

# A METHOD FOR THE DETERMINATION OF NITROGEN IN CLAYS, WITH APPLICATION TO THE BURIAL DIAGENESIS OF SHALES

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**ABSTRACT:** A new operationally defined method for the measurement of fixed inorganic nitrogen ( $N_{fix}$ ) associated with clays has been tested and applied to a sequence of mixed-layer illite/smectite (I/S) (ranging from 40 to 68% illite in I/S) in shales from a drill site in Terrebonne Parish, Louisiana. This new method has distinct advantages over other methods in that it is simple and can accommodate small sample sizes (10 mg).  $N_{fix}$  is measured, using a carbon-nitrogen analyzer, on a sample that has been ashed for 8 hr at 450°C to remove organic and non-fixed inorganic nitrogen. Total nitrogen is measured on an separate untreated sample. Content of organic carbon and nitrogen can be assessed by the weight-percent difference between untreated and ashed samples. Fourier-transform infrared spectroscopy confirmed the presence of nitrogen as ammonium in untreated and heat-treated samples.

$N_{fix}$  content of the < 0.2  $\mu$ m fraction of the shale sequence correlates positively ( $R^2 = 0.91$ ) with the percent of illite in the mixed-layer I/S. Corresponding with the increase in percent of illite in I/S with depth, an increase in  $N_{fix}$  content is also seen with increasing depth of burial. Nitrogen from thermal breakdown of organic-matter during later diagenesis probably provides the  $N_{fix}$  found in I/S. In the range of diagenesis studied here,  $N_{fix}$  concentration appears to depend on the available fixing capacity of illite. Because nitrogen content varies with organic-matter type, however, caution should be used when assuming this relationship for other diagenetic environments.

## INTRODUCTION

The relationship between fixed inorganic nitrogen in sedimentary rocks and the extent of diagenesis of clay minerals and organic matter has recently gained new attention from those interested in geochemical indicators of hydrothermal and diagenetic events (Daniels and Altaner 1990; Williams and Ferrell 1991; Compton et al. 1992; Williams et al. 1992). Most studies on the fixing of inorganic nitrogen ( $N_{inorg}$ ) in sedimentary rocks have focused either on (1) the fate of nitrogen in the early diagenetic and biogenically mediated environments (Müller 1977; Waples 1983), (2) the fate of nitrogen in low-grade metamorphic ore and coal deposits (Sterne et al. 1982; Daniels and Altaner 1990; Bottrell and Miller 1990), or (3) occurrences of minerals with unusually high proportions of isomorphous ammonium ( $NH_4^+$ ) substitution (Juster et al. 1987; Compton et al. 1992; Williams et al. 1992).

In previous studies, total and inorganic nitrogen in sediments and rocks has been analyzed by one or more methods, including (1) measurement of total nitrogen ( $N_{tot}$ ) using a C-N analyzer (e.g., Waples and Sloan 1980), (2) Kjeldahl digestion and distillation (e.g., Bremner 1965), (3) Fourier-transform infrared (FTIR) spectroscopy (e.g., Sterne et al. 1982), (4) X-ray diffraction (e.g., Daniels and Altaner 1990), and (5) ion chromatography (Krohn et al. 1988). Each method works well under appropriate conditions. Unfortunately,  $N_{tot}$  measurements are not extremely diagnostic, because they do not differentiate between  $N_{inorg}$  and organic nitrogen ( $N_{org}$ ). The  $N_{tot}$  measurement does have utility, however, in that  $N_{org}$  is often determined by difference between  $N_{tot}$  and measurements of  $N_{inorg}$ .  $N_{inorg}$  has been traditionally measured using the last four methods listed above.

The Kjeldahl method, which can distinguish  $N_{inorg}$  (as fixed  $NH_4^+$ ) from  $N_{tot}$ , is by far the most commonly used method. Although providing reasonable accuracy and limits of detection, the Kjeldahl technique requires large sample quantity and involves specialized apparatus and many reagents (Bremner 1965). The technique of IR spectroscopy uses the absorption of the IR-active normal-planar-bending vibrational mode ( $\nu_2$ ) of the tetrahedral  $NH_4^+$  molecule at 1430  $cm^{-1}$  (Farmer 1974). This technique has the advantage of directly measuring the presence of nitrogen as  $NH_4^+$ , which is present as a compensating interlayer cation in 2:1 layer-silicate structures. The IR technique works well in samples with particularly high amounts of  $NH_4^+$ , however; published studies have assessed the detection limits at levels of about 0.1% nitrogen by weight (Kydd and Levinson 1986). Nitrogen measurement by XRD uses the difference in the higher-order (third and fifth) basal (001) reflections of 2:1 interlayered clay structures. In this case, the nearly isomorphous substitution of  $NH_4^+$  for  $K^+$  in the illite structure is manifested in the XRD peaks at 45.5° and 44.9° 2 $\theta$ , respectively (Cu K $\alpha$ ,

radiation). The method is therefore a direct measure of nitrogen present as fixed  $NH_4^+$ . XRD works well for samples with unusually high proportions of  $NH_4^+$  like clays associated with coal, but the limit of detecting the  $NH_4^+$ -illite peak is high, and the technique can not be applied effectively to the typical shale with low  $NH_4^+$ . The ion chromatographic method (Krohn et al. 1988) appears to be able to distinguish mineral-bound ammonium but requires HF-HCl digestion. This method may offer a viable alternative in the analysis of nitrogen, but the technique has not been used extensively.

The intricacies of the Kjeldahl method and the high limits of detection associated with XRD and IR methods are probably why there are few  $N_{inorg}$  measurements in the geological literature. The purpose of this paper is to introduce a new operationally defined method for determining fixed nitrogen ( $N_{fix}$ ) in sedimentary rocks. This simple method should result in a greater number of measurements, leading to better understanding of the nature of  $N_{inorg}$ ,  $N_{org}$ , and the diagenetic evolution of sedimentary rocks. In an effort to begin this assessment of nitrogen in sedimentary rocks, this paper examines the relationships between the nitrogen content of clay minerals in Miocene shales from the Gulf of Mexico and their diagenesis.

## METHODS

The samples we used include a sequence of mixed-layer illite/smectites (I/S) from a well in Terrebonne Parish, Louisiana. Drill cuttings from Miocene shales (Flemming Formation equivalent) were collected over the depth range of 1220–5764 m. XRD analysis of the I/S in the shales indicate a range in Reichweite (R) ordering of I/S layer types from R = 0 to R = 0.5 and a range of 40–68% 10 Å (illite-type) layers in the mixed-layer structure. Details of the XRD operating conditions are given by Schroeder (1992a).

All samples were pretreated for removal of labile organic matter, carbonates, and iron oxide and oxyhydroxide coatings. The following treatments are needed for the technique. (1) Each sample is gently crushed with a mortar and pestle and disaggregated with an ultrasonic device, then sieved through a 45  $\mu$ m mesh. (2) The fine fraction is then further size fractionated to the < 2  $\mu$ m fraction (equivalent spherical diameter) using a centrifuge (Hathaway 1956). (3) Labile organic matter is removed using 30%  $H_2O_2$ . Digestions are performed for about 30 minutes at 50°C with ~ 2 g of sample, 15 ml of  $H_2O_2$ , and 30 ml of distilled water (DW). The sample is cooled and centrifuged to settle all particles. In this first step and all later steps described below, after treatment the supernatant is discarded, and the sample is doubly centrifuged and rinsed with DW. The organic-matter digestion step is then repeated. (4) Carbonates are removed by heating the sample to 80°C for 1/2 hour in a sodium acetate-acetic acid buffer at pH 4 (see, Moore and Reynolds 1989). This step is essential to remove carbonate carbon, which may interfere with the measurement of organic carbon and to remove carbonate ion, whose IR absorbance band interferes with that of the ammonium ion (Kydd and Levinson 1986). (5) Both iron oxide and hydroxide coatings are removed using a 0.3 M Na citrate bicarbonate solution (buffered). A solution is prepared using 100 g sodium citrate dihydrate, 95.3 g sodium bicarbonate, 1.1 l  $H_2O$ , and HCl to adjust the solution to a pH of 7.6. Approximately 0.5 g of sample is mixed with 1.2 g sodium dithionite, then 50 ml of the citrate/bicarbonate solution is added. Samples are treated for 8 hr and rinsed. (6) Samples are then sized by centrifugation to the < 0.2  $\mu$ m fraction (Hathaway 1956).

Carbon and nitrogen are measured using an ERBA® NA-1500 analyzer. The technique, as described by Waples (1983) and Cutter and Radford-Knoery (1991), burns 5–10 mg of sample in an oxygenated atmosphere at 1010°C. The evolved gases are passed over tungstic oxide and reduced copper catalyst and converted to  $N_2$  and  $CO_2$ . The gases are then separated using a chromatographic column and measured using a thermal conductivity detector. Sample concentrations are calculated relative to a sulfanilamide standard. The limit of detection is 0.01% N by weight. Repetitive measurement of a known mixture of ammonium chloride-quartz standard gives an average of 0.109% N with a standard deviation of  $\pm$  2%.

$N_{tot}$  is measured using an untreated sample in a standard tin foil capsule.  $N_{fix}$  is measured using a sample that has been placed in a silver foil capsule and ashed

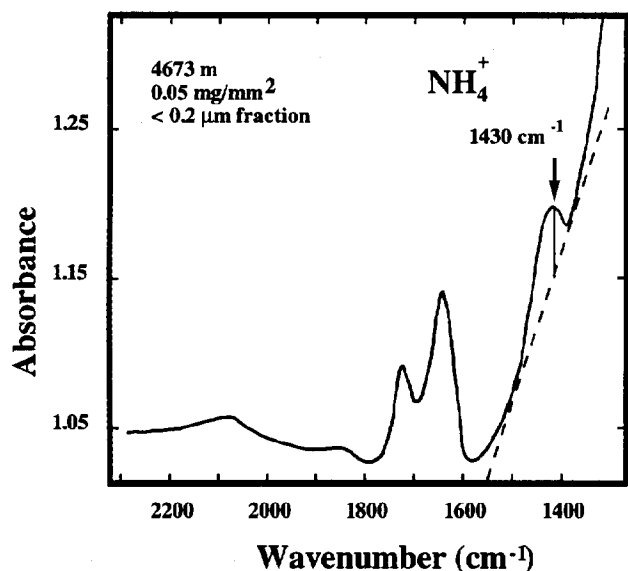


FIG. 1.—Infrared absorption spectrum of the  $< 0.2 \mu\text{m}$  fraction of Miocene shale cuttings from 4673 m depth. The spectrum was collected using a BIORAD FTS-60 FTIR spectrometer equipped with a MCT detector. Spectral resolution was set at  $4 \text{ cm}^{-1}$  with a time-average signal collected over 256 scans. Approximately 10.0 mg of sample was mixed with 150 mg KBr and pressed to provide a sample density of  $0.05 \text{ mg/mm}^2$ . The method of absorbance measurement at  $1430 \text{ cm}^{-1}$  assumes a linear baseline correction. Absorbance and baseline each are shown with solid and dashed lines, respectively.

for 8 hr at  $450^\circ\text{C}$  to remove  $N_{\text{org}}$  and loosely fixed  $N_{\text{inorg}}$ .  $N_{\text{org}}$  is defined here as the difference between  $N_{\text{tot}}$  and  $N_{\text{fix}}$ , although we realize that  $N_{\text{org}}$  by this definition contains a component of loosely fixed  $N_{\text{inorg}}$ .

The temperature of  $450^\circ\text{C}$  to remove organic carbon and nitrogen is based upon the exhaustive study of Krom and Berner (1983). To study the effects of heat treatment on the measurement of  $N_{\text{inorg}}$ , FTIR spectroscopic studies were performed to detect the presence of the fundamental asymmetric bend of the  $\text{NH}_4^+$  tetrahedron, whose absorption band is at  $1430 \text{ cm}^{-1}$ . One sample (from 4361 m) was selected and split into two sets of five aliquots (2 and 10 mg, respectively). Each set was heated to  $25^\circ$ ,  $225^\circ$ ,  $325^\circ$ ,  $375^\circ$ , and  $500^\circ\text{C}$ , respectively, for 8 hr. The first set was measured for carbon and nitrogen on the C-N analyzer using the silver foil method. Absorption spectra were collected for the second set using pressed KBr pellets mixed in a ratio of 15:1 (KBr to sample). Absorbances were measured by peak heights, using a standard linear baseline technique (Fig. 1).

#### RESULTS AND DISCUSSION OF METHODOLOGY

To use ashing methods to determine fixed inorganic nitrogen, two potential problems must be addressed. The first is whether organic nitrogen is volatilized entirely upon heating. Fortunately, concomitant measurement of carbon can provide evidence for the presence of organic matter. This is why carbonate carbon was removed from these samples. It is generally observed that the  $C_{\text{org}}/N_{\text{org}}$  ratio is relatively constant, provided that there has been no significant change in the type of organic matter that is being deposited in the sediments. This is evidenced in a plot of  $C_{\text{tot}}$  versus  $N_{\text{tot}}$  for the Gulf Coast Miocene shale clay fraction, which shows a  $C_{\text{tot}}/N_{\text{tot}}$  of about 3.8 (Fig. 2A). This plot also shows that much of the  $C_{\text{tot}}$  and  $N_{\text{tot}}$  associated with the  $< 0.2 \mu\text{m}$  fraction is from organic matter, even after  $\text{H}_2\text{O}_2$  treatment. A plot of carbon vs. nitrogen after the ashing treatment (Fig. 2B) shows only background noise levels of carbon, with virtually no correlation between carbon and nitrogen ( $R^2 = 0.15$ ).

The complete removal of organic carbon and nitrogen at  $450^\circ\text{C}$  is supported by the multiple heating experiments using the sample from 4261 m. Results are shown in Figure 3, a plot of weight percent carbon and nitrogen vs. temperature of heating. While almost all of the carbon is lost at  $325^\circ\text{C}$ , at least one third of the nitrogen remains to a temperature of  $450^\circ\text{C}$ . The complete loss of nitrogen at  $500^\circ\text{C}$  indicates complete volatilization of all forms of nitrogen.

The data above point to a second potential problem with heat treatments, which

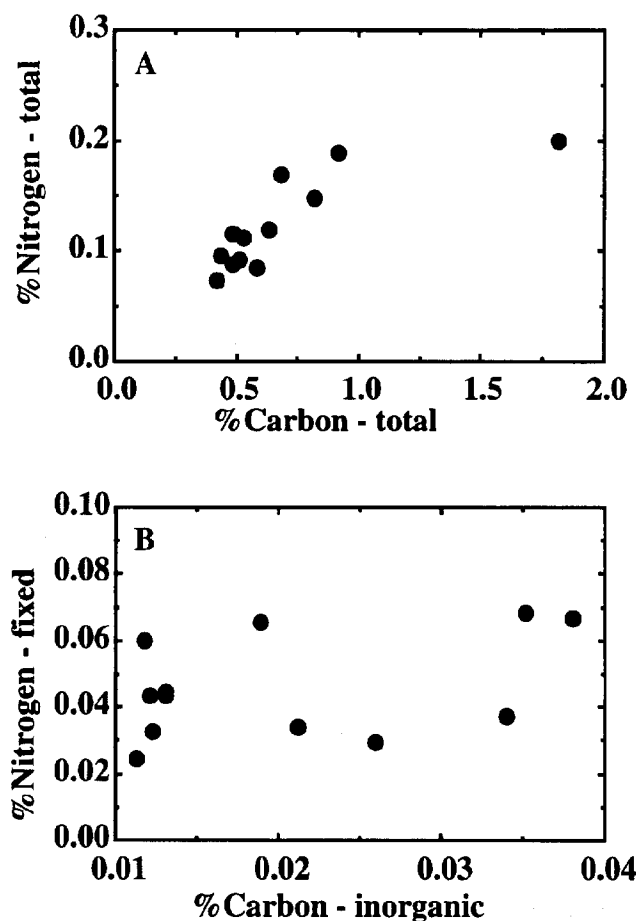


FIG. 2.—A) Total nitrogen content vs. total carbon content of the  $< 0.2 \mu\text{m}$  fraction of Miocene shales. These data include the non-ashed samples, after treatment by hydrogen peroxide. The C/N ratio is about 3.8. B) Nitrogen content vs. carbon content after ashing for 8 hr at  $450^\circ\text{C}$ . Virtually all the carbon has been removed (note difference in carbon scale between A and B).

concerns the volatility of  $\text{NH}_4^+$  loosely fixed as a compensating interlayer cation in the low-charge illite-type sites and the smectite-type sites of the I/S structure. Figure 3 shows that with progressive laboratory heating of the sample from 4261 m there is a measurable loss of nitrogen even at  $225^\circ\text{C}$ . The presence of  $\text{NH}_4^+$  in the I/S structure with progressive heating was evaluated by analysis of FTIR spectra. Figure 1 shows the absorption spectrum of the unheated ( $25^\circ\text{C}$ ) sample. The absorption band at  $1430 \text{ cm}^{-1}$  is readily seen. With progressive heating, however, the intensity of the absorption band decreases rapidly (Fig. 4). This indicates that  $\text{NH}_4^+$  is lost even with moderate heating to  $225^\circ\text{C}$ . It is likely, therefore, that nitrogen loss during early heating is not only due to volatilization of organic matter but also to loss of adsorbed and loosely fixed interlayer  $\text{NH}_4^+$ . This adsorbed  $\text{NH}_4^+$  is presumably present on the organics themselves, in the interlayer sites bounded by smectite layer types, and/or on the edges of the clays.

These results are independently supported by the work of Russell and White (1966), who showed that  $\text{NH}_4^+$  in montmorillonite starts to decompose into ammonia and hydrogen ions at  $300^\circ\text{C}$ . More recently, Roche et al. (1986) studied the nature of nitrogen in a black shale by continuous analysis of the pyrolysis products by mass spectrometry. They showed clearly (Roche et al. 1986, their figure 7) the evolution of three populations of  $\text{NH}_3$  evolved during stepwise pyrolysis. Included are peak populations produced at about  $225^\circ$ ,  $475^\circ$ , and  $650^\circ\text{C}$ , which are related to nitrogen associated with adsorbed, organic, and fixed sources, respectively. It should be noted that Kydd and Levinson (1986) operationally defined a temperature of  $550^\circ\text{C}$  for the removal of all organic matter. Their work focused on ammonium halos in carbonate-hosted ore deposits. In their application, clay minerals are not a significant component of the rock, and this temperature

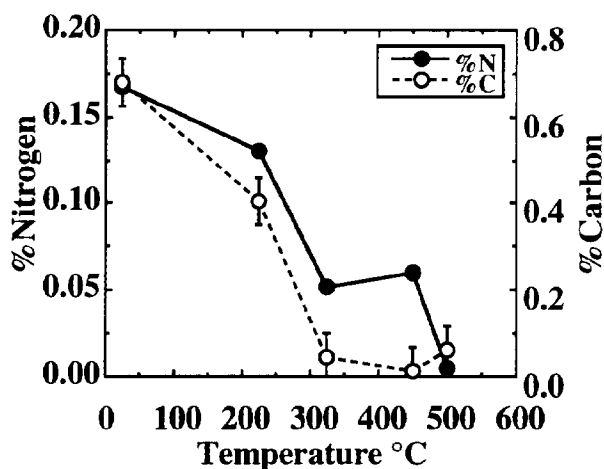


FIG. 3.—Heating experiments for  $< 0.2 \mu\text{m}$  fraction of the shale from 4261 m depth. Plotted are the weight percent nitrogen (solid) and carbon (open) as determined by the C-N analyzer vs. maximum temperature of heating.

may be more appropriate. In a similar study of black-shale-hosted quartz-vein gold deposits, Bottrell and Miller (1990) also used a temperature of  $550^\circ\text{C}$  to differentiate organically held nitrogen. In the case of our shale studies of the pretreated  $< 0.2 \mu\text{m}$  fraction, where minimizing the volatility of ammonium from diagenetic 2:1 structures is of key concern, the data indicate that  $450^\circ\text{C}$  is sufficient to release organic nitrogen and retain a component of inorganic nitrogen.

When using FTIR, the limit of detection of the  $\text{NH}_4^+$  absorption band in clays is reached when nitrogen values are less than 0.1% N, a limit previously demonstrated by Kydd and Levinson (1986). Thus, the ability of the C-N analyzer to measure nitrogen contents accurately down to 0.01% makes it the analytical tool of choice for the study of low N-bearing clays. The C-N analyzer also requires half as much sample as the FTIR method. Two remaining questions about the ashing method are: (1) What is the optimum ashing temperature for determination of fixed inorganic nitrogen in shale? and (2) What form of nitrogen remains after ashing? In this study and for the use of this new ashing method,  $N_{\text{fix}}$  must therefore be operationally defined.

Although it appears that all organic matter can be liberated at temperatures lower than  $450^\circ\text{C}$ , as shown in this study by the removal of all carbon, Krom and Berner (1983) have shown that in a wide variety of samples an 8 hr treatment at  $450^\circ\text{C}$  is necessary to remove most forms of organic carbon. The optimum temperature is probably dependent upon the type and proportion of organic matter present. On the basis of this study and the work of Krom and Berner (1983) and Roche et al. (1986),  $450^\circ\text{C}$  is therefore a reasonable compromise between mini-

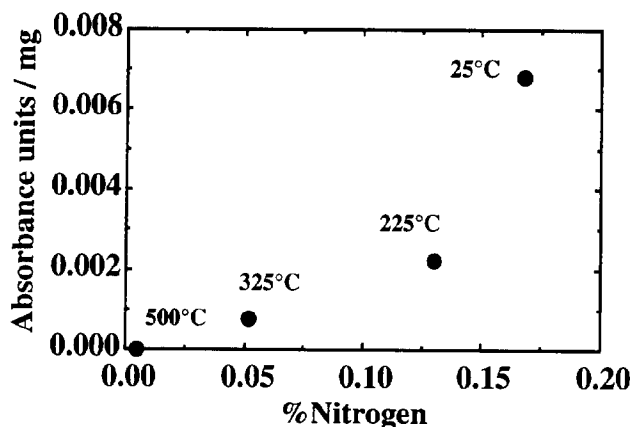


FIG. 4.—Absorbance of  $1430 \text{ cm}^{-1}$  band for  $< 0.2 \mu\text{m}$  fraction of the shale from 4261 m depth vs. nitrogen content as determined by the C-N analyzer. Each data point is identified by the maximum temperature of heating.

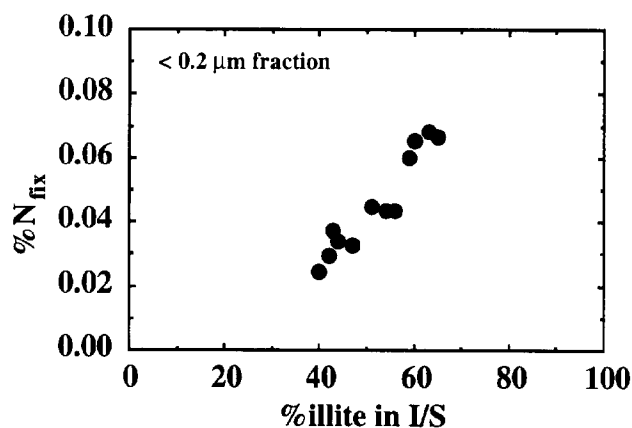


FIG. 5.—Fixed inorganic nitrogen ( $N_{\text{fix}}$ ) content vs. percent illite in mixed-layer illite/smectite of the  $< 0.2 \mu\text{m}$  fraction of Gulf Coast Miocene shales. The N:I/S ratio is about 0.002.

mizing volatilization of  $\text{NH}_4^+$  from interlayer sites and maximizing oxidation of organic matter. Low-temperature ashing techniques may further minimize  $\text{NH}_4^+$  volatilization (Gluskoter 1965), but this procedure was not available for this study.  $N_{\text{fix}}$  is defined here as the nitrogen that remains after ashing at  $450^\circ\text{C}$  for 8 hr.

The answer to the second question above (what is  $N_{\text{fix}}$  a measure of?) is best answered by analysis of the clay-mineral reactions that occur during early and late diagenesis. This aspect is discussed below where the method is applied to the fine fraction of Miocene shales in a Gulf Coast diagenetic sequence.

#### RESULTS AND DISCUSSION OF GULF COAST DATA

The exact relationship between the generation of biogenic and thermogenic  $\text{NH}_4^+$  from organic matter and the fixing of  $\text{NH}_4^+$  into the interlayer sites of clay minerals is still not well understood. This is partly due to the complex factors involved in generation of  $\text{NH}_4^+$  (see, e.g., Compton et al. 1992) and partly due to the complex reaction mechanisms involved in the diagenesis of 2:1 clay minerals (see, e.g., Schroeder 1992b). Despite the uncertainties in the mechanisms of illitization and  $\text{NH}_4^+$  generation, there exists an extremely high correlation between  $N_{\text{fix}}$  in the fine fraction of shales and the extent of diagenetic maturation of the 2:1 clay minerals.

Figure 5 shows that in this study the percent  $N_{\text{fix}}$  of the  $< 0.2 \mu\text{m}$  fraction correlates positively ( $R^2 = 0.91$ ) with the percent illite layers in the I/S of Miocene shales. Because the percentage of illite in I/S increases with depth, an increase in  $N_{\text{fix}}$  is also seen with increasing depth of burial. This correlation has been observed in other shales, including those from the Miocene Monterey Formation (Compton

TABLE 1.—Depths, whole rock (W.R.) and fine-fraction nitrogen and carbon contents and illite content of Miocene shale cuttings, taken from Terrebonne Parish, Louisiana

Depth (m)	%N <sub>fix</sub> W.R.	%C <sub>org</sub> W.R.	%N <sub>fix</sub> < 0.2 μm	%C <sub>org</sub> < 0.2 μm	%N <sub>fix</sub> < 0.2 μm	%C <sub>org</sub> < 0.2 μm	% Illite in I/S	Illite Layers
1220	0.076	1.26	0.024	0.011	0.049	0.410	40	0.44
1577	0.073	0.71	0.029	0.026	0.055	0.557	42	0.42
2568	0.068	0.66	0.034	0.021	0.061	0.419	44	0.44
2779	0.069	0.62	0.037	0.034	0.055	0.477	43	0.46
3172	0.063	0.57	0.033	0.012	0.055	0.474	47	0.54
3483	0.120	0.53	0.045	0.013	0.066	0.515	51	0.55
3758	0.070	0.77	0.044	0.012	0.071	0.473	54	0.58
4178	0.085	0.94	0.044	0.013	0.076	0.622	56	0.57
4361	0.081	0.73	0.060	0.012	0.108	0.670	59	0.59
4673	0.106	1.29	0.065	0.019	0.083	0.800	60	0.61
5093	0.107	1.64	0.068	0.035	0.121	0.881	63	0.64
5368	0.094	1.79	0.067	0.039	0.110	0.944	65	0.64
5764	0.106	0.93	0.127	0.000	0.073	1.230	68	0.67

\* The total fraction of illite-type layers in the  $< 0.2 \mu\text{m}$  fraction = {weight fraction of discrete illite + [weight fraction of I/S × (percent illite in illite/smectite)]}.

et al. 1992) and the Upper Paleocene Midway Group and Lower Eocene Wilcox Group (Cooper and Abedin 1981; Williams et al. 1992). This close relationship suggests that the nitrogen from thermal breakdown of organic matter during later diagenesis provides the  $N_{\text{fix}}$  found in the I/S. Within the range of diagenesis for the Miocene shale studied here, the linear relationship above indicates that  $N_{\text{fix}}$  content is dependent upon the available fixing capacity of illite sites rather than upon nitrogen availability. This is supported by the observation that  $N_{\text{tot}}$  and  $C_{\text{org}}$  of the bulk shale show no trend with depth of burial (Table 1).

A study by Williams and Ferrell (1991) has shown that at higher temperatures in regions of contact metamorphism, the  $N_{\text{fix}}$  content of illite is limited by nitrogen availability. Williams et al. (1992) have more recently suggested that in sandstone adjacent to shales, a larger proportion of nitrogen is fixed into illites in the sandstone. They ascribe this to a greater availability of  $\text{NH}_4^+$  that has migrated from depth into and through more permeable layers. Unfortunately the authors did not differentiate the percent I/S associated with the respective adjacent shales and sandstones. Howard (1981, 1987) has shown that shale/siltstone fabrics in the Oligocene Frio Formation and the Eocene Queen City Formation in Texas contain a higher percentage of illite in I/S in the less permeable shale parts. Howard (1987) suggested that the rate of potassium fixation is first limited by the rate at which layer charge can be created, i.e., the rate of illite crystal growth and/or the rate at which high layer charge can develop in existing 2:1 layer structures. The differences between the degree of illitization in shale and siltstone/sandstone sequences may reflect not only the availability of potassium and  $\text{NH}_4^+$  but also the relative concentrations of all competing cations in solution (see, e.g., Lasaga and Kirkpatrick 1981). It still remains uncertain, however, whether the proportion of  $\text{NH}_4^+$  fixed in illites is limited by the availability of  $\text{NH}_4^+$  or the rate at which illite-type sites can be created.

One possible approach to assessing the relationship between  $N_{\text{fix}}$  content and extent of illitization would be to examine the  $N_{\text{fix}}$  to illite-in-I/S ratio ( $N_{\text{fix}}/I/S$ ) world-wide. If  $N_{\text{fix}}/I/S$  is similar from basin to basin, then availability of fixing sites is probably the rate-limiting step. If  $N_{\text{fix}}/I/S$  is variable, then one must consider not only the availability of  $\text{NH}_4^+$  but also other kinetic factors, such as diffusion-coefficient partitioning due to the relative concentration of competing cations in solution, and the presence of different organic-matter types with varying nitrogen contents. Since the new method proposed here also measures organic carbon content, the  $C_{\text{org}}/N_{\text{org}}$  ratio should serve as an index to monitor differences in organic-matter type.

## CONCLUSIONS

A new method is offered for the determination of fixed inorganic nitrogen in clay minerals. The technique is operationally defined as the nitrogen that remains associated with the clay structure after 8 hr of heat treatment at 450°C. This new method provides distinct advantages over other methods in that it is simple and can accommodate small sample sizes (10 mg). Independent analysis of the  $\text{NH}_4^+$  concentrations using FTIR reveals that for the samples studied, a measurable quantity of inorganic fixed nitrogen is retained after heating.

A high correlation exists between the proportion of fixed nitrogen in the < 0.2  $\mu\text{m}$  fraction of Gulf Coast Miocene shales and the percent illite in I/S. The relationship between nitrogen content and degree of illitization is dependent upon both the availability of nitrogen and fixing sites in authigenic illite-type layers. However, the relative importance of each is not well understood for shales in the same sedimentary basin or between different basins worldwide. Use of the inorganic nitrogen to illite-in-I/S ratio ( $N_{\text{fix}}/I/S$ ) may offer an approach to assess this relationship.

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