

Illite-smectites and the influence of burial diagenesis on the geochemical cycling of nitrogen

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ABSTRACT: Fixed nitrogen in illite-smectites (I-S) has been measured for Miocene shales from a Gulf of Mexico oil well. Fixed N values for the $<0.2\ \mu\text{m}$ fraction increase with depth from 150 ppm (1000 m) to a maximum of 360 ppm (3841 m). This increase is coincident with illitization from 41% I in I-S to 75% I in I-S. Below 3841 m, fixed N values decrease to 190 ppm (4116 m) while I-S is maintained with a slight increase from 77 to 82%. The changes in fixed N with increasing illitization are consistent with the notion that illitization proceeds via both transformation and dissolution/precipitation reaction mechanisms. The trend of decreasing fixed N in illitic I-S is compatible with surface-controlled crystal growth and Ostwald ripening mechanisms for illitization. The trend may also be linked to the timing of maximum NH_4^+ release from kerogen maturation during oil generation. The changing rate of NH_4^+ liberation from organic matter and multiple illitization reaction mechanisms can result in complex N geochemical cycling pathways throughout early diagenesis to metamorphism.

Evidence for the geochemical cycling of nitrogen (N) spans from the study of nutrients in ocean sediments (Mayer & Rice, 1992) to the study of high-grade metamorphism (Honma, 1996). The principal source of N for oceanic sediments is generally considered to be organic matter and NH_4^+ -bearing feldspars and micas (Berner & Berner, 1996). Initially, buried organic N is released partly through denitrification of proteins and peptides, amino acids and amino sugars that progressively become more associated with the humic fraction of organic matter (Aller & Benninger, 1981). Under early anoxic diagenetic conditions $\sim 1\%$ by mass of the total organic N reacts to form NH_4^+ (Berner & Berner, 1996; Tissot & Welte, 1978). After early diagenesis, N originally buried as organic matter resides mainly in the asphaltene and cyclic-aromatic

fractions of kerogen and the generated NH_4^+ is fixed into the interlayer sites of negatively charged 2:1 phyllosilicates. It has also been assumed that during later diagenesis, thermally generated NH_4^+ is simply fixed along with K^+ into the interlayer site of illite and that the NH_4^+ content of rocks remains relatively unchanged as burial conditions enter into intermediate grade metamorphism (Bebout & Fogel, 1992).

The ability to measure fixed N in typical marine shales (which normally contain concentrations <500 ppm) until now has been a limiting factor for extensive investigations. The development of the simple differential ashing method for measurement of fixed N in clays (Schroeder & Ingall, 1994) now makes it possible to bridge the gap between N studies of early diagenetic sediments and studies of NH_4^+ in metamorphic rocks. By presenting fixed N data which are typical for marine shales, we report here both a validation of the ashing method used to measure N in shales and apply our results for insights to the exogenic cycling of N. We suggest

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that N can be both fixed and liberated from illitic clays by several reaction mechanisms during burial diagenetic conditions.

SAMPLES AND ANALYTICAL METHODS

Samples were supplied as cuttings from the Texaco #3 Wildcat Federal Block 451, OCS-G 1733, Brazos area, offshore Texas and were selected using gamma and SP electric logs. Palaeontological data provided by Texaco and well logs indicate the sampling intervals (ranging from 1005 m to 4116 m) are from Middle and Upper Miocene shales. Sampling was limited to shales to aid in the assumption that the samples have been maintained in a quasi-isochemical system (i.e. the importing and exporting of chemical constituents is primarily diffusion controlled and dominated by the host rock).

The procedures for sample preparation, C and N analysis and X-ray diffraction (XRD) quantitative bulk mineralogy are described fully in Schroeder & Ingall (1994), and Hurst *et al.* (1997), respectively. Percentages of illite in illite-smectite (I-S) and ordering were estimated by comparing observed XRD patterns over the range of 3 to 50°2 θ (both in the air-dried and the Ca-saturated, ethylene glycol saturated state) with synthetic patterns generated using NEWMOD[®] (Reynolds, 1985). The method developed by Środoń (1980) was also employed.

The procedures for quantitative clay mineralogy are described fully in Schroeder (1992a). Briefly summarized, quantification proceeded via the following steps: (1) the <0.02 μ m fraction mounts were prepared from sedimented slurries, in an infinitely thick, Ca-saturated, ethylene glycol saturated state; (2) the percentages of I in I-S were determined; (3) NEWMOD instrument-sensitive parameters were tuned to the Scintag[®] diffractometer optics; (4) remaining tunable sample-sensitive NEWMOD parameters (e.g. mean defect-free distances) were empirically determined to try to reproduce the observed data; (5) reference intensity ratios (RIR) (Chung, 1975) were calculated for each model step over the range of 22–35°2 θ , using kaolinite as the reference standard; (6) a least-squares minimization technique was used to fit the relative contributions of the model patterns to the observed patterns; (7) appropriate RIRs were applied to obtain relative abundances of each clay mineral; and (8) as a final

check, model XRD patterns were mixed using the computed percentages, and then compared visually to verify a reasonable degree of fit (results available in McLain, 1997).

The ashing method involves measuring C and N using an ERBA[®] CN analyser. Samples are pre-treated for the removal of labile organic matter, carbonates and iron oxides to facilitate dispersion (for references see Schroeder, 1992a). Total C and N values for the bulk samples were obtained by using standard tin capsules. Fixed N values were measured after 8 h of sample ashing at 450°C in silver capsules. Fixed N values are, therefore, operationally defined. The only new variation to the ashing method described fully in Schroeder & Ingall (1994) is that each silver capsule is now placed inside a tin capsule after the ashing period and before introduction to the CN analyser (McLain, 1997). This last step facilitates sample handling and adds a catalyst for subsequent combustion.

RESULTS

Table 1 shows the XRD results, including bulk mineral and semi-quantitative clay (<0.2 μ m) mineral abundances. There are no systematic anomalies in bulk mineralogy, lending credence to the assumption that no major changes in the composition of the sediment input source (i.e. provenance) occurred over the studied interval. Two phases of discrete illite (I) were modelled by trial and error to approximate the observed XRD data. The amount of discrete illite with a small coherent scattering domain shows an irregular increase with depth. Some irregularity reflects difficulty in resolving discrete illite and I-S with >80% I in I-S. The amount of I in I-S increases systematically with depth from 41 to 82%, with a change in ordering type (*reichweite* = *R*) from *R* = 0 to *R* = 1 at 3841 m. The total number of illite sites (calculated as wt% I + % I in I-S \times wt% I-S) shows a strong trend of increasing degree of illitization with increasing depth (Fig. 1). The illitization trend is notably independent of bulk composition.

Table 2 presents the C and N contents for carbonate-free whole-rock samples. Table 2 also contains the C and N percentages of the unashed fine fraction and their respective atomic C/N ratios. The operationally defined organic C/N ratio and fixed N contents, derived by difference between the

TABLE 1. Quantitative whole-rock and semi-quantitative clay mineralogy as determined by X-ray diffraction. Reichweite (*R*), % I in I-S and total % illite layers are determined using <0.2 μm fraction.

Depth (m)	Whole rock					Clay fraction					<i>R</i>	% I in I-S	% illite sites
	% qtz	% kspar	% plag	% calc	% pyr	% kao	% ill LCSD	% ill SCSD	% I-S				
1005	12	2	2	3	2	—	—	—	—	—	—	—	
1880	—	—	—	—	—	6	1	39	53	0	41	65	
2036	11	0	1	8	1	8	2	39	52	0	47	65	
2719	10	2	4	9	1	8	3	31	58	0	53	65	
2796	19	3	4	13	1	4	3	43	50	0	56	74	
3328	15	1	3	12	1	4	3	41	52	0	59	75	
3404	18	1	2	17	1	7	7	26	66	0	63	69	
3841	11	0	3	8	0	6	0	62	32	1	75	86	
3903	14	0	2	10	0	4	1	63	32	1	77	89	
4049	13	1	1	14	0	9	2	36	53	1	80	80	
4116	15	0	2	13	1	9	2	74	14	1	82	87	

% = percentage by weight; qtz = quartz; kspar = K-feldspar; plag = plagioclase; calc = calcite; pyr = pyrite; kao = kaolinite; ill = illite; LCSD = large scattering domain ($N = 6-14$); SCSD = small scattering domain ($N = 3-6$); see text for determination of % illite sites.

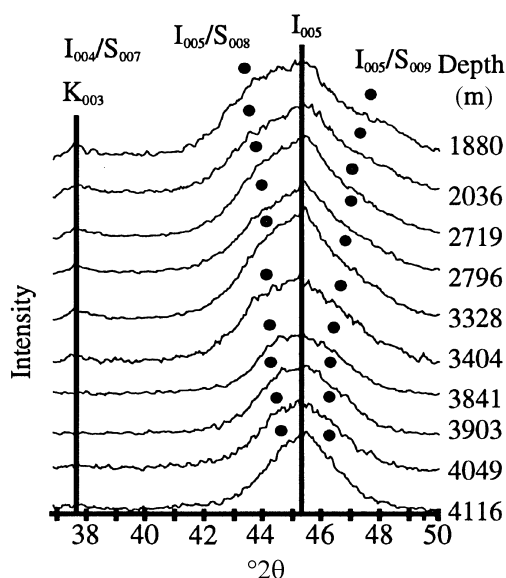


FIG. 1. XRD data for the 37 to 50°2 θ (Cu-K α) region used in part to determine the % illite in I-S. Subscript notation represents the order of the discrete and mixed-layer 00 l reflections. The discrete kaolinite and illite peak location are denoted by the vertical solid lines. The circles mark the location of the respective mixed-layer peaks.

ashed and unashed samples, are presented in the last two columns of Table 2.

Whole-rock N content shows no notable trend with depth. Whole-rock C values decrease with depth from ~1.3 to 0.8%, which results in a concomitant decrease in the atomic C/N ratio. Whole-rock C/N values range from 27 to 13, which is typical of Gulf Coast shales, (Tissot & Welte, 1978; Schroeder & Ingall, 1994). Neither the unashed fine fraction C/N values nor the organic C/N values show any systematic trend with depth. The ratios for the fine fraction organic C/N ratios, however, are an order of magnitude lower than the whole-rock C/N ratios. This difference indicates the organic fraction intimately associated with clay mineral surfaces is enriched in N.

Trends of fine fraction fixed N are found in both Table 2 and Fig. 2. Repeated measurements of a dilute standard (NH₄Cl-quartz mixture) and a sample with the lowest N content revealed a reliable detection level >100 ppm and limits of precision to effectively ± 10 ppm. These levels/limits are similar to those reported by Schroeder & Ingall (1994). Fixed N values (which were observed over the range of 140 to 360 ppm) are, therefore, reported to only two significant figures. Fixed N depth trends can be best described as increasing from a background level of ~140 ppm at 1800 m, to a level of 360 ppm at 3841 m. Fixed N values then

TABLE 2. Percentages of C and N in whole rock and fine clay mineral fraction (<0.2 μm) from Miocene Gulf Coast shale cuttings. Measurements made on carbonate free-basis.

Depth (m)	Whole rock			Clay fraction				
	% Cl total	% N total	C/N total	% C total	% N total	C/N total	C/N org	N fixed ppm
1005	1.283	0.064	23.4	—	—	—	—	—
1880	—	—	—	0.234	0.069	4.0	4.3	160
2036	1.215	0.054	26.3	0.162	0.067	2.8	3.2	150
2719	—	—	—	0.237	0.096	2.9	3.3	230
2796	0.927	0.054	20.0	0.244	0.103	2.8	3.2	210
3328	0.964	0.067	16.9	0.348	0.125	3.2	2.8	260
3404	0.966	0.071	15.9	0.154	0.096	1.9	1.8	210
3841	0.834	0.075	13.0	0.231	0.100	2.7	3.5	360
3903	0.815	0.063	15.1	0.446	0.112	4.6	5.6	250
4049	0.891	0.079	13.2	0.652	0.103	7.4	8.1	190

% = percent by weight; total = C and/or N measurement from the unashed sample; N fixed = measurement from the ashed sample; org = organics, based on difference between total values and fixed values.

decrease with increasing depth to 190 ppm at 4049 m (Fig. 2). The trend of decreasing fixed N between 3841 and 4049 m is subtle. The same trend in fixed N values was independently reproduced, however, using another CN analyser in a different laboratory. Calibration issues precluded the use of that data set (i.e. the measurements were precise, but lacked accuracy). We conclude, therefore, that the trend seen in Fig. 2 is real.

DISCUSSION

Fixed N in illite-smectites

The results of this study provide insights into several ongoing debates including: (1) use of fixed N as an indicator of hydrocarbon migration pathways (Williams *et al.*, 1992); (2) illitization reaction mechanisms operating during burial diagenetic conditions (Eberl, 1993; Schroeder, 1992b); and (3) the assumption that the NH_4^+ content of mudrocks remains unchanged as burial conditions enter into intermediate grade metamorphism (Bebout & Fogel, 1992). To address any one of these issues, it is clear that additional clay mineral, fixed N and stable N isotope studies (e.g. Williams *et al.*, 1995) will be useful. Figure 2 however, serves as a starting point and includes all published data for which measurements of both fixed N and %I in I-S were made on illitic clays from the same shale.

Measuring fixed N in typical shales. The ability to measure fixed N concentrations at levels ≥ 100 ppm in shales is now validated by the ashing method. Virtually every shale is now suitable for testing the theory that authigenic clays may trace migration pathways of hydrocarbons (Williams *et al.*, 1992). The catalytic effect that clay surfaces have on hydrocarbon formation may be instrumental in removing NH_3 from aromatic heterocycles and providing protons to produce NH_4^+

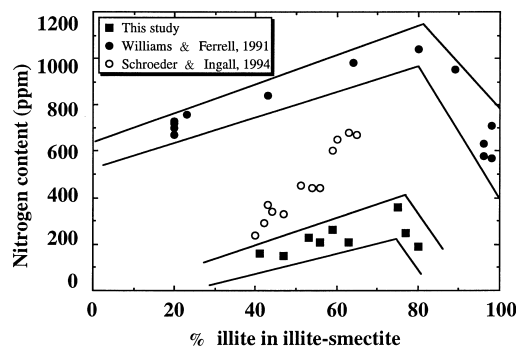


FIG. 2. Comparison of fixed N vs. % illite in I-S for three studies. All show initial increase in fixed N with degree of illitization. In this study and the one by Williams & Ferrell (1991), fixed N decreases after reaching a maximum close to 80% I in I-S. Solid lines are visual aids to highlight the trends. Fixed N measurements are reproducible within ± 10 ppm.

(Johns & McKallip, 1989). Clay surfaces may serve to increase NH_4^+ activity locally to levels greater than those predicted by Juster *et al.*, (1987), who predicted that phases in equilibrium with $\text{N}_2\text{-H}_2\text{O}$ fluids at higher temperatures will contain less NH_4^+ than those at lower temperatures.

One difficulty associated with using the differential ashing method is the inability to know whether the fixed N measured resides in detrital illite, authigenic discrete illite or the I portion of I-S. The problem of accounting for the N contribution from detrital illite can be addressed by making the first-order approximation for steady-state sediment input and single provenance for the studied Miocene interval. This is partially supported by bulk mineralogy trends presented in Table 1. It is also reasonably assumed by most researchers (e.g. Sucha & Siranova, 1991) that interlayer K^+ and NH_4^+ fixed by negative layer charges >0.6 per half unit-cell are held tightly during burial diagenesis and laboratory treatments. The basin, therefore, has been receiving a relatively constant contribution of NH_4^+ from the detrital components. Furthermore, this contribution is likely to be small due to the high metamorphic grade of the muscovite surviving transport to the Gulf of Mexico. Bebout & Fogel's (1992) data support this notion indirectly by showing the average N concentration in amphibolite-grade Californian rocks to be ~ 130 ppm. This value notably coincides with our baseline N levels. Changes above this baseline, therefore, are interpreted to reflect only authigenic increases/decreases in fixed N of both neoformed illite and I in I-S.

Implication for illitization reaction mechanisms. In our study, the fixed N content of authigenic illitic clays initially increases with depth of burial to reach a maximum at 3841 m. Then the fixed N content decreases at greater depth, with little change in the degree of ordering and % I in I-S (Fig. 2). This trend suggests that the NH_4^+ fixed during illitization is dependent upon the timing of maximum hydrocarbon release or the type of reaction mechanism operating during the later stages of illitization.

One simple way to account for variations in the amount of fixed N would be to relate the total available N in the whole rock to the fixed N content illitic clays. This assumes that the amount of NH_4^+ potentially available in pore waters would be proportional to the total amount of N in the shale. Table 2, as well as the Schroeder & Ingall (1994)

data set, show typical C and N values for marine shales. These data also show that there is little or no relationship between the bulk N content and amount of fixed N in the authigenic illitic clays. This suggests that variation in fixed N is not directly related to the availability of total N. If variations in pore-water NH_4^+ cannot be explained fully by the bulk N trend, then there may be a thermodynamic explanation that involves the reaction mechanisms responsible for illitization.

Eberl (1980) has shown that the transformation reaction mechanism (i.e. formation of illite through the collapse of smectite) prefers ions with the greatest energy of adsorption, which is inversely related to ionic radius. However, the larger the size of the monovalent cations, the lesser the energy that is required to dehydrate the cation. Because NH_4^+ (1.43 Å) has a slightly larger radius than K^+ (1.33 Å), NH_4^+ should be fixed preferentially. If illite is still forming via a transformation mechanism during the later stages of diagenesis (i.e. $>80\%$ I in I-S), then previously collapsed illite layers should have sequestered dehydrated NH_4^+ preferentially. This in effect leaves behind a greater proportion of K^+ available for fixation during later stages of transformation. Counteracting the competition for interlayer site occupancy is the nature of smaller dehydrated K^+ size. The K^+ fits better into the ditrigonal interlayer sites than does NH_4^+ (Bailey, 1984).

The decrease in fixed N beyond 80% I in I-S, seen in Fig. 2, may in part be explained by a second possible reaction pathway that involves the crystal growth and dissolution of neoformed illite. In the case of illite nucleation and growth, the electrochemical rules established by Eberl (1980) and assumed above for the transformation mechanism need not apply. If earlier transformed smectite and illite layers with relatively higher NH_4^+ contents could be permitted to dissolve, and earlier neoformed illite redissolved (through the reaction mechanism of Ostwald ripening, Barronet, 1982) then the composition of the illite layers formed later reflect the thermodynamically favoured K^+ ions. Our results suggest that during the growth of illite formed later, the fixing of K^+ is favoured thermodynamically over NH_4^+ .

In quasi-isochemical (i.e. semi-closed system) Gulf Coast shales, the ionic strength of pore water decrease initially with increasing depth of burial (Land & Macpherson, 1992). At the same time, temperature increases and illitization proceeds up to

80% I in I-S. The effect of pore-water dilution and formation temperature increase on K^+ and NH_4^+ activities can be evaluated through a simple comparison activity coefficient (γ) in freshwater to seawater ionic strength chloride solutions (0 to 1 M). These effects are shown in Fig. 3 which was derived via the extended Debye-Hückel law (Nordstrom & Munoz, 1994). Figure 3 shows formation waters with an initial ionic strength of 0.7 (seawater), that are diluted to 0.5 (equivalent to the Gulf of Mexico Na acetate type waters described by Land & Macpherson, 1992), would result in a slight decrease of γ_{K^+} relative to $\gamma_{NH_4^+}$. This effect however, is largely offset by rising temperatures as sediments become more deeply buried. The effect of higher temperature is to increase γ_{K^+} relative to $\gamma_{NH_4^+}$. Although the changes in Fig. 3 are small, the temperature effect appears to favour K^+ fixation over NH_4^+ fixation as part of a crystal growth reaction mechanism, particularly as diagenetic conditions proceed through the oil window (50–120°C).

A comparison is made between our data and the data for illitization of the Pierre shale studied by Williams & Ferrell (1991) (Fig. 2) for two reasons. Firstly, it enables a compilation of all published studies that present both fixed N and illitization data for the same sample suite. Secondly, the Pierre shale suite has a notably different thermal history than the burial diagenetic shales studied here. The maximum temperature of the dyke-intruded shale approached 400°C and the duration of the heating event was of the order of hundreds of years (Pytte & Reynolds, 1988). One explanation for the decrease in fixed N at temperatures >200° could be the stability of NH_4^+ vs. NH_3 . Both Williams & Ferrell (1991) and Bottrell & Miller (1990) suggest that the non-ionic nature of NH_3 (which is thermodynamically favoured above 200°C) cannot compete with K^+ in newly formed illite layers.

Another important factor controlling the amount of NH_4^+ vs. K^+ fixed into authigenic illite may be differences in reaction pathways. Rates of transformation, nucleation and crystal growth are highly dependent upon temperature and saturation state (Steefel & Van Cappellen, 1990). The further from equilibrium (i.e. super saturation) a system is, the more likely neoformation would occur. Lynch & Reynolds (1984) contend that the dyke-intruded Pierre Shale experienced significant dissolution of smectite and nucleation of illite, which is consistent with the idea that the illitic clays next to the dyke

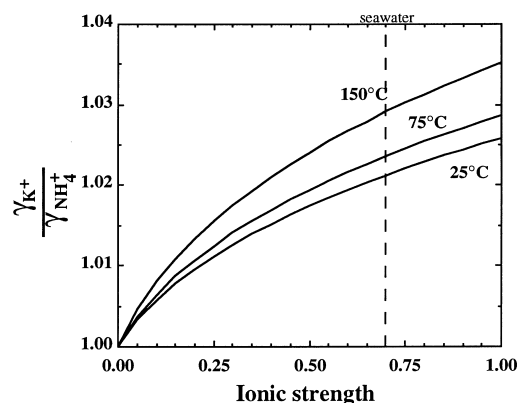


FIG. 3. Ratio of activity coefficients (γ) for K^+ to NH_4^+ calculated for chloride solutions over a range of 0 to 1 M. Each curve represents the ratio calculated at temperatures of 25, 75 and 150°C using the extended Debye-Hückel equation. The effect of dilution at constant temperature is to lower γ_{K^+} relative to $\gamma_{NH_4^+}$ and the effect of increasing temperature at constant ionic strength is to raise the ratio.

experienced conditions far from equilibrium. In contrast, the illitic clays forming under burial diagenetic conditions probably formed closer to equilibrium conditions. This situation would favour the operation of surface-controlled illite growth (which potentially includes Ostwald ripening).

Therefore, with the decrease in both the rate of illitization and the amount of I-S available for reaction at depths below 3841 m (Table 1), it appears that conditions are optimized for the formation and crystal growth of K-illite and the destruction of NH_4 -illite. The mechanism of Ostwald ripening is predicted to enhance the formation of K-illite. Our observations are consistent with the observations and reaction mechanisms described in Eberl's (1993) third and deepest zone of illitization. Extrapolation of fixed N and authigenic illite relationships presented by Williams & Ferrell (1991) to burial diagenetic conditions needs to be supported through more extensive basin scale studies in order to suggest that the maximum amount of NH_4^+ is fixed when thermal breakdown of the organic matter is in the 'oil window'.

Implications for nitrogen cycling

Data presented in Fig. 2, along with evidence for the multiple reaction mechanisms operating

throughout illitization (Eberl, 1993; Schroeder, 1992b) have ramifications for understanding of the geochemical cycling of N. It has been proposed that the NH_4^+ content of rocks remains unchanged as burial conditions enter into intermediate grade metamorphism (Bebout & Fogel, 1992). Our data show that prior to metamorphism, the timing and nature of N transfer between the 'organic' and 'inorganic' reservoirs is linked dynamically to the step-wise, overlapping multiple reactions of illitization and the biogenic/thermal breakdown of organic matter.

Mechanisms responsible for N fixing into smectitic and illitic clays span from: (1) adsorption/desorption of NH_4^+ and N-rich organic species on smectites (Table 2); (2) NH_4^+ fixation by smectite transformation to illite; (3) neoformation of NH_4^+ -illite during hydrocarbon generation; (4) release of NH_4^+ by smectite dissolution and small illite crystals (i.e. Ostwald ripening), to (5) NH_4^+ fixation by amphibolite-grade muscovite formation. Paralleling this sequestering sequence is the yielding of NH_4^+ from various pools of organic matter including the early diagenetic microbial degradation of proteins and humic acids, the thermal denitrification of aromatic heterocycles, and the metamorphic denitrification of kerogen-bound asphaltene.

The diagenetic modification of organic matter associated with clay surfaces is partly evidenced by the order of magnitude difference seen in the C/N ratio of the whole rock vs. the C/N ratio of fine fraction (Table 2). The opportunities for changes in the availability of N from organic matter for fixation into minerals appear to be abundant. The degree to which these modifications can affect isotope systematics cannot be addressed in this study, but appears to warrant additional investigation (e.g. Williams *et al.*, 1995).

CONCLUSIONS

The occurrence of maximum fixed N content in authigenic illitic clays near the onset of 80% I in I-S in Gulf of Mexico shales and contact metamorphism of shales (Williams & Ferrell, 1991) is consistent with the notion that the timing of maximum NH_4^+ release from kerogen maturation coincides with the initial formation of regularly-ordered ($R = 1$) I-S. These trends also suggests that illitization undergoes a fundamental change in reaction pathways that may include a range of

mechanisms from transformation to Ostwald ripening (Eberl, 1980).

From the standpoint of changes in mudrock composition throughout sedimentation to metamorphism and the geochemical cycling of N, the fixing of N via illitization can be characterized by numerous step-wise and overlapping reaction mechanisms, involving transformation via cation exchange, dissolution, neoformation and surface-controlled crystal growth and Ostwald ripening. Illitization involves smectites, mixed-layer illite-smectites, detrital and authigenic discrete illite and true mica phases, each of which serve as an inorganic N reservoir. Further studies should look to couple measurements of fixed N, characterization of authigenic and detrital clay phases (e.g. % I in I-S, reichweite and polytype determinations) and N isotope data to establish the role of illitization better, and NH_4^+ generation reaction pathways in the cycling of N.

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