

AMMONIUM SILICATE DIAGENESIS AND ITS INFLUENCE  
ON THE INTERPRETATION OF FIXED-AMMONIUM  
ANOMALIES AS AN EXPLORATION TOOL

Progress Report

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## ABSTRACT

The study of nitrogen ( $\text{NH}_4^+$ ) diagenesis associated with hydrocarbon occurrences is intended to aid in predicting favorable areas of petroleum exploration and recovery by establishing a better understanding of the interaction of organic maturation products with clastic sedimentary sequences. Our research has indicated that fixed- $\text{NH}_4$  in clays preserves anomalous  $\text{NH}_4^+$  abundances, thus recording a significant reaction in the maturation of hydrocarbons which correlates with the "oil window". Fixed- $\text{NH}_4$  concentrations are independent of total organic carbon content, but increase with organic maturity in source rocks (up to  $T=140^\circ\text{C}$ ). We have found anomalously high fixed- $\text{NH}_4$  concentrations in oil and gas reservoirs, and in sandstones that may have acted as migration conduits for a nearby oilfield. The remainder of the project period will be spent completing publications, and finalizing the interpretation of results on fixed- $\text{NH}_4$  in the Salton Sea (SSDP) and Monterey Fm. The data we have collected from these areas will allow us to examine the effect of high temperatures and high-N organic matter (prevalent on the west coast) on levels of  $\text{NH}_4$ -fixation. We will also develop some preliminary ideas on the mechanism of  $\text{NH}_4^+$  oxidation responsible for high- $\text{N}_2$  (gas) reservoirs such as Sorrento Field, Colorado.

## INTRODUCTION

An understanding of fixed- $\text{NH}_4$  in the nitrogen cycle of deeply buried organic-rich sedimentary environments is potentially useful in evaluating hydrocarbon maturity and tracing migration pathways. N-compounds have previously been considered insignificant components of hydrocarbons, because kerogen generally contains only  $\approx 2\%$  N, while oil contains  $< 0.5\%$  N. However, Hunt suggests (1979) that thermogenic-N is released during the catagenetic stage of organic maturation (or "oil window") and that N has not been accounted for in the diagenetic environment. In the reducing environments associated with organic matter accumulations, N is predominantly in the form of ammonium ion ( $\text{NH}_4^+$ ).  $\text{NH}_4^+$  substitutes for  $\text{K}^+$  in aluminosilicates such as clay minerals, feldspars and zeolites. When  $\text{NH}_4^+$  becomes integral to a silicate structure, it is called "fixed- $\text{NH}_4$ " and it is protected from environmental fluctuations that might affect dissolved, organic, and exchangeable forms of N. Once the ion is fixed it may become a relatively permanent indicator of the chemical environment existing when the mineral formed. Due to its low hydration energy,  $\text{NH}_4^+$  may be preferentially incorporated in authigenic minerals.

Previous work showed that fixed- $\text{NH}_4^+$  is commonly concentrated in authigenic silicate minerals formed near sedimentary exhalative ore deposits hosted by organic-rich shales. The  $\text{NH}_4^+$  is thought to be leached from organic matter in the sediments as hydrothermal fluids migrate through the strata and is incorporated in silicate minerals at the site of ore deposition. This discovery formed the basis for our current project, which is to determine at what stage of thermal maturity N is released from organic matter in the deep subsurface and whether or not "fixed- $\text{NH}_4$ " concentrations could be used in hydrocarbon exploration.

## ACCOMPLISHMENTS DURING REPORTING PERIOD 7/1/89 - 10/30/90

### **1. Results of Preliminary Experiments**

Our initial research plan specifically addressed the conditions favoring the substitution of  $\text{NH}_4^+$  in clay minerals, because clays are the primary host minerals in diagenetic environments. We tested several techniques for the preparation and analysis of samples for fixed- $\text{NH}_4$ . The best results were obtained by standard Kjeldahl digestion and distillation methods, so two distillation units were built in our laboratory.

To determine the quantities and relative rates of  $\text{NH}_4$ -fixation for the dominant types of clay minerals, we conducted experiments using Clay Minerals Society standards of illite, smectite, and mixed-layered I/S (60/40 ordered) in a 0.05M  $\text{NH}_4\text{Cl}$  aqueous solution. Three reaction vessels were kept at temperatures of 25, 60, and 80°C, respectively, to simulate early diagenetic temperatures, and experiments were conducted at pH 4 and 8. Reducing conditions were maintained by steady flushing of the vessels with Ar (gas) to remove  $\text{O}_2$ . Samples were taken periodically over 128 days.

Results showed that the highest rates of  $\text{NH}_4$ -fixation occurred in mixed-layered I/S (Standard ISMT-1) at pH=4 (rate=12 mg/kg/day). The quantity of  $\text{NH}_4^+$  fixed is directly proportional to temperature, but equilibrium was not attained in any case. The increase in fixed- $\text{NH}_4$  concentrations in I/S with time and temperature may be due to progressive ion exchange, or illite authigenesis. The fixing capacity of smectite (Standard SWY-1) was highly variable over time, most likely because of the low layer charge allowing for weak attraction of cations. Unless the smectite layers collapse, the ratios of interlayer cations apparently fluctuate. Discrete illite (Standard Silver Hill Illite) showed a very low  $\text{NH}_4$ -fixing capacity because the interlayers are already electrically balanced and collapsed. These experiments indicate that charge heterogeneity associated with I/S mixed-layered clays and the conversion of smectite to illite are important in controlling the quantities of fixed- $\text{NH}_4$ .

### **2. Surface vs Subsurface Fixed- $\text{NH}_4$**

Many studies have examined the role of N interacting with sediments in near-surface organic-rich environments. During the early diagenesis of N supplied by the bacterial decay of organic matter, dissolved  $\text{NH}_4^+$ -N normally increases with depth. We examined fixed- $\text{NH}_4$  concentrations in shallow cores near a Holocene oil seep in the Green Canyon area, offshore Gulf of Mexico, to see if the presence of migrating hydrocarbons had a significant impact on fixed- $\text{NH}_4$  concentrations. Results were compared to two producing reservoirs at ~4 km depth in Fordoche Field, Pointe Coupee Parish, Louisiana. The comparison was made in order to examine the effect of progressive diagenesis/thermal maturation on fixed- $\text{NH}_4$ , and to see if anomalously high fixed- $\text{NH}_4$  concentrations occurred near crude oil accumulations.

We found that fixed- $\text{NH}_4$  concentrations within mudstones are twice as high at depth than in surface sediments and that intervals of the sandstone from which oil is extracted contain anomalously high fixed- $\text{NH}_4$  concentrations. Total organic carbon (TOC) in the deep reservoirs is only one third the TOC

content of Green Canyon samples. This may reflect the release of CO<sub>2</sub> and CH<sub>4</sub> from organic matter that occurs with increasing burial. We suggested (Williams et al., 1989) that during catagenesis, the rapid thermal cracking of hydrocarbons allows the release of N (as NH<sub>4</sub><sup>+</sup>) in relatively large quantities and this is reflected in the higher fixed-NH<sub>4</sub> concentrations of clays. The NH<sub>4</sub><sup>+</sup>(aq) migrates along the same path as the hydrocarbons and some continued release of N occurs as hydrocarbons continue to mature and degrade throughout migration. The lack of fixed-NH<sub>4</sub> anomalies in surface samples associated with migrating hydrocarbons may be due to low temperatures, lack of authigenic mineral growth to capture significant quantities of NH<sub>4</sub><sup>+</sup>, oxidation, and/or microbial attack of NH<sub>4</sub><sup>+</sup>. Our case study shows that although NH<sub>4</sub><sup>+</sup> may be provided by the degradation of hydrocarbons, the right geochemical and mineralogical conditions must exist to preserve the anomaly.

### **3. Fixed-NH<sub>4</sub> in Oil, Gas and Dry Wells**

After establishing that fixed-NH<sub>4</sub> concentrations were apparently anomalous in deep subsurface (4km) sandstones that contained migrated crude oils, the next step was to compare the fixed-NH<sub>4</sub> concentrations in the crude oil reservoir to those in a gas well and in a non-productive sandstone with similar depositional and burial histories. We examined two stratigraphically equivalent cores from the Wilcox Group in Fordoche Field; one from a well producing crude oil, and one from an abandoned gas well at the edge of the field. A dry hole from Fordoche was not available, so we used samples from a wildcat in Hurricane Creek Field, Allen Parish, that intersects an equivalent interval with sediments similar to those in Fordoche Field.

Because there are significant depositional differences between sandstones and mudstones that affect organic content and mineralogy, samples were divided by lithology for comparison. Rock Eval pyrolysis was used to determine organic matter type and level of maturity. The mudstones of both areas contain mixed type II (marine) and type III (terrestrial) organic matter that is marginally mature to mature (T<sub>max</sub> 436 - 445°C). The burial temperatures range from 113 - 120°C in the Fordoche Field cores and 88-140°C in the core from Hurricane Creek Field.

Concentrations of fixed-NH<sub>4</sub> from organic-rich mudstones show a general increase with depth, coincident with increasing organic maturity. Reservoir sandstones containing crude oils show a two-fold increase over background, while fixed-NH<sub>4</sub> concentrations in the gaseous portion of the reservoir are three times background. Two out of five sandstone intervals sampled in the dry hole at Hurricane Creek contain anomalously high concentrations of fixed-NH<sub>4</sub> (similar to concentrations found in the crude oil reservoir at Fordoche Field). These same two sandstones have substantially higher pyrolysis indices (Production Index and Hydrogen Index) than other sandstones in the section (PI >0.2; HI >250), which is additional evidence to suggest that hydrocarbons may have migrated through these sandstones.

### **4. Ammonium substitution relative to illite authigenesis.**

One difficulty with the results discussed for the diagenetic studies of fixed-NH<sub>4</sub> is that proposed increases in thermogenic-N from the breakdown of hydrocarbons occur coincident with temperatures (depths) that cause the

illitization of smectite. Because of the coincidence of these two processes that act to enhance fixed-NH<sub>4</sub> concentrations of a sample, we could not say with certainty whether the observed increases in fixed-NH<sub>4</sub> result from increased pore fluid NH<sub>4</sub><sup>+</sup>, or simply the increased uptake of available NH<sub>4</sub><sup>+</sup> by authigenic illite.

To resolve this problem, we studied samples from the contact aureole of the basaltic Walsen dike, which intrudes the Cretaceous, organic-rich Pierre Shale near Walsenburg, Colorado. Shallow burial of the section allowed minimal advancement of diagenetic reactions prior to dike emplacement and sampling from a thin stratigraphic interval minimized depositional variations in mineralogy and organic matter type. Samples were taken at increasing distances from the dike, along a well-defined geothermal gradient that was established previously by thermal modeling (Pytte and Reynolds, 1989). The kinetics and stoichiometry of the smectite to illite transformation were well defined within the contact aureole and organic matter maturity was determined by vitrinite reflectance (Bostick and Pawlewicz, 1984).

Our analyses of fixed-NH<sub>4</sub>, mineralogy, and hydrous pyrolysis indicators of organic matter maturity provided new insights on the fixation process. Fixed-NH<sub>4</sub> concentrations increase (to ≈1100 mg/kg clay) with the quantity of authigenic illite formed during the smectite->illite transformation, but the maximum NH<sub>4</sub>-fixation per unit of illite formed occurs within the "oil window" where thermal breakdown of organic matter is rapid.

At a distance of 5 m from the dike, where temperatures reached 250-300°C, fixed-NH<sub>4</sub> concentrations drop to about 500 mg/kg clay. Statistical correlations suggest that in the 6 samples taken within 5 m of the dike, NH<sub>4</sub><sup>+</sup> is associated with feldspar rather than authigenic illite. The change in affinity of NH<sub>4</sub><sup>+</sup> for one host mineral over another may have an effect on total fixed-NH<sub>4</sub> concentrations. While this study confirms the association of high NH<sub>4</sub>-substitution with mature hydrocarbons, it also points out the necessity of considering variations in host mineralogy when interpreting fixed-NH<sub>4</sub> anomalies.

#### Goals For Next Reporting Period

The remaining six months of the current grant period will be spent completing the following investigations, and finalizing publication of results.

##### **1. Fixed-NH<sub>4</sub> under a high temperature gradient: Salton Sea (CA)**

Fixed-NH<sub>4</sub> was analyzed in samples from the US DOE Salton Sea Scientific Drilling Project, where the geothermal gradient is steep and well defined (Sass et al., 1988). Samples were provided by the DOE Core and Sample Repository (Grand Junction, CO) from the interval between ≈600-3000 m depth. Fixed-NH<sub>4</sub> concentrations in this core decrease with depth. Although samples above 1200 m show significant quantities of fixed-NH<sub>4</sub>, samples below this depth are metamorphosed (T>300°C), and fixed-NH<sub>4</sub> concentrations approach the minimum detection limit. This is easily explained by the stability field of NH<sub>4</sub><sup>+</sup>. Ammonia (NH<sub>3</sub>) is the dominant form of N at high temperatures and low pH, and it does not interact with silicate minerals as NH<sub>4</sub><sup>+</sup> does. Mineralogic examination of the samples representing temperatures from 200-300°C may reveal

$\text{NH}_4^+$  to be hosted by feldspar rather than illite (muscovite), as was observed in the near dike samples from Walsenburg.

### **2. Fixed-NH<sub>4</sub> in a high organic-N source area: Monterey Fm**

We have examined fixed-NH<sub>4</sub> from two cores located in productive areas of the Monterey Fm, California. One core from the Lost Hills Oil Field does not intersect a reservoir and one core from the Santa Maria Basin is from a producing offshore oil well. The clay mineralogy from each core is being examined in detail. In the offshore well, the % illite in mixed-layered illite/smectite increases from ~10% to ~80%. Fixed-NH<sub>4</sub> concentrations relative to the changes in clay mineralogy indicate maximum NH<sub>4</sub>-substitution within the interval of hydrocarbon production, and thus supports our model for the use of fixed-NH<sub>4</sub> as an exploration tool. The Monterey Fm samples contain extremely high fixed-NH<sub>4</sub> concentrations, up to 13,000 mg/kg clay (1.30 wt.%). Concentrations that high are almost detectable by XRD (indicated by the 003 peak shift to lower angles), but the high silica content of the samples interfere with this analysis.

Rock Eval pyrolysis analyses of the Monterey Fm are commonly confusing as indicators of organic matter maturity. Conventional interpretation of these parameters would indicate that the Monterey source rocks are too immature to have generated oil, even in places where major discoveries have been made. Pyrolysis results on the Lost Hills samples show a general increase in organic maturity with depth, but maturity parameters of the deepest samples still indicate immature kerogen. One explanation for this may be indicated by our observation of a strong correlation between fixed-NH<sub>4</sub> and the Hydrogen Index for samples from the Lost Hills core. It is possible that the very high fixed-NH<sub>4</sub> concentrations could inflate the S<sub>2</sub> pyrolysis peak which is used to indicate the hydrogen content of the kerogen. Ammonium is released from silicates beginning at 400°C with a maximum release at 650°C (Kydd and Levinson, 1986).

Samples from the other oil well are still under investigation. Splits of the samples have been sent to Chevron Research Laboratories in La Habra, California for a complete chemical analysis, and ion chromatographic analysis of fixed-NH<sub>4</sub> concentrations for comparison to our method.

### **3. Fixed-NH<sub>4</sub> in a high-N gas reservoir: Sorrento Field (CO)**

At the request of an oil company interested in determining the origin of high-N gas in the Sorrento Field in southern Colorado, we sampled 12 cores across the field and examined the fixed-NH<sub>4</sub> concentrations and bulk mineralogy. Analyses revealed no fixed-NH<sub>4</sub> anomalies; samples contained fixed-NH<sub>4</sub> concentrations approximately equal to background levels of fixed-NH<sub>4</sub> that we observed in the Wilcox cores. This leads us to believe that something is acting to alter the speciation of N released from hydrocarbons in this area so that  $\text{NH}_4^+$  is no longer the dominant form of N. N<sub>2</sub> (gas) is non-reactive with minerals, therefore one would expect only background levels of fixed-NH<sub>4</sub> (from detrital minerals) where N<sub>2</sub> gas predominates. We are interested in pursuing the question of N speciation and its effect on fixed-NH<sub>4</sub> as a tracer of hydrocarbons.

### Most Recent Publications

Williams, L.B. and Ferrell, R.E. Jr., 1990, Ammonium-fixation and thermal maturity in the contact aureole of the Walsen Dike, Colorado, *Geology*, in review.

Williams, L. B., Wilcoxon, B.R., Ferrell, R.E., and Sassen, R., 1990 Nitrogen as an indicator of hydrocarbon maturation and migration, *AAPG Bulletin*, in review.

Williams, Lynda B., Ferrell, Ray E., Chinn, Elizabeth .W., and Sassen, Roger, 1989, Fixed-ammonium in clays associated with crude oils, *Applied Geochemistry* 4:6:605-616.

Williams, Lynda B., and Ferrell Ray E. Jr., 1990, Chemical and Mineralogical controls on ammonium substitution in authigenic illite, *Geological Society of America, Abstracts with Programs*, 22:7:A206.

Williams, Lynda B., 1990, Nitrogen diagenesis related to organic maturation in Gulf Coast sediments, *AAPG Bull.* 74/5:792.

Note: The Houston Geological Society has invited us to publish a review article of this work in their journal. The article is in preparation but should be published in early 1991.

### References Cited in Text

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Kydd, R.A. and Levinson, A.A., 1986, Ammonium halos in lithogeochemical exploration for gold at the Horse Canyon carbonate-hosted deposit Nevada, U.S.A.: use and limitations, *Applied Geochemistry*, 1: 407-417.

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