values are well constrained. The resulting parameter set models the observed data for the different wells quite satisfactorily (Fig. 8). The contribution of each of
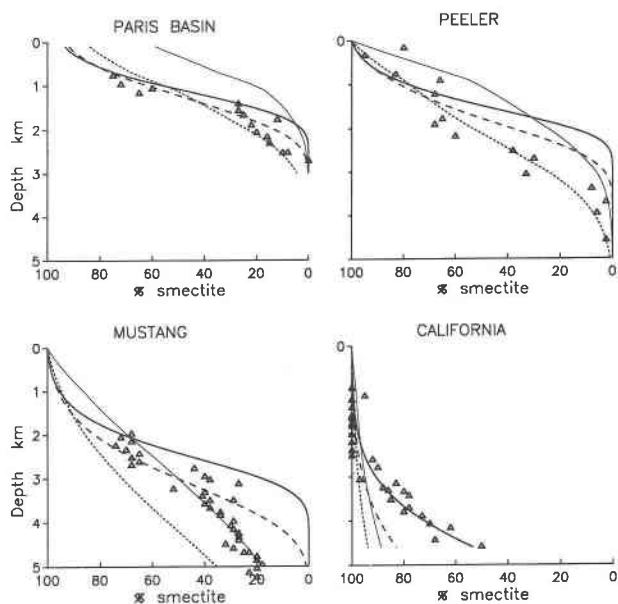

Fig. 6. Comparison of calculated smectite contents using the kinetic values derived using the one-step reaction model for each well. Heavy solid line shows predictions using the derived values for the California well ($E = 50$ kJ/mol, log $A = 14$); dashed line denotes compositions derived using the Paris Basin kinetic values ($E = 37.5$ kJ/mol, log $A = 9$); dotted line shows Peeler values ($E = 20.7$ kJ/mol, log $A = 2.7$); light line is Mustang Island values ($E = 16$ kJ/mol, log $A = 1.8$).

the two reactions to smectite content (i.e., S and $M/2$) are also displayed. In order to obtain the aggregate smectite content curve (solid line) of the sequence, one must add the smectite content of the dotted and dashed curves for a given depth. In most cases the agreement between the observed and the predicted values is satisfactory.

Given these kinetic parameters, one can simulate the I/S reaction in the older Paris Basin (210 Ma). Initially we use the present-day thermal gradient of 32.5 °C/km. It can be seen in Figure 9 that the shape of the curve is in good accord with the data points, indicating that the trend is correct and that the two-step reaction model is adequate, but the reaction does not seem to have advanced far enough.

A second simulation was made using a higher gradient, 45 °C/km, with much greater success. It seems that the kinetic values for a two-step reaction give good results for the older Paris Basin (210 Ma at the deepest observation point), but allowance should be made for a slightly higher overall (integrated over the total period of sedimentation) temperature. As mentioned above, it is possible that there has been erosion of an upper part of the section in early Tertiary times as the section studied outcrops in Eocene sediments, but burial of several hundred meters for such a short period of time will not greatly affect the maturity of the clays in the sequence studied. There are, however, other data that suggest significantly higher temperatures than those of the present. The ma-
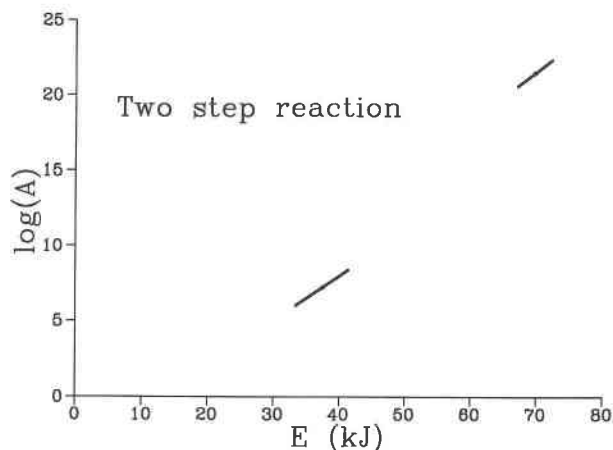
Fig. 7. Confidence domains of the best fit values of kinetic factors using a two-step reaction model for $R = 0$ and $R = 1$ mineral reaction series.
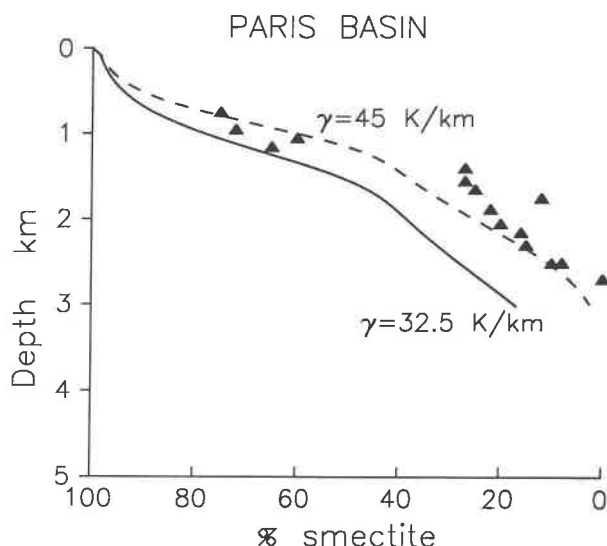

Fig. 9. Calculated composition-depth curves for the Paris Basin well using the present geothermal gradient (solid line) of 32.5 °C/km and dashed line for 45 °C/km.
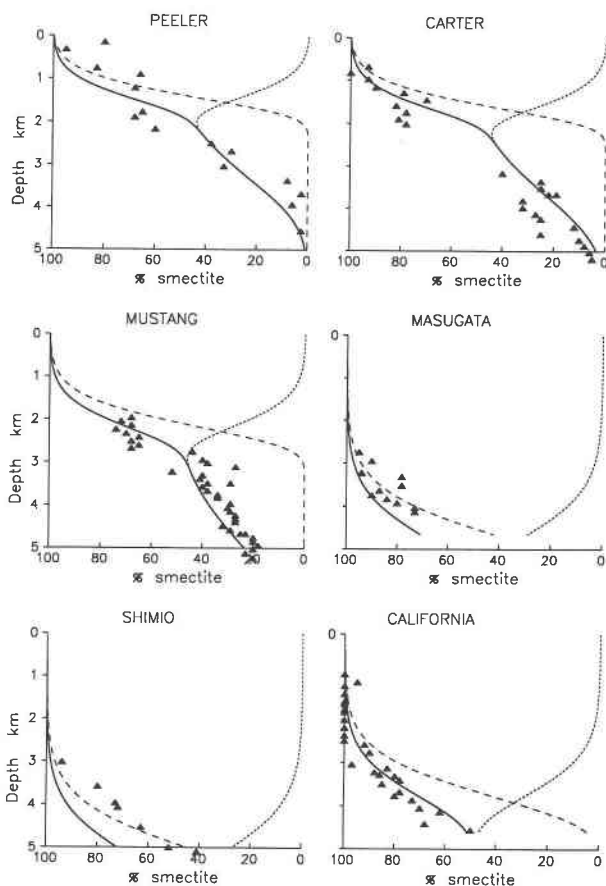

Fig. 8. Calculated and observed smectite contents of the I/S minerals for the six test wells using the two-step reaction model. Solid line is the total smectite content; dashed line is the contribution resulting from the first reaction involving the $R = 0$ phase; dotted line is the smectite contribution from the second $R = 1$ reaction.

turity of organic material in the Jurassic sediments (type II) observed by Espitalié (1986) and Price (1983) suggests that higher maximum temperatures have occurred in the basin, by about 30 °C. Fluid inclusions (Guilhaumou and Gaulier, 1991) also indicate higher maximum temperatures of sediments at 2000-m depth. This, then, suggests a thermal history of the Paris Basin different from that given by the present gradient. In using a higher average thermal gradient for the clay maturation sequence, one can adequately explain observed clay compositions in the Paris Basin.

DISCUSSION AND CONCLUSIONS

The use of a two-part reaction model seems plausible given the knowledge of the XRD structural data, the crystal morphology differences for the two I/S minerals ($R = 0$ and $R = 1$), the results of laboratory experiments, and the very poor results from a one-step reaction model for the data from the various sedimentary basins studied here. The broad range in ages of the sediments used in the present study reinforces the overall validity of the model. If reasonable fits can be made for data in the 4–210 Ma range, it is highly likely that the model can be used in general applications, whatever its imperfections might be.

Questions can be raised concerning the relatively low activation energies for both of the steps in the change from smectite to illite. One can compare the derived activation energies of 70 and 37 kJ/mol for the two parts of the burial diagenesis series with those obtained in syntheses of the smectite to illite reaction in laboratory experiments. Experiments using synthetic or natural clays (Eberl and Hower, 1976; Roberson and Lahann, 1981; Howard and Roy, 1985) indicated values ranging from 120 to 15 kJ. As a comparison, Chermack (1989) deter-

mined a value of 155 kJ for experiments on the reaction kaolinite + K+ → muscovite.

In all of the experimental studies the temperatures exceeded 200 °C, well above those experienced by the diagenetic sedimentary mineral series investigated. The fitted activation energies for the two-part reaction in the smectite to illite conversion lie within the experimental estimations, but their range is so great that they do not validate nor do they invalidate the results obtained by modeling the natural mineral reactions.

It is known from studies on other silicate mineral reactions that energies of 80–100 kJ are necessary for reactions involving disruption of bonds in silicate structures (Lasaga, 1981) such as those indicated by Chermack (1989) for the change from kaolinite to muscovite. Such small values as 37–70 kJ/mol are more characteristic of ion exchange or mineral dissolution than transformation. This might suggest that dissolution of unstable phases such as micas and potassium feldspar, which provide K from the detrital component of a sediment, are very important to reactions in diagenesis, whereas those of bond breaking and transformation might be more typical of higher energy situations such as hydrothermal alteration and experimental modification of silicate mineralogy in the laboratory. The very slow rate of change in the smectite to illite reaction of diagenetic rocks seems to indicate that the controlling mechanism is not the same as that in high-temperature environments.

Whatever the model proposed here lacks in accounting for reaction mechanisms and order of the overall reactions, it does appear to be a useful tool to describe the smectite to illite transformation over large ranges of reaction times, 4–200 Ma.

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