Clays and Clay Minerals, Vol. 44, No. 1, 77–87, 1996.

EVALUATION OF KINETIC MODELS FOR THE SMECTITE TO ILLITE TRANSFORMATION

W. CRAWFORD ELLIOTT[1] and GERALD MATISOFF[2]

[1]Department of Geology, Georgia State University, Atlanta, Georgia 30303

[2] Department of Geological Sciences, Case Western Reserve University
Cleveland, Ohio 44106

Abstract—Three different models have been reported previously to describe the kinetics of the transformation of smectite to illite (Pytte 1982; Velde and Vasseur 1992; Huang et al. 1993). In order to evaluate the general utility of these models to calculate the timing and extent of this transformation, each model was applied to four different geologic settings (Denver Basin, Gulf Coast, the Salton Sea Geothermal System, and Paris Basin) in which the ages, geothermal gradients and potassium ion activities vary markedly. The model results are compared to the measured percentages of illite in illite/smectite (I/S) and the K/Ar ages of I/S (if available) to test the utility of a given model to a particular basin.

Although individual models can be applied to study this transformation within a specific setting, none of these models was successful in simulating the transformation for all four basins. The Salton Sea was simulated best using the model by Huang et al. (1993), which incorporated an increased geothermal gradient during the last 20,000 years. These results indicate that a large fraction of illite formed due to this increased geothermal gradient, and underscores that temperature is a dominant kinetic factor in forming illite. The Denver Basin was simulated well by the models of Velde and Vasseur (1992) and Pytte (1982). The Gulf Coast was simulated very well by the model of Huang et al. (1993) using a term that terminates the transformation at 75% illite. For the Paris Basin, the results are mixed. The models can be refined by comparing the calculated and measured ages of illite such as the K/Ar ages of I/S to understand the thermal history of a particular basin. The calculated ages of illitization derived from these refined models can be used to indicate the time at which source rocks became thermally mature to form oil and gas.

Key Words—Illite, Kinetics, Models, Smectite.

INTRODUCTION

The kinetics of the smectite to illite transformation, smectite illitization, have been deduced through noting the increase in the percentage and ordering of illite layers within illite/smectite (I/S) in response to various geologic processes such as progressive burial (Hower et al. 1976); thrust sheet burial (Hoffman et al. 1976; Altaner et al. 1984); contact metamorphism (Pytte 1982; Pytte and Reynolds 1988); and increased geothermal gradients (Jennings and Thompson 1986; Inoue et al. 1988). While increased temperature appears to be a common factor triggering smectite illitization, the ion activities of potassium and other cations (Ca^{2+}, Na^+ and Mg^{2+}) also affect the rate of this transformation and the formation of authigenic illitic clays in reservoirs (Roberson and Lahann 1981; Howard and Roy 1985; Huang 1992; Huang et al. 1993). Time is the least understood factor affecting the rate of this transformation. The duration of the transformation has been estimated at various temperatures only through mathematical modeling, and it should decrease with increasing temperature (Pytte 1982; Pytte and Reynolds 1988; Elliott et al. 1991).

In addition to the effects of temperature, time, and potassium content on the rate of smectite illitization; the stoichiometry and mechanism of the transformation is still in debate. Aluminum conserved, and non-aluminum conserved, reactions have been proposed to describe the transformation in the Gulf Coast shales (Hower et al. 1976; Boles and Franks 1979). These reactions, as derived by Boles and Franks (1979), are shown below:

Al-conserved:

$$\begin{aligned} 3.93\ K^+ + 1.57\ \text{Smectite} \rightarrow\ & \text{Illite} + 1.57\ Na^+ \\ & + 3.14\ Ca^{+2} \\ & + 4.28\ Mg^{+2} \\ & + 4.78\ Fe^{+3} \\ & + 24.66\ Si^{+4} \\ & + 57\ O^{-2} \\ & + 11.40\ OH^- \\ & + 15.7\ H_2O \qquad [1] \end{aligned}$$

Non Al-conserved:

$$\begin{aligned} 4.5\ K^+ + 8\ Al^{+3} + \text{Smectite} \rightarrow\ & \text{Illite} + Na^+ + 2\ Ca^{+2} \\ & + 2.5\ Fe^{+3} + 2\ Mg^{+2} \\ & + 3\ Si^{+4} + 10\ H_2O \qquad [2] \end{aligned}$$

In the Al-conserved reaction (Equation [1]), 1.57 moles of smectite react to form only 1 mole of illite. This leads to an illite volume produced that is considerably less than the smectite that has reacted because silica and water are lost. The non Al-conserved reac-

https://doi.org/10.1346/CCMN.1996.0440107 Published online by Cambridge University Press

tion (Equation [2]) is commonly expressed by the following reaction (Altaner 1989):

$$K^+ + X - \text{Smectite} \rightarrow \text{Illite/smectite} + \text{Quartz} + X^+ \quad [3]$$

Recently, a third reaction suggested that the transformation occurs as a consequence of the reduction of silica activity at the onset of quartz precipitation (Abercrombie et al. 1993):

$$\text{K-feldspar} + \text{K-smectite} \rightarrow 2\ \text{Illite} + 4\ SiO_2(aq) \quad [4]$$

The rate of the transformation certainly depends on the activity of potassium and temperature, and one or both of these two parameters have been considered explicitly in the extant mathematical models of the transformation (Pytte 1982; Velde and Vasseur 1992; Huang et al. 1993). However, these models do not account explicitly for the activities of Al, Si, pH or $p(H_2O)$ nor for the simultaneous dissolution of K-feldspar, which clearly are important parameters as seen in the reactions above (Equations [1], [2], [4]).

With respect to the mechanism, there are two end-member hypotheses. As seen through X-ray diffraction, smectite transforms to illite as a solid-state transformation on an intact alumino-silicate lattice to illite via a series of interstratified phases of illite/smectite (Reynolds and Hower 1970; Hower 1981; Bethke and Altaner 1986). Following the Gulf Coast studies, the type of stacking order of mixed layer I/S and the percentage of illite layers in I/S have been used successfully as semi-quantitative geothermometers for basins of Mesozoic age and younger (Hoffman and Hower 1979; Pollastro 1993). Alternatively through transmission electron microscopy examination, smectite is seen to transform to "fundamental" illite particles either by a dissolution-reprecipitation process (Boles and Franks 1979; Nadeau et al. 1984; Ahn and Peacor 1986) or by Ostwald ripening (Morse and Casey 1988; Eberl et al. 1990; Eberl 1993). While the "fundamental" particles have been shown to have been an artifact of sample preparation, three distinct crystalline forms, flakes, laths, and hexagonal plates, have been observed through electron microscopy (Inoue et al. 1988; Ahn and Buseck 1990). The occurrences of these forms of illite as well as isotopic studies have suggested the transformation is composed of at least two sequential reactions, for example K-exchange followed by neoformation, as opposed to a continuous transformation (Whitney and Northrup 1988; Lanson and Champion 1991). Additionally, Eberl (1993) argued that the transformation is proceeding via an Ostwald ripening in I/S at the deepest depths (3–4 km) in the Gulf Coast well CWRU #6 based on the increase in the amount of 2–5 μm fraction, a concomitant decrease in the <0.1 μm fraction, and a loss of radiogenic Ar ($^{*40}Ar$) from I/S.

Mathematical modeling has the potential to increase our understanding of the kinetics and the mechanism(s) of this transformation. Through this approach, if a model simulates well the transformation for a given geologic setting and/or settings, then this model could be used to understand the effects of time (duration), potassium concentration, and temperature on the extent of the transformation. In addition, agreement between simulation results and data support the postulated transformation mechanism. Since the transformation involves the uptake of potassium, a portion of which is radiogenic ^{40}K, the timing and duration of the transformation can be calculated from the models and can be used to test them. Once verified, the model may be applied to predicting when rocks are heated to form oil and gas such as in the Wattenberg Field, Denver Basin (Elliott et al. 1991; Huang et al. 1993).

The main purpose of this study was to apply each of these models to calculate the timing and extent of illitization in the Denver Basin, the Gulf Coast, the Salton Sea Geothermal System, and the Paris Basin. The ages of these geologic settings vary from 210 Ma (Paris Basin) to 3 Ma (Salton Sea). The geothermal gradients and the potassium concentrations are specified for each setting and also vary markedly among the geologic settings being studied. The model results are compared to the measured percentages of illite in I/S and the K/Ar ages of I/S (if available) to evaluate further the utility of each of the kinetic expressions. The application of these kinetic expressions of smectite illitization to widely different geologic settings are good tests of these models.

The Models

Presently, there are three prominent published models of the smectite to illite transformation (Pytte 1982, hereafter referred to as the Pytte model; Velde and Vasseur 1992, hereafter referred to as the Velde and Vasseur model; and Huang et al. 1993, hereafter referred to as the Huang et al. model). All these models employ or tacitly assume a non Al-conserved reaction (Equations [2] and [3]) first posed by Hower et al. (1976) in which a loss of smectite is set equal to a gain in illite on a molar basis. Pytte and Huang et al. both conclude that their models simulate smectite illitization well for the Gulf Coast. Pytte's model has been applied to calculate the amount of illite formed in a K-bentonite resulting from diffusion of potassium into a thick bentonite followed by a reaction to form illite (Altaner 1985, 1989; Elliott 1988; Elliott et al. 1991). The Velde and Vasseur model was applied successfully to the Paris Basin and to several younger basins.

In all three models, the loss of smectite, and consequently a gain in illite, is calculated using an Arrhenius-type kinetic expression derived either from experimental syntheses of illite or from iterative curve

Table 1. Parameters used in the kinetic models.

	Pytte	Huang et al.	Velde and Vasseur
α	4	2	1
β	1	1	—
Ea (kJoules/mole)	125.52	117.15	37.24, 67.78
A (sec^{-1})	90,000	80,800	6.9×10^{-5}, 4.25×10^{-11}

fitting to calculate the rate of transformation (Pytte 1982; Pytte and Reynolds 1988; Velde and Vasseur 1992; Huang et al. 1993). The models differ primarily with respect to the overall order of the kinetic expression and to the term describing the dependency of potassium concentration for the transformation. In the Pytte and Huang et al. models, the kinetic expressions are non-first order: third order overall (Huang et al.) and fifth or sixth order overall (Pytte). The Velde and Vasseur model is the most recent example of a first order overall kinetic expression (Dutta 1986; Bethke and Altaner 1986), and it does not have a term for potassium concentration.

In Pytte's model, the kinetic expression used to calculate the amount of smectite lost (S), is given by:

$$\frac{\partial S}{\partial t} = -\kappa S^{\alpha}\left(\frac{[K^+]}{[Na^+]}\right)^{\beta} \qquad [5]$$

where

α = smectite order parameter (dimensionless),
β = potassium order parameter (dimensionless),
and
κ = Arrhenius-type illitization reaction rate constant ($time^{-1}$):

$$\kappa = A\exp\left(-\frac{E_a}{RT}\right) \qquad [6]$$

where

E_a = activation energy (Joules/mole),
A = pre-exponential constant ($time^{-1}$),
R = gas constant (8.314 Joules/mole K),
and
T = absolute temperature (K).

The overall reaction order is defined by the sum of α and β. We employed Pytte's fifth order value ($\alpha = 4$ and $\beta = 1$). The potassium concentration of the pore solutions is expressed as a ratio to sodium concentration ($[K^+]/[Na^+] = 0.1$). The values for activation energy, E_a, and the pre-exponential constant, A, used in Pytte's model are listed in Table 1.

In Huang et al.'s model, a kinetic expression similar to Equation [5] is also used to calculate the loss of smectite:

$$\frac{\partial S}{\partial t} = -\kappa S^{\alpha}[K^+]^{\beta} \qquad [7]$$

However, Equation [7] differs from Equation [5] in two ways. First, the potassium concentrations, $[K^+]$, of the pore solutions are specified, as opposed to being expressed as an ion ratio as in Equation [5]. Second, the overall order ($\alpha = 2$ and $\beta = 1$) and the values of E_a and A used to calculate the smectite illitization rate constant, κ, are different from those used by Pytte in Equation [5].

The Velde and Vasseur model considers the transformation of smectite to illite to be a two-step sequential reaction process described by Equations [8] and [9] below. First, smectite in I/S is converted to random ordered I/S (Equations [8]); then from random ordered I/S to ordered I/S (Equation [9]):

$$\frac{\partial S}{\partial t} = -\kappa_1 S \qquad [8]$$

$$\frac{\partial M}{\partial t} = \kappa_1 S - \kappa_2 M \qquad [9]$$

In Equation [8] the decrease of smectite, S, in random ordered illite/smectite (R = 0 I/S with <50% illite layers) is assumed to be first order and becomes illite in random ordered I/S. The amount of ordered illite/smectite, M, formed from random ordered I/S is calculated using Equation [9]. While Velde and Vasseur expressed the extent of the transformation in terms of smectite, we chose to calculate the amount of illite (I) formed, using Equation [10].

$$\frac{\partial I}{\partial t} = \kappa_2 M \qquad [10]$$

The cumulative amount of illite is the sum of the amount of I and M/2. The values for the activation energy and the pre-exponential rate constants used for κ_1 (Equations [8] and [9]) and κ_2 (Equations [9] and [10]) are listed in Table 1. These expressions are solved sequentially at a given time step for a given temperature.

In the models of Pytte and of Velde and Vasseur, the values for E_a, A, α, and β were selected to optimize the agreement of the calculated percent illite in I/S to measured percent illite for a given well or geologic occurrence for example, in Walsenberg Dike, Colorado (Pytte 1982). In the model of Huang et al., E_a, A, α, and β were established through experimental syntheses of illite from smectite. The values of E_a, A, α, and β used in each of the models are summarized in Table 1.

Table 2. Parameters specific to geologic settings.

	Denver Basin	Gulf Coast	Salton Sea	Paris Basin
K^+ (ppm)	$K^+/Na^+ = 0.1$	200	3200	—
Δt (Ma)	1	0.1	0.01	1
Geothermal Gradient (°C/km)	25	25	35, 72	32.5, 45

The differential equations (Equation [5], and Equations [7–10]) were solved using explicit finite difference approximations similar to Altaner (1985, 1989) and to Elliott (1988) except that changes in the potassium ion activity due to diffusional transport were not considered. The time increments, Δt; the potassium concentrations; and the geothermal gradients used for each model to simulate the transformation in each basin are summarized in Table 2. The burial history used for each basin was based on previously published curves: the Denver Basin (Elliott et al. 1991), the Gulf Coast (Huang et al. 1993), the Salton Sea Geothermal Field (Huang et al. 1993), and the Paris Basin (Velde and Vasseur 1992).

The mean age of illitization was also calculated from each model for each basin (Aronson and Hower 1976). The mean age of illitization is calculated using Equation [11]:

$$\text{Mean Age} = \sum_{i=1}^{SA}\left[\left(\frac{I_i}{I_{Total}}\right)\cdot(SA - i)\right] \qquad [11]$$

where

SA = stratigraphic age,

I_i = fraction of illite (%illite in I/S) formed at each time step i (Ma) from i = 1 to SA,

and

I_{Total} = total amount of illite formed.

The mean age of illitization is the sum of the product of the fraction of illite formed at each time step and the age of that time step. The product, $[(I_i/I_{Total})\cdot(SA - i)]$ is defined as the K/Ar age increment, since it represents the contribution to the K/Ar age from the illite formed during the *i*th time step. The mean age of illitization is equivalent to the area under a curve defined by the plotting the K/Ar age increment at each time step versus the stratigraphic age at each time step (see Elliott et al. 1991, Figures 8A–8D), and this area is directly comparable to the measured K/Ar age of I/S. In this study, the K/Ar age increment is plotted as a function of depth for all four basins (Figure 2).

APPLICATION OF THESE MODELS

The models developed by Pytte (Equation [5]), Huang et al. (Equation [7]) and Velde and Vasseur (Equations [8–10]) were applied to diverse burial settings: the Denver Basin; the Gulf Coast; the Paris Basin; and the Salton Sea Geothermal Field. Heretofore, Pytte's model was applied to the Gulf Coast and the Denver Basin, but it had not been used to simulate the transformation in the Salton Sea and the Paris Basin. The model by Huang et al. was successful in simulating the transformation in the Salton Sea and the Gulf Coast, but it was not applied to simulate the transformation either in the Paris or Denver Basins. The model by Velde and Vasseur was used to simulate the transformation in the Paris Basin, but it has not yet been applied to the other geologic settings.

The amount of illite is calculated at each time step for a given duration in the burial history using temperatures derived from burial curves, geothermal gradients, and values for the concentration of potassium in the pore solution. From the amounts of illite formed at each time step, the mean ages of illitization are calculated (Equation [11]) for comparison to measured K/Ar ages of I/S. The amount of smectite lost, or illite gained, is strongly dependent on the inputs of temperature and, consequently, on the burial curves and geothermal gradients used to describe each basin. The burial curves, geothermal gradients and potassium pore solution activities already specified by the authors in the calibration of their models were used in our calculations. This allowed us to verify that our models generated the same results that other authors did with their calculations and permits an effective comparison of the different kinetic expressions to each other in a variety of geologic settings. These basin specific parameters such as the burial curve and geothermal gradients, are summarized in Table 2.

For the Gulf Coast and the Salton Sea, the geothermal gradients and the burial curves developed by Huang et al. were used in this study. These burial curves record the time-depth history of a rock of a given age at one location in the basins. In the models of Velde and Vasseur and the application of the Pytte model to the Denver Basin, a series of burial curves are constructed to simulate the burial of one unit of a given stratigraphic age at various depths in these basins (Elliott et al. 1991, Figure 2D; B. Velde personal communication 1993). In the Denver Basin, the burial of the Mowry bentonite, stratigraphic age of 97 Ma, was studied. For the Paris Basin, the burial of an argillaceous rock deposited 210 Ma was studied. For these two basins, a standard burial curve is developed to simulate the burial history at the deepest part of each basin. Then a series of burial curves were constructed, whose depths at a given time, are fractions of the standard curve to simulate the burial at less deeply buried areas within these basins. These burial curves were not corrected for erosion or compaction.

For the Gulf Coast setting, two sets of simulations for each model were run. For one set of simulations, the transformation was stopped once it reached 75% illite. Hower et al. (1976) showed that the amount of illite layers in I/S may be limited to about 75% in the Gulf Coast sediments because [K^+] is limited to the amount of K-feldspar in shales undergoing dissolution at depth. Huang et al. stopped the simulation at 75% by setting [K^+] to zero. In our study, one set of simulations used a kinetic expression that was modified by setting the maximum amount of K_2O in illite to 75% of the total K_2O content of illite (i.e., 75% of 9.13 wt. % K_2O in illite), which causes the transformation to shut-down at 75% illite in I/S. In the other set, the simulations were allowed to run to completion without limiting the amount of K_2O formed.

RESULTS

The percentages of illite layers in I/S with depth published previously for the Denver Basin, the Salton Sea, the Gulf Coast, and the Paris Basin were reproduced using the published kinetic parameters, geothermal gradients and burial curves specified by the authors in their models, respectively (Elliott et al. 1991; Huang et al. 1993; Pytte 1982; Velde and Vasseur 1992). Thus, our translations of the three models were precise. Each model was then applied to "the" each basin to see how well each model simulated the measured percentages of illite in I/S. The results are shown by geologic setting in Figure 1.

Salton Sea Geothermal Field

In the Salton Sea Geothermal Field, the model by Huang et al. best simulated the increase in the amount of illite layers in I/S with depth using a high geothermal gradient (76°C/km) during the last 20,000 years (Figure 1). By comparing the results generated using a lower geothermal gradient (32.5°C/km) throughout the entire burial simulation versus the results generated using a higher geothermal gradient (76°C/km) during the last 20,000 years, it is apparent that a significant fraction of the illite layers in I/S was formed during the last 20,000 years due to the increased geothermal gradient. However, even with the increase in the geothermal gradient to 76°C/km for the last 20,000 years, the percentages of illite in I/S calculated using the models by Velde and Vasseur and Pytte did not simulate the measured data very well. With regard to the model of Velde and Vasseur, this might be due to the combined effect of short time increments, Δt of 10,000 years, and the low values of the preexponential constants, A_1 and A_2 (Table 2); even though the smectite rate parameter (α) is unity and lower than the smectite rate parameter used by Huang et al. However, the difference between the results calculated using the Pytte model versus the model of Huang et al. is probably due to the value of the smectite rate parameter, α, because the values of E_a and A in these two models are comparable to each other. Since the thermal event occurs only during the last 20,000 years, the illite formed during these last two time steps contributes little to the calculated mean age of illitization (K/Ar age) as seen in comparing the mean ages calculated with and without the increased geothermal gradient (Table 3).

Gulf Coast

Two types of simulations were performed using each of the three models for six total simulations: one stopped the amount of illite layers formed at 75% and one continuing normally. When the simulation was not stopped at 75%, the models by Pytte and Velde and Vasseur best simulated the measured percentages of illite in I/S with depth while the model by Huang et al. formed a significantly larger amount of illite (Figure 1). However, when the simulations were stopped at 75%, the model by Huang et al. best simulated the measured percentages of illite in I/S with depth (Figure 1). The amounts of illite calculated using the model by Velde and Vasseur are comparable to the results calculated using the Pytte model (Figure 1), and the break in slope at 50% illite is a consequence of the formation of ordered I/S (Equation [9]).

Denver Basin

For the Denver Basin, the model by Velde and Vasseur best simulated the increase in the percent illite in I/S with depth in Mowry bentonites (Figure 1). Again, the break in slope at 50% illite corresponds to a second, slower, kinetic expression used to simulate the formation of ordered I/S. This second expression (Equation [9]) is slower as indicated by the values of E_a and A used in the kinetic expression (Table 1). The percentages of illite in I/S calculated using Pytte's model are slightly greater than the measured percentage of illite in I/S at all depths, although the simulated values and trend were previously judged as satisfactory (Elliott 1988). The results calculated using the model of Huang et al. do not agree well with the measured data. This is attributed to the lower value of the smectite rate parameter, α (Equation [7]).

Paris Basin

In the Paris Basin, the transformation was simulated for an argillaceous rock whose stratigraphic age is 210 Ma as presented originally by Velde and Vasseur (1992). As shown in Figure 1, the percentages of illite in I/S calculated using the model by Huang et al. best simulated the measured data for the deepest burial depths (2–2.3 km), whereas the model of Velde and Vasseur best simulated the measured data at shallow depths (1 km).

https://doi.org/10.1346/CCMN.1996.0440107 Published online by Cambridge University Press

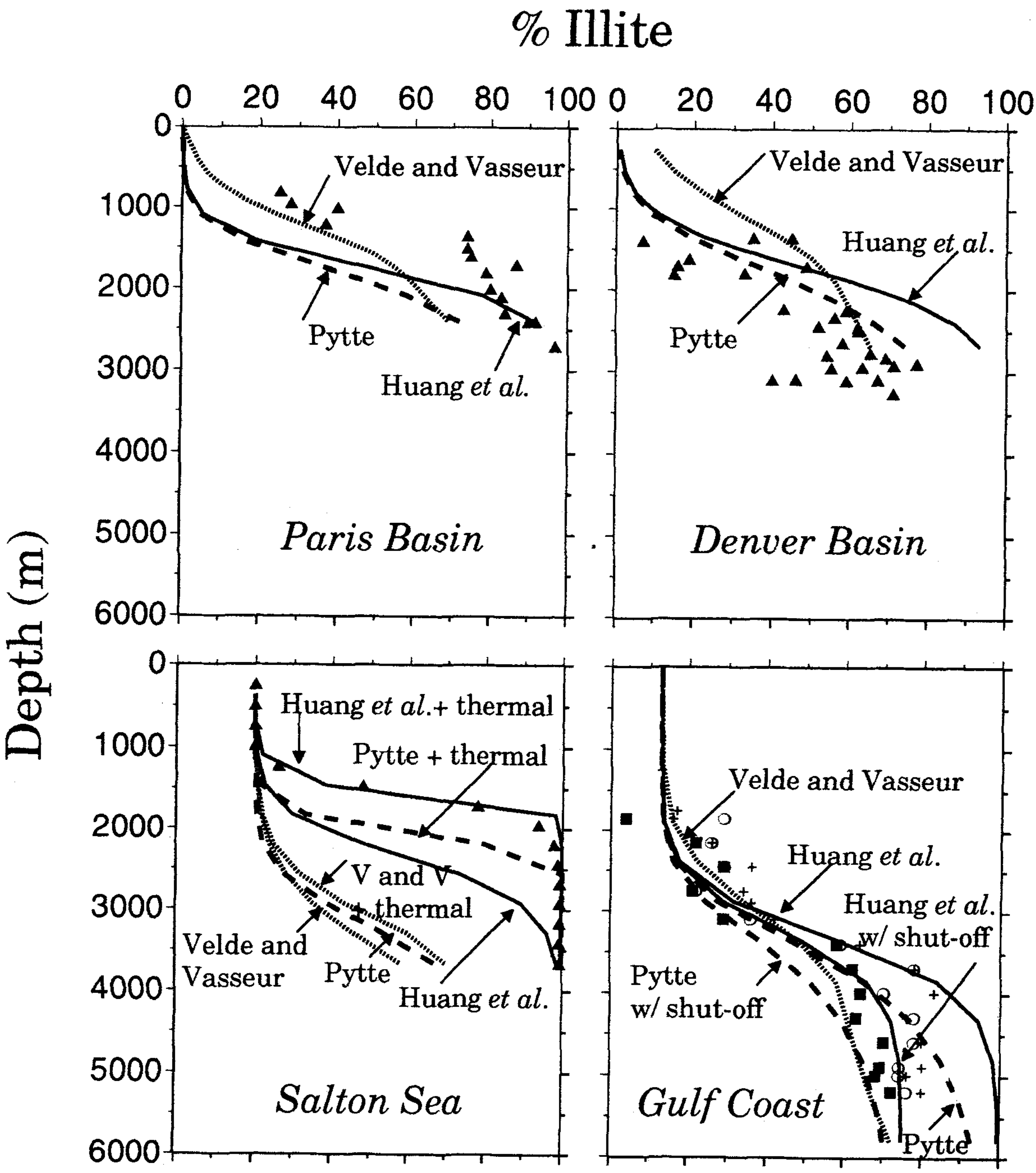

Figure 1. Percent illite in I/S with depth in each of four geologic settings. Measured values are designated by symbols (▲) while curves are computed using the models as described in the text. For the Gulf Coast, the symbols refer to different size fractions defined by Huang et al. (1993): ■ = 0.5–2.0 μm; ○ = 0.1–0.5 μm; + = <0.1 μm.

Table 3. Calculated K/Ar ages for maximum burial (Ma).

Model	Denver Basin	Paris Basin	Salton Sea w/thermal	Salton Sea no thermal	Gulf of Mexico w/shut-off	Gulf of Mexico no shut-off
Pytte	53.1	78.3	0.25	0.38	14.7	15.3
Velde and Vasseur	55.9	98.7	0.34	0.38	—	16.4
Huang et al.	53.7	79.2	0.83	0.85	17.2	17.5

https://doi.org/10.1346/CCMN.1996.0440107 Published online by Cambridge University Press

Mean Age of Illitization

The mean ages of illitization were calculated using Equation [11] for the formation of I/S at the deepest burial depth in each basin for each model. These ages are summarized in Table 3. For the Denver Basin, the calculated ages of the deepest buried I/S using the three models are similar (mean = 54.2 ± 1.5 Ma) and they agree with the measured K/Ar ages of I/S from Cretaceous Mowry Formation bentonites (Elliott et al. 1991). For the Gulf Coast, the calculated ages of the deepest buried I/S (mean = 16.4 ± 1.1 Ma) agree with the K/Ar ages of I/S (18 Ma) measured by Aronson and Hower (1976). Stopping the reaction at 75% illite layers leads to only slightly younger calculated mean ages of illitization (Table 3). This is because there is little additional illite produced above 75% layers by any of the models. Thus, for the Denver Basin and the Gulf Coast, the ages of I/S calculated from the models do not permit discrimination among the models.

However, for the Paris Basin and the Salton Sea Geothermal Fields, the calculated age measurements of the deepest buried I/S differ among the models, and it is conceivable that measured K/Ar ages of I/S would be useful in identifying the best model. For the Paris Basin, the calculated ages of I/S range from 98.7 Ma using the model of Velde and Vasseur to 78.3 and 79.2 Ma for the other models (Table 3). For the Salton Sea, the calculated ages of I/S range from 0.83–0.85 Ma using the Huang et al. model to 0.25–0.38 Ma using the other models.

The portion of illite that contributes to the K/Ar age (K/Ar age increment) versus depth is plotted for the deepest buried I/S in each basin (Figure 2). These calculations (Equation [11]) reveal the depths where the illitization transformation is proceeding most rapidly. For the Salton Sea, the model curves and the ages calculated using the model by Huang et al. indicate that more illite is formed at shallower depths relative to the other two models. Hence the age of illitization predicted by this model would be the oldest as illustrated in Table 3. The rapid rise of the curve from Huang et al.'s model at 1–2 km is also the depth at which the transformation is proceeding most rapidly (Figure 1).

For the Paris Basin, more illite is projected to be formed at deeper depths from the models by Huang et al. and Pytte, and more illite is formed at shallower depths in the model by Velde and Vasseur (Figure 2). This is also reflected in the calculated ages. The calculated ages by the Velde and Vasseur model are older than those calculated using the models of Pytte and Huang et al. It would have been very useful to have K/Ar data for the Paris Basin to compare the calculated ages to the measured K/Ar ages of I/S (free of detrital illite) because the measured ages might permit distinguishing the best model(s).

The calculations of percentages of illite in I/S and K/Ar ages of I/S are dependent on temperature. The temperature dependency of the illite content is governed primarily by the Arrhenius rate expression (Equation [6]). Although the K/Ar age depends on the formation of illite, its value depends on the depth integrated sum of the illitization increment (Equation [11], Figure 2). Accordingly, the relationship between %illite in I/S and K/Ar age of I/S reflects the cumulative effects of the transformation rate kinetics (Equations [5–10]), and the burial and thermal history in that geologic setting. Therefore, a plot of the percentages of illite in I/S against the K/Ar age of the I/S may enable testing these different models.

Although there are not any measured K/Ar ages with depth from bentonites available for the Paris Basin, the Salton Sea Geothermal Field or the Gulf Coast, the K/Ar ages and percent illite in I/S in bentonites from the Denver Basin are shown with calculated results from the three models (Figure 3). In general, the K/Ar ages of I/S increase with increasing percent illite in I/S, but as noted above, the relationships are non-linear and different for each model in each basin (Figure 3). There is a minimum in the calculated K/Ar ages at a small percent illite value which is a consequence of the non-linear burial curve in the Denver Basin which undergoes uplift during the last 60 Ma.

The results generated using the Huang et al. model underestimate the K/Ar age for all percent illite values, which forms more illite later. The Pytte and Velde and Vasseur models both have mixed results. The curve computed using the Pytte model also underestimates the K/Ar age for all %illite values, although the difference is smaller at higher percent illite concentrations. The curve computed using the Velde and Vasseur model predicts K/Ar ages in the right range for lower percent illite contents, although the trend of the curve may not agree with the trend from the measured data. In addition, the Velde and Vasseur model shuts down at 50% illite because the second reaction (Equations [9, 10]) is slower in contrast to the first reaction.

DISCUSSION

The percentages of illite calculated by the three models are highly sensitive to temperature, E_a, A, and α. This was observed in previous studies as well (Pytte 1982; Elliott et al. 1991). Higher values of the reaction order such as higher values of α typically terminated the transformation sooner, and this is seen by comparing the results of the Pytte model to the Huang et al. model. For example, in the results of the Denver Basin shown in Figure 1, the calculated amount of illite formed using the lower order model of Huang et al. is greater than the amount of illite formed using the model of Pytte (α = 4). In the model of Velde and Vasseur, α is effectively equal to one, so the values for A and E_a are the significant factors governing the rate of

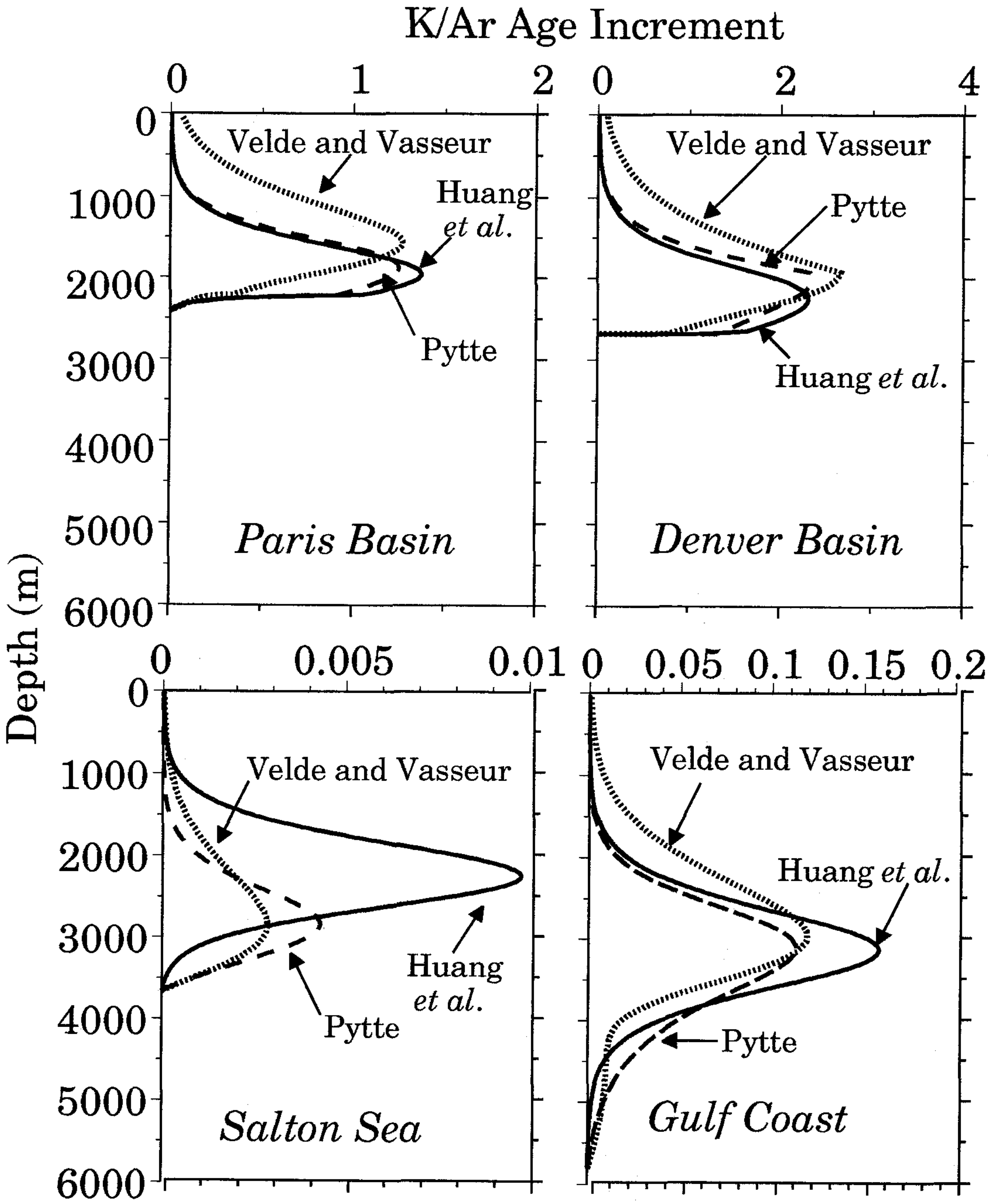

Figure 2. The contribution to the K/Ar age from the illite formed during each burial step is termed the K/Ar age increment. Peaks indicate those zones which contributed the most to the K/Ar age. The mean age of illitization is the area under the curves and corresponds to the measured K/Ar age.

transformation. The small amounts of illite formed by that model in the Gulf Coast and Salton Sea are explained by the low values of A and E_a. The model of Velde and Vasseur was more successful in simulating the formation of illite in the two older settings (Denver Basin, Paris Basin) compared to the Salton Sea and the Gulf Coast.

The models are also very sensitive to the geothermal gradient (Pytte and Reynolds 1988; Elliott et al. 1991; Velde and Vasseur 1992; Huang et al. 1993). The large fraction of illite formed during the last 20,000 years in the Salton Sea in response to a twofold increase in the geothermal gradient clearly indicates that temperature is a dominant kinetic factor.

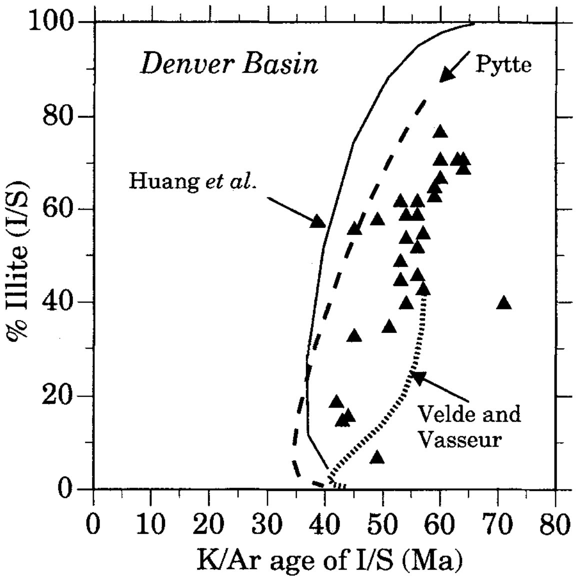

Figure 3. Comparison of modeled (curves) and measured (▲) %illite in I/S with K/Ar age of I/S in the Denver Basin from Elliott et al. (1991).

This is also apparent from Equation [6], the Arrhenius rate expression, where an increase in temperature leads to an exponential increase in the rate of reaction. For example, a factor of 10 increase in the reaction rate at about 300K requires only a 15K increase in temperature for the Pytte model and a 16K increase in the Huang et al. model, and about a 55K and 28K increase for the two reactions in the Velde and Vasseur model.

As shown in Figure 1, none of the models satisfactorily simulated smectite illitization in all four different geologic settings: the Denver Basin, the Gulf Coast, the Paris Basin and the Salton Sea Geothermal System. The model by Huang et al. was most successful in simulating the transformation in the Salton Sea, the Gulf Coast, and the deeper part of the Paris Basin. The model by Velde and Vasseur approximated the measured percentages of illite in I/S better than the model by Huang et al. in the shallow part of the Paris Basin. In addition, the model by Velde and Vasseur best simulated the formation of I/S in the deepest part of the Denver Basin. These results indicate that the transformation cannot be effectively described by a single kinetic expression in all geologic settings so none of the models may be blindly applied to any basin. However, the models can be further calibrated for a particular basin using measured chronologic data such as K/Ar ages on I/S separated from bentonites and K-bentonites, and then other variables such as the geothermal gradient through geologic time, potassium concentration and possibly burial history can be examined using the model.

As an example of how a model was used to understand the kinetics of the transformation, we applied the model of Pytte to simulate the transformation within a thick (1 meter) middle Ordovician K-bentonite from the shallow-buried portion of the southern Appalachian Basin (Elliott 1988). We found that the extent including the percent illite layers in I/S, of the transformation was simulated best using a very saline fluid ($[K^+]$ = 3200 ppm) as opposed to a potassium concentration approximately 200 ppm typically found in shales (Altaner 1985). The source of the potassium is controversial and is thought to be external to the K-bentonite (Elliott and Aronson 1987; Bethke and Marshak 1990; Oliver 1992). In this case, the use of the model at least demonstrates a possible way for illite to be formed in the Appalachian Basin.

Conceptually, the model by Velde and Vasseur departs from the other models mentioned in describing the transformation. They recognized two reactions: 1) formation of random ordered I/S from smectite; and 2) formation of ordered I/S from random ordered I/S. Moreover, each reaction has a specified kinetic expression (Equations [8–9]). However, this model does not consider potassium content, and yet experimental studies and field studies have shown this to be an important parameter (Altaner et al. 1984; Whitney and Northrup 1988; Huang et al. 1993).

The models we examined conserve illite after it forms. They are all based on the non Al-conserved reaction posed by Hower et al. (1976). These models simulate the formation of illite more analagous to a solid-state transformation mechanism as opposed to a dissolution/reprecipitation process (Boles and Franks 1979). Ostwald ripening is not considered by these models. There are inherent difficulties in evaluating Ostwald ripening and the dissolution/reprecipitation mechanisms through mathematical modeling. The amounts and the times of the gains and losses of either smectite or illite, including stable and radiogenic isotopic changes, must be specified during the formation of I/S. Even if it is assumed that Ar is totally lost during dissolution, it is still necessary to specify when and how much illite is dissolving to make more illite in the model, as well as specifying the activation energy and pre-exponential rate constants for dissolution/reprecipitation and ripening processes. If this could be done, then the calculated ages and percentages of illite in I/S can be used to decide whether I/S is formed through a dissolution/reprecipitation or a solid-state transformation process.

Finally, the models have only considered temperature and potassium ion activity in forming illite in the context of a non Al-conserved reaction mechanism (Equation [2] or [3]). In terms of dissolution/reprecipitation or Al-conserved reactions, the ion activities of Al and Si and/or the dissolution rate of K-feldspar must also be considered and at this point, the models can not be used to exclude this mechanism or other reactions (Equations [1] and [4]). Models based on Equations [1] and [4] need to be written and compared to the models described in this paper. After these results are compared to the results presented herein, then the models can be used to test hypotheses describing both the reaction and the mechanism of this transformation.

CONCLUSIONS

Although individual models can be applied to study the I/S transformation, none of these models was successful in simulating the transformation in all four basins. The Salton Sea was simulated best using the model by Huang et al. incorporating an increased geothermal gradient during the last 20,000 years. These results indicate that a large fraction of illite formed due to this increased geothermal gradient, which underscores that temperature is a dominant kinetic factor in forming illite. The Denver Basin was simulated well by the models of Velde and Vasseur and Pytte. The Gulf Coast was simulated very well by the model of Huang et al. using a term that shuts down the reaction at 75% illite. In the Paris Basin, the results are mixed. We conclude that none of the existing kinetic expressions for the simulations of I/S transformation can be universally applied. The reasons for this are unknown. It may be a consequence of any or all of the following: 1) improperly defined transformation mechanism; 2) improperly chosen activation energies or pre-exponential factors; and 3) neglecting to consider ion activities of K^+ and other ions in the pore solution that enhance or impede the rate of the transformation. However, once a model is formulated for a given basin, that model can be used to study a basin's thermal history and constrain parameters such as the past geothermal gradient and potassium concentration. The models can be further calibrated by comparing the calculated and measured ages of illitization for example, the K/Ar ages of I/S. The calculated ages of illitization can be used to indicate the timing at which source rocks are being heated to form oil and gas.

The models examined in this study conserved illite after forming it during a tacitly assumed solid-state transformation mechanism. Thus, in their present forms, the kinetic expressions cannot be used to test whether illite forms by a dissolution/reprecipitation mechanism. To evaluate dissolution/reprecipitation and Ostwald ripening, it is necessary to specify the times and the amounts of gains and losses of illite and smectite, respectively, and make assumptions regarding loss of radiogenic argon and potassium in the interlayer sites. The ages and extent of illite formation from this model could be compared to the model results discussed herein to compare the two illite forming mechanisms.

ACKNOWLEDGMENTS

We thank E. J. Essene, D. R. Pevear, W.-L. Huang, and B. Velde for helpful discussions and comments. W. C. Elliott's effort was supported partially by NSF grants EAR83-065666 to J. L. Aronson, #EAR89-16473 to Elliott, and #EAR91-05112 to S. M. Savin. CWRU contribution #202.

REFERENCES

Abercrombie HJ, Hutcheon IE, Bloch JD, de Caritat P. 1993. Silica activity and the smectite to illite reaction. Geology 22:539–542.

Ahn JH, Peacor DR. 1986. Transmission and analytical electron microscopy of the smectite-to-illite transition. Clays & Clay Minerals 34:165–179.

Ahn JH, Buseck PR. 1990. Layer stacking sequences and structural disorder in mixed layer illite/smectite: image simulations and HRTEM imaging. Am Mineral 75:267–275.

Altaner SP. 1985. Potassium metasomatism and diffusion in Cretaceous K-bentonite from the disturbed belt, northwestern Montana and in the Middle Devonian Tioga K-bentonite, eastern U.S.A. [Ph.D. dissertation]. University of Illinois: Urbana. 193p.

Altaner SP. 1989. Calculation of K diffusional rates in bentonite beds. Geochem Cosmochim Acta 53:923–931.

Altaner SP, Hower J, Whitney G, Aronson JL. 1984. Model for K-bentonite formation: evidence from zoned K-bentonites in the Disturbed Belt, Montana. Geology 12:412–415.

Aronson JA, Hower J. 1976. The mechanisms of burial metamorphism of argillaceous sediments: 2. Radiogenic argon evidence. Geol Soc Am Bull 87:738–744.

Bethke CM, Altaner SP. 1986. Layer-by-layer mechanisms of smectite illitization and application to a new rate law. Clays & Clay Miner 34:136–145.

Bethke CM, Marshak S. 1990. Brine migration across North America -The Plate Tectonics of Groundwater. Ann Rev Earth Planet Sci 18:257–315.

Boles JR, Franks SG. 1979. Clay diagenesis in Wilcox sandstones of southwestern Texas: implications of smectite diagenesis on sandstone cementation. J Sed Petrol 49:55–70.

Dutta NC. 1986. Shale compaction, burial diagenesis and geopressures: A dynamic model solution and some results in thermal modelling in sedimentary basins. In:Burruss J, editor. Therm Model Sed Basins. Paris:Technip. 149–172.

Eberl DD. 1993. Three zones for illite formation during burial diagenesis and metamorphism. Clays & Clay Miner 41: 26–37.

Eberl DD, Srodon J, Kralik M, Taylor BE, Peterman ZE. 1990. Ostwald ripening of clays and metamorphic minerals. Science 248:474–477.

Elliott WC. 1988. Bentonite illitization in two contrasting cases: the Denver basin and the southern Appalachian basin [Ph.D. dissertation]. Case Western Reserve University: Cleveland, OH. 236p.

Elliott WC, Aronson JL. 1987. Alleghanian episode of K-bentonite illitization in the Southern Appalachian basin. Geology 15:735–739.

Elliott WC, Aronson JL, Matisoff G, Gautier DL. 1991. Kinetics of the smectite to illite transformation in the Denver basin: clay mineral, K/Ar, and mathematical model results. Am Assoc Petrol Geol Bull 75:436–462.

Hoffman J, Hower J. 1979. Clay mineral assemblages as low-grade metamorphic geothermometers, application to the thrust faulted Disturbed Belt of Montana, U.S.A. In: Scholle PA, Schluger PR, editors. Aspects of Diagenesis. SEPM Special Publication 26:55–79.

Hoffman J, Hower J, Aronson JL. 1976. Radiogenic dating of thrust faults in the Disturbed Belt, Montana. Geology 4: 16–21.

Howard JJ, Roy D. 1985. Development of layer charge and kinetics of experimental smectite alteration. Clays & Clay Miner 33:81–88.

Hower J. 1981. X-ray diffraction of mixed layer clay minerals. In:Longstaffe FJ, editor. Clays and the Resource Geologist:Mineral Soc Can Short Course Handbk 7:39–59.

Hower J, Eslinger EV, Hower M, Perry EA. 1976. Mechanism of burial metamorphism of argillaceous sediments: 1. mineralogical and chemical evidence. Geol Soc Am Bull 87:725–737.

Huang W-L. 1992. Illitic clay formation during experimental diagenesis of arkoses. In:Houseknecht DW et al, editors. Origin, Diagenesis and Petrophysics of Clay Minerals in Sandstones. SEPM Special Publ. 47:49–63.

Huang W-L, Longo JM, Pevear DR. 1993. An experimentally derived kinetic model for smectite-to-illite conversion and its use as a geothermometer. Clays & Clay Miner 41: 162–177.

Inoue A, Velde B, Muenier A, Touchard G. 1988. Mechanism of illite formation during smectite to illite conversion in a hydrothermal system. Am Mineral 73:1325–1334.

Jennings S, Thompson GR. 1986. Diagenesis of Plio-Pleistocene sediments of the Colorado River delta, southern California. J Sed Petrol 56:89–98.

Lanson B, Champion D. 1991. The I/S-to-illite reaction in the late stage diagenesis. Am J Sci 291:473–506.

Morse JW, Casey WH. 1988. Ostwald precesses and mineral paragenesis in sediments. Am J Sci 288:537–560.

Nadeau PH, Wilson MJ, McHardy WJ, Tait J. 1984. Interstratified clay as fundamental particles. Science 225:923–925.

Oliver J. 1992. The spots and stains of plate tectonics. Earth Sci Rev 32:77–106.

Pollastro RM. 1993. Considerations and applications of the illite/smectite geothermometer in hydrocarbon bearing rocks of Miocene to Mississippian age. Clays & Clay Miner 41:119–133.

Pytte A. 1982. The kinetics of the smectite to illite reaction in contact metamorphic shales [M.A. Thesis]. Dartmouth College: Hanover, N.H. 78p.

Pytte A, Reynolds RC. 1988. The thermal transformation of smectite to illite. In:Naeser ND, McCulloh TH, editors. Therm Hist Sed Basins. Berlin:Springer-Verlag. 133–140.

Reynolds RC, Hower J. 1970. The nature of interlayering in mixed layer illite-montmorillonite. Clays & Clay Miner 18: 25–36.

Roberson HE, Lahann RW. 1981. Smectite to illite conversion rates. Effect of solution chemistry. Clays & Clay Miner 29:129–135.

Velde B. Personal communication. 26 April 1993. Department of Geologie, URA, 1316 CNRS, Ecole Normale Superieure, 24 Rue L'homond, 75005 Paris, FRANCE.

Velde B, Vasseur G. 1992. Estimation of the diagenetic smectite-to-illite transformation in time-temperature space. Am Mineral 77:967–976.

Whitney G, Northrup HR. 1988. Experimental investigation of the smectite to illite reaction: dual reaction mechanisms and oxygen isotopic systematics. Am Mineral 73:77–90.

(Received 19 August 1994; accepted 23 May 1995; Ms. 2565)