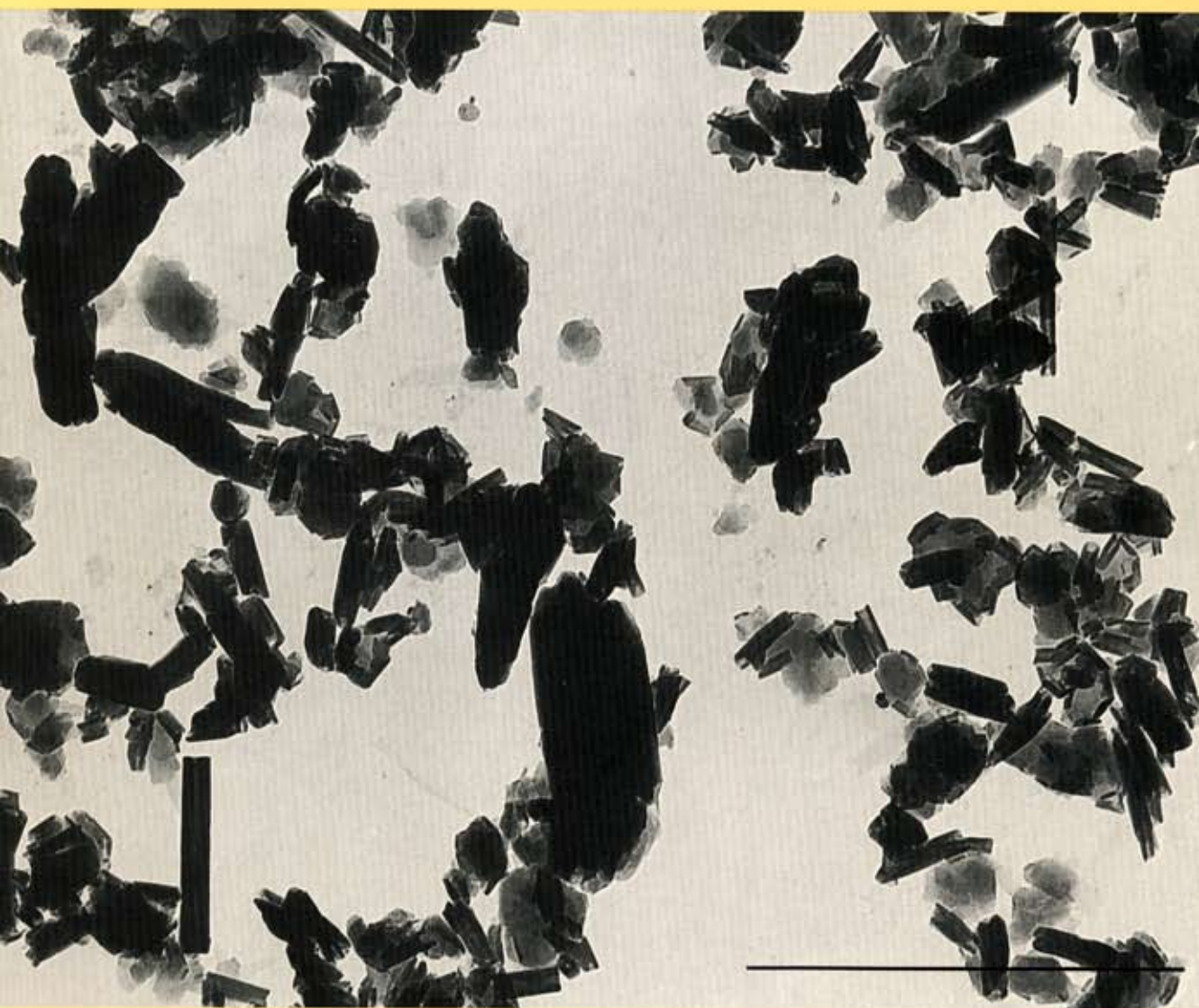THE 29TH INTERNATIONAL GEOLOGICAL CONGRESS
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A MULTIPLE REACTION MECHANISM (MRM) MODEL FOR ILLITIZATION DURING BURIAL DIAGENESIS

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ABSTRACT

A multiple reaction mechanism model is proposed for the illitization process during burial diagenesis. Reaction mechanisms include: 1) transformation, 2) dissolution/precipitation and 3) Ostwald ripening. End-member low-charge and high-charge smectites and illites are components used with the mechanisms above. Average compositions, determined by chemical analysis and fitting into structural formula, for smectite and illite, as well as mixed-layer illite/smectites (I/S) compare reasonably well with those determined by blending end-members, using proportions of I/S determined by X-ray diffraction. Implications of this model for the study of radiogenic isotope age dates of shales are also examined.

INTRODUCTION

New evidence from the far-IR and ^{27}Al NMR study of mixed-layer illite/smectite (I/S) in the burial diagenetic environment supports the existence of heterogeneous 2:1 layer compositions. Far-IR spectroscopy provides evidence for two distinct fixed K interlayer environments (an Al-rich illite and an Al-Fe-Mg illite, Schroeder, 1992a). ^{27}Al NMR and Fe content relationships reflect the presence of Al-rich octahedral domains, segregated from Fe-rich octahedral domains (Schroeder, 1992b). These observations are consistent with independent chemical (Hower and Mowatt, 1966; Srodon et al., 1986) and TEM studies (Inoue et al., 1987; Ahn and Buseck, 1990) that indicate the presence of heterogeneous I/S crystal-chemical structures. At the same time, experimental δ^{18}O studies of hydrothermally altered I/S suggests that more than one reaction mechanism is operating during illitization (Whitney and Northrop, 1988). Using these constraints, this paper introduces a model for the mechanisms of illitization during burial diagenesis. The purpose of this model is to provide a basis for understanding the mechanisms and ultimately, the kinetics of the overall illitization reaction. Although actual kinetic modeling of the illitization

reaction is beyond the scope of this study, the general ideas of published kinetic models are briefly discussed in light of the crystal-chemistry of I/S.

The basic tenant of the multiple reaction mechanism (MRM) model is that three mechanisms are potentially involved in the overall reaction for illitization. These three mechanisms include: 1) I/S transformation, which is defined as the *in situ* remodeling of the existing 2:1 layer structure. Interlayer cations can be exchanged and fixed and minor solid-state re-mobilization of inter chemical components occurs. 2) I/S dissolution - precipitation, where the dissolution of smectite occurs contemporaneously with the nucleation and crystal growth of illite, and 3) Ostwald ripening, where newly formed crystallites of illite dissolve to form larger authigenic illite crystals. Evidence for Ostwald ripening during late stage diagenesis has recently appeared through crystallite size and shape studies, using XRD, TEM and morphometrics (Eberl and Srodon, 1988; Lanson and Champion, 1991). The theory for the physical chemistry of all the reaction mechanisms above is now being integrated into the field of mineral-water interface geochemistry (Hochella, 1990). It is likely that the approaches currently being used for the study of mineral-water interface reactions will be appropriate for understanding the illitization process.

BACKGROUND, METHODS AND RESULTS

On the basis of on thermodynamic data, Eberl, (1980) has demonstrated preferential tendencies for different cations to fix into interlayer sites of clay minerals (usually based upon hydration energies, ionic radii and charge properties of cations). Using the differential fixing properties it has been revealed that most smectitic clays are composed of both low- and high-charge layer sites. Lindgreen et al., (1991), for example, used Mg^{2+} and K^+ cations, to show distinct differences in the percentage of illite in I/S in North Sea shales. The greater hydration energy of Mg^{2+} compared to that of K^+, results a higher number of illitic layers (10Å) in the K^+ saturated version of the same sample. The difference between the percentage of 10Å layer types in the Mg^{2+} saturated and the K^+ saturated forms was therefore used to gauge the number of high-charge smectite sites. Using this operational definition of high-charge, Lindgreen et al., (1991) found that irrespective of the amount of illite in I/S, about half of the smectites were high-charge.

End-member smectite and illite compositions were derived using the evidence offered by IR, NMR, TEM, XRD and chemical study of various smectitic and illitic clay types. Estimates for their compositions appear below in Table 1. Presented in the first box, are compositions of idealized low- and high-charge smectite (LC-smectite and HC-smectite). Also presented are compositions for idealized low and high layer charge illites (LC-illite and HC-illite). Mixing equal proportions of LC- and HC-smectite and LC- and HC-illite, gives compositions that closely depict average compositional values

TABLE 1

Structural formula per $O_{10}(OH)_2$

LC-smectite	$Na^+_{0.3}$ ($Al^{3+}_{1.41}$ $Fe^{3+}_{0.3}$ $Mg^{2+}_{0.3}$) ($Si^{4+}_{3.97}Al^{3+}_{0.03}$)
HC-smectite	$Na^+_{0.6}$ ($Al^{3+}_{1.17}Fe^{3+}_{0.4}$ $Mg^{2+}_{0.5}$) ($Si_{3.7}^{4+}Al^{3+}_{0.3}$)
LC-illite	$K^+_{0.6}$ ($Al^{3+}_{1.02}Fe^{3+}_{0.53}$ $Mg^{2+}_{0.6}$) ($Si^{4+}_{3.55}Al^{3+}_{0.45}$)
HC-illite	$K^+_{0.9}$ ($Al^{3+}_{1.88}Fe^{3+}_{0.05}$ $Mg^{2+}_{0.1}$) ($Si^{4+}_{3.1}Al^{3+}_{0.9}$)
Ave. smectite	$Na^+_{0.45}$ ($Al^{3+}_{1.29}Fe^{3+}_{0.35}$ $Mg^{2+}_{0.4}$) ($Si^{4+}_{3.84}Al^{3+}_{0.16}$)
Ave. illite	$K^+_{0.75}$ ($Al^{3+}_{1.45}Fe^{3+}_{0.29}$ $Mg^{2+}_{0.35}$) ($Si^{4+}_{3.33}Al^{3+}_{0.67}$)
0.60 smectite 0.40 illite	$K^+_{0.30}Na^+_{0.27}$ ($Al^{3+}_{1.35}Fe^{3+}_{0.33}$ $Mg^{2+}_{0.38}$) ($Si^{4+}_{3.64}Al^{3+}_{0.36}$)
1220 m 0.4 I in I/S	$K^+_{0.17}Na^+_{0.18}$ ($Al^{3+}_{1.32}Fe^{3+}_{0.43}$ $Mg^{2+}_{0.38}$) ($Si^{4+}_{3.63}Al^{3+}_{0.37}$)
0.50 smectite 0.50 illite	$K^+_{0.38}Na^+_{0.23}$ ($Al^{3+}_{1.37}Fe^{3+}_{0.32}$ $Mg^{2+}_{0.38}$) ($Si^{4+}_{3.59}Al^{3+}_{0.42}$)
3483 m 0.5 I in I/S	$K^+_{0.23}Na^+_{0.17}$ ($Al^{3+}_{1.40}Fe^{3+}_{0.38}$ $Mg^{2+}_{0.34}$) ($Si^{4+}_{3.57}Al^{3+}_{0.43}$)
0.32 smectite 0.68 illite	$K^+_{0.51}Na^+_{0.14}$ ($Al^{3+}_{1.40}Fe^{3+}_{0.31}$ $Mg^{2+}_{0.37}$) ($Si^{4+}_{3.59}Al^{3+}_{0.42}$)
5764 m 0.68 I in I/S	$K^+_{0.29}Na^+_{0.28}$ ($Al^{3+}_{1.48}Fe^{3+}_{0.30}$ $Mg^{2+}_{0.31}$) ($Si^{4+}_{3.49}Al^{3+}_{0.51}$)

for smectite and illite, respectively (Newman and Brown, 1987, see Tables 1.15 and 1.22). This mixing example, demonstrates the limitation of normative fitting of chemical data into structural formulae. A normalized structural formula does not allow for discrimination between an I/S with homogeneous layer compositions and an I/S composed of a mixture of different layer compositions.

Using the end-member's composition in Table 1, a MRM model is proposed. The first reaction proposed, is a transformation reaction that involves the formation of LC-illite at the expense of HC-smectite,

HC-smectite + 0.6 K⁺ + 0.13 Fe³⁺ + 0.1 Mg²⁺ -

LC-illite + 0.6 Na⁺ + 0.15 Si⁴⁺ (1).
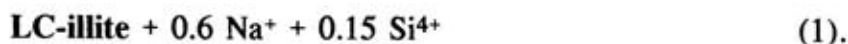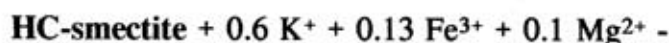
The compositions were derived so as to conserve the overall Al content. It is envisioned that during this reaction some minor solid-state transformation occurs. Al^{3+} may migrate from the octahedral sheet to the tetrahedral sheet

and displace Si^{4+}; thus transferring layer charge closer to the interlayer sites of the 2:1 structure. This process could be facilitated by increased K^+ adsorption and dehydration that is accompanied by increasing temperatures. The combined effect of the localization of K^+ closer to the intra-sheet structure and lengthy periods of geologic time may allow Al-Si exchange, even though Al-Si diffusion rates are typically small in silicates (Freer, 1981).

The second reaction involves the dissolution of LC-smectite and the precipitation of HC-illite,

LC-smectite + 0.90 K^+ + 1.34 Al^{3+} -

**HC-illite + 0.30 Na^+ + 0.25 Fe^{3+} + 0.2 Mg^{2+} + 0.87 Si^{4+}** (2).
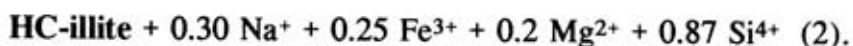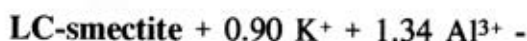
Implied in this reaction is a the complete dismantling of the smectite structure, major importing and exporting of reactants and nucleation of illite crystallites.

The final mechanism is a conservative reaction involving Ostwald ripening illite crystallites where,

HC-illite (crystallites) - HC-illite (crystals) (3).

Although there are marked differences in the conservation and mobility of chemical components in each reaction, when the overall reaction is written using the average compositions (see Table 1), qualitatively and quantitatively the average reaction (equation 4) is notably similar the reactions proposed by Hower et al., (1976) and by Boles and Franks, (1979).

Ave. smectite + 0.75K^+ + 0.67Al^{3+} -

Ave. illite + 0.45 Na^+ + 0.06Fe^{3+} + 0.05 Mg^{2+} + 0.51 Si^{4+} (4).
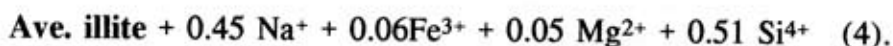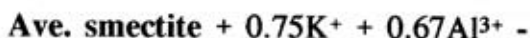
For comparative purposes, the chemical components of the I/S fraction for three samples from a Gulf of Mexico well (see Table 2 of Schroeder 1992b) have been cast into a normalized structural formula. These include samples from depths of 1220, 3483 and 5764 m, which contain 40, 50, and 68 % illite layers, respectively. Listed above each formula in Table 1 is an average structural formula assuming the same proportions of average illite and average smectite as XRD proportions of illite (10Å) and smectite (17Å) layers. Upon comparison of measured and calculated formulae, there is a striking agreement for both the octahedral and tetrahedral compositions. The disagreement between interlayer values is likely attributed to the large error associated with the measurement of Na_2O. The corroboration of the normalized structural formulae for I/S and the formulae derived by mixing idealized end-members give credence to the MRM model and provides a basis for examining the MRM model in light of larger geochemical problems.

Relevance of the MRM model is therefore briefly explored below with regard to kinetic models that have been proposed for illitization and attempts to utilize radiogenic isotope systematics in shales.

DISCUSSION

To date, attempts to derive kinetic expressions for the illitization reaction, (i.e., the conversion of 17Å smectite layers to 10Å illite layers) have encountered only limited success. The two general approaches that have been used to model illitization kinetics include; 1) laboratory hydrothermal experimentation (Eberl and Hower, 1976; Eberl and Hower, 1977; Eberl et al., 1978; Howard and Roy, 1985) and 2) empirical fitting of illite trends observed in different geologic settings by way of known thermal histories (Bethke and Altaner, 1986; Bethke et al., 1986; Pytte, 1988). Each have provided great insights to the problem of kinetic modeling of illitization, however as discussed below, application of the rate information has been restricted.

Experimental hydrothermal studies (Eberl and Hower, 1976; Howard and Roy, 1985) have derived activation energies (E_a) for the conversion of smectite to illite (often expressed as the loss of smectite layers or expandability, where expandability = 100 - percentage illite in I/S). These studies revealed a wide range of E_a, (3 to 30 Kcal/mole) and consequently, a wide range in rate constants for illitization. When assuming a first or second order rate expression to describe the complete illitization reaction, there is typically poor agreement between observed rates of illitization (e.g., when using a first order law, reaction rates predict faster rates than observed). The larger E_a values are typical of energies required for major bond breaking processes, while the smaller values are typical of cation fixation process. If the overall loss of expandable layers occurs as a result of several more elementary reactions, as proposed by the MRM model, there is now offered an explanation as to why there have been difficulties ascribing a single first order law for the overall illitization reaction.

The empirical approach to predict the rates of illitization from observed expandability trends in geologic settings with different time-temperature histories, has resulted in two proposed rate laws. The first, by Bethke and Altaner, (1986), uses a Monte Carlo model to simulate interactions among clay layers. Their approach to describing a rate law is to consider the total number of smectite layers (N) to be a summation of changes in different types of smectite layers (N_i),

$$\frac{dN}{dt} = \Sigma \frac{dN_i}{dt} \qquad (8),$$

where, i refers to different layer types and t = time. This is combined with an assumed first order rate of loss with respect to the number of smectite

layer types present (analogous to the kinetic expression derived for the organic matter decomposition in marine sediments by Westrich and Berner, 1985),

$$\frac{dN_i}{dt} = k_i N_i \qquad (9),$$

where k_i = the rate constant ($k_i = A \exp(\frac{-Ea_i}{RT})$). Solutions to their rate law use three smectite layer types; each with different E_{ai} (i=0,1,2). Using this model, they were able to successfully reproduce the features seen in expandability trends from sediments that have experienced a range of different thermal histories. Bethke and Altaner, (1986) attempt to explain their results by a layer-by-layer transformation model. Although the assumption of a single reaction mechanism may be incorrect, the concept of multiple rate laws to describe the overall illitization is compatible with the MRM model.

A different form of a rate law for illitization, based on higher order reaction kinetics, was first proposed Pytte and Reynolds, (1988). Smectite layer loss is calculated using the kinetic rate expression,

$$\frac{dN}{dt} = -k\, N^a\, (\tfrac{K}{Na})^b \qquad (10)$$

where, (a + b) is the order of the reaction and K and Na are the solution activities for potassium and sodium set by equilibrium between K-feldspar and albite. Coefficients for their kinetic model are derived from estimated times and peak temperatures experienced by argillaceous rocks and observed expandability's. Using trends from rocks whose maximum burial temperatures ranged from 70° C to 250° C and whose duration of heating ranged from 10 years to 300×10^6 years, their testing of the expression revealed a best fit with a fifth order solution (a=4 and b=1).

The expression of Pytte and Reynolds, (1988) has been recently applied in a study of the Denver Basin by Elliot et al., (1991). Their results indicate that the kinetic expression reasonably approximates the measured rates of expandability change throughout portions of the Denver Basin that have experienced different burial histories. Curiously, they found their best simulation with eighth order kinetics (i.e., a=8).

Despite the application of high order reaction kinetic models, in numerous geologic settings there remain the contradictory observational and theoretical evidence that elementary geochemical reactions simply do not follow fifth to eighth order reaction kinetics. Laws with reaction orders this high, as noted by (Elliot et al., 1991), are so unrealistically high, they do not permit a physical interpretation of the kinetic mechanisms. Elementary reactions typically follow first or second order rate laws (Burton et al., 1951; Lasaga, 1981; Baronnet, 1982; Steefel and Cappellen, 1990). It seems

likely therefore, that the kinetic expression used by Pytte and Reynolds, (1988) and Elliot et al., (1991) represent some overall set of more fundamental reactions. The MRM model seems to offer an approach for understanding the overall reaction in terms of the physical laws that govern specific chemical reactions.

The MRM model may provide insights to the mixed results that are yielded by radiogenic Rb-Sr and K-Ar studies of shales. A detailed examination of observed radiogenic isotope trends in the burial diagenetic environment is not intended here, but the MRM concept offers a means to partially resolve age date differences obtained by different radiogenic systems. The example to follow, discusses the Rb-Sr and K-Ar systems.

Perry and Turekian, (1974) were the firsts to consider the nature of diagenetic effects on Sr isotopes in Miocene Gulf Coast shales. The uncertainty in their age dates was attributed to a homogenization of the shale, primarily as a result of illitization and both carbonate and feldspar diss/ppt. Rb clearly shows a preference for fixation into illite sites with increasing depth of burial (see <0.5 μm data in Table 1 of Perry and Turekian, (1974)). Morton, (1985) subsequently has investigated Rb and Sr evidence from older Oligocene Gulf Coast sediments in Texas and documented a constant age grouping of $23.6 \pm 0.8 \times 10^6$ years for the samples deeper in the sequence. He suggests that this age represents the mean time of illitization.

Attempts to use the K-Ar system for dating shales has received as equally mixed results as the Rb-Sr system (Weaver and Wampler, 1970; Perry, 1974; Aronson and Hower, 1976; Elliot et al., 1991). Reasons for this have been attributed to contamination effect of atmospheric Ar and the physical mixing of older K found in detrital micas with newer K retained by the formation of diagenetic illite. Using the K-Ar technique Aronson and Hower, (1976) minimized the contamination problem and obtained a mean age of $18.4 \pm 2.0 \times 10^6$ years for stratigraphically equivalent samples in a well nearby to that of Morton's, (1985). Interestingly, the Rb-Sr model ages are slightly greater than the K-Ar model ages. Some of the age difference can be attributed to pitfalls stated above. However, if there is differential fixing of the K compared to the fixing of Rb during illitization then this may account for the observe age differences. As discussed above and by Eberl, (1980), the hydrated ionic radii and hydration energies for K and Rb would suggest that K would be fixed preferentially first. If the release and sequestering of Rb-Sr and K-Ar associated with the proposed MRM model (I/S transformation, diss/ppt and Ostwald ripening) differs, then the measured isotopic signatures may reflect the dominance of a reaction mechanism. This is an issue to be tested with the MRM concept and clearly must be addressed in view of other contemporaneous reactions involving Rb-Sr and K-Ar (e.g., carbonate and feldspar diss/ppt).

In summary, the MRM model, supported by the crystal-chemical evidence of this study, appears to provide a more robust basis for the predictive kinetic modeling of illitization and understanding radiogenic isotopic systematics of shales.

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