ORGANIC/INORGANIC INTERACTIONS OF NITROGEN IN OILFIELDS
PART 1: GEOCHEMISTRY

Progress Report

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Lynda B. Williams

Department of Geology
Arizona State University
Tempe, Arizona 85287-1404

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ABSTRACT

A detailed investigation of the geochemistry of nitrogen in oilfields is being conducted in order to test the model that N is generated from hydrocarbons during thermal maturation and is incorporated into authigenic clay minerals in the sediments through which the oil and brines migrate. If the model is correct, there should be fixed-NH₄ anomalies that can be correlated across an oilfield to indicate the pathway of migration into the trap. The preliminary data from this research shows that fixed-NH₄ anomalies are associated with producing intervals in twelve cores examined across a multi-reservoir oilfield. Trends in fixed-NH₄ values across the field do not reflect present brine NH₄⁺ concentrations. Fixed-NH₄ anomalies are greatest in the structurally high areas of the anticlinal trap, while brine NH₄⁺ concentrations are greatest near a fault that is a likely entry point for oil into the trap. Limited isotopic data show ~3‰ variation in δ¹⁵N across one reservoir with the heavier values found in the same well as the maximum fixed-NH₄ anomalies.

Results generated in the next grant period will allow construction of a three dimensional map of fixed-NH₄ anomalies that should indicate migration conduits and possibly identify compartments of by-passed oil. Isotopic analyses will help define the direction of migration, and may be useful in making oil-source rock correlations.

INTRODUCTION

The initial investigation of fixed-NH₄ in clay minerals (grant DE-FG05-87ER13748) showed that fixed-NH₄ concentrations increase as authigenic illite forms with increasing temperature or depth of burial (Williams and Ferrell 1991). Anomalously high fixed-NH₄ concentrations occur near hydrocarbon reservoirs (Williams et al., 1989), and in sandstones that may have acted as hydrocarbon migration conduits (Williams et al., 1992). These observations, lead to the suggestion that fixed-NH₄ concentrations in a diagenetic environment may be used to indicate levels of hydrocarbon maturation within a source rock and to trace paths of hydrocarbon migration. The model derived from the initial study suggests that N is released from hydrocarbons during maturation and throughout migration as hydrocarbons are degraded. Nitrogen is predominantly in the form of NH₄⁺ which substitutes for K⁺ in authigenic minerals. The interaction of organically derived N with inorganic components (rock and brines) in the diagenetic environment allows high levels of NH₄⁺ substitution in authigenic minerals (predominantly clay)

which may be useful in geochemical exploration.

With support from the current grant (DE-FG02-91ER14218), a detailed investigation of this model is underway. The goal of the current research is to better understand the interaction of organogenic-N with minerals in oilfields, in order to evaluate the usefulness of fixed-NH₄ anomalies in siting productive wells and in establishing areas containing by-passed oil. A detailed study of Fardoche Field; an oilfield in the Louisiana Gulf Coast Basin (Figure 1), is proceeding as planned. This field is a typical Gulf Coast oilfield with basin stratigraphy and structure representative of the majority of known hydrocarbon accumulations. Therefore the results for this field should be applicable to many other oilfields.

The nitrogen geochemistry of the oilfield is the primary responsibility of this investigator. Seventy five percent time has been devoted to this work, and the same level of effort will be maintained for the remainder of the grant. Collaborative work is being done on the mineralogy and microbiology of Fardoche Field by Drs. Ray Ferrell and Maud Walsh at Louisiana State University (DE-FG05-87ER13748). The approach for the geochemical investigation is to chemically characterize all components of the hydrocarbon environment that could have an influence on NH₄⁺ fixation. Primary analyses include Kjeldahl digestion and distillation of core samples for determination of fixed-NH₄ concentrations, and extraction of fixed-N for isotopic analysis. The isotopic composition of fixed-NH₄ is being examined and compared to that of the oil, associated kerogen, and formation waters (brines) in order to better understand the interplay of nitrogen among its various hosts. Other analyses necessary to interpret the fixed-NH₄ data include Rockeval pyrolysis, CHN analysis of total-N, chromatographic analysis of the oil, bitumen and kerogen, and some major element chemistry. The results will allow generation of a three dimensional map showing detailed variations in the N-geochemistry across a multi-reservoir oilfield.

If the fixed-NH₄ analysis of Fardoche Field supports our early hypotheses, an examination of oil, brine and rock samples from an oilfield in northern Louisiana (the Nebo-Hemphill Field) is planned for comparison. It has been suggested that this field contains oils from the same source area as the Fardoche Field, and that the oils have migrated more than 100km (Sassen, 1990). If this is the case, there should be significant differences in the N-isotopic composition of both the organic and inorganic-N.

Figure 1. Location of Fordoche Field, Pointe Coupee Parish, Louisiana

ACCOMPLISHMENTS DURING REPORTING PERIOD 9/15/91 - 5/15/92

Fordoche Field

One dozen cores were sampled from across Fordoche Field, and Fordoche extensions to the north, east and west of the main trap. Samples were collected from three sandstone reservoirs that are separated stratigraphically by hundreds to thousands of feet of organic-rich mudstone. Every lithologic facies represented was sampled in detail yielding a total of 163 samples. Sandstones were predominantly sampled in order to evaluate fixed-NH₄ variations within the heterogeneous sand bodies. Pictures were taken of the cores before they were crushed to separate out clay minerals. Whole rock powders were prepared for fixed-NH₄ analysis and nitrogen extraction. A split of the whole rock powders was examined by X-ray diffraction for an estimation of bulk mineralogy.

A trip was made to Fordoche Field in February 1992 to collect fresh oil and brine samples. Eight wells were sampled. At each well one liter of oil and two liters of brine were collected; pH, temperature and alkalinity were measured. Brine samples were prepared in the field for C and S isotopic analysis, and N-species were analyzed in the laboratory one day after collection. Kjeldahl distillation was done at a later date in order to extract the N from brines for isotopic analysis. Isotopic analysis of the inorganic-N compounds are being performed at The University of Calgary, and isotopic analysis of the organic-N compounds in the oils are being done at Argonne National Laboratory.

Completed analyses include whole rock mineralogy and fixed-NH₄ concentrations for the Fordoche Field whole rock samples. More than 250 µg of nitrogen was extracted from all samples and concentrated as ammonium sulfate crystals for isotopic analysis. Rockeval pyrolysis has been performed on 87 samples representing each lithology sampled. Rockeval provides a good estimate of the total organic carbon content of each facies. Total-N was determined by CHN analyzer on the same 87 samples. Organic nitrogen contents can be determined by difference between total-N and fixed-N.

By ratioing the fixed-NH₄ concentrations to the clay mineral content of each sample a rough estimate of the levels of NH₄ -fixation can be obtained. Interpretations based on this estimate are preliminary, and may be revised once clay mineral data are available. Ammonium is primarily fixed in authigenic minerals (Williams and Ferrell, 1991), therefore detrital clay will interfere with the analysis of fixed-NH₄ ratioed to total clay contents. Nevertheless, if we assume that the clay minerals are predominantly authigenic (as was indicated in our initial investigation)

then a preliminary interpretation of the data can be made. These data must be evaluated in the context of stratigraphic and structural influences. For the remaining discussion, the term "fixed-NH₄ value" will refer to fixed-NH₄ *concentrations* normalized to the clay content.

Variations in the fixed-NH₄ value for each core shows that a fixed-NH₄ anomaly exists in every producing horizon. In some cases the anomaly is slightly below the actual production perforation, which may be where the NH₄-enriched brines are concentrated. Lithological differences exist across the field that affect porosity, permeability and the general suitability of the sandstones as hydrocarbon reservoirs. Lithological variability is further complicated by anticlinal folding and a listric growth fault which transects the field (Figure 2). The fixed-NH₄ values could be affected by these structural and stratigraphic variations. This is indicated by broad variations in background fixed-NH₄ values among the wells and reservoirs (Figure 3). Structural contour maps of the reservoir sandstones indicate that two domes exist along the anticlinal axis at the depth of the W-8 and W-12 sandstones. Higher fixed-NH₄ values (2X background) are associated with wells located within these domes. The highest fixed-NH₄ values (3X background) are associated with an abandoned gas well in the southeastern end of the field (El Plant 7). The contour of the oil/water interface indicates that the two domes are oil (and gas) saturated. Wells that intersect the reservoir sandstones within the water dominant areas contain fixed-NH₄ values that are generally lower than in the hydrocarbon saturated zones, but they still show high fixed-NH₄ values in the intervals of oil production. Cores that represent non-productive sections of the reservoir contain some intervals of sandstone with moderate NH₄-anomalies which could be interpreted as migration conduits. All of these samples are from the edges of the field, and most likely represent the maximum extent of the NH₄-enriched brines.

The anomalous fixed-NH₄ values do not reflect present day brine NH₄⁺ concentrations. Concentrations of NH₄⁺ in the brines are clearly highest near the major listric fault, and decrease with distance away from the fault to the southeast (Figure 4). This is essentially opposite from the trend observed in fixed-NH₄ values. The high brine NH₄⁺ concentrations could result from oil being generated in source rocks at depth, and migrating up the listric fault. As oil is being extracted from the field, the brine NH₄⁺ concentrations would decrease in the domes where it was previously trapped. The encroachment of fresh formation water would dilute the pore water NH₄⁺ concentrations. Notably the lowest concentration of brine NH₄⁺ (23 mg/l) is found on the north side of the fault in the Sparta B reservoir. This is difficult to reconcile with the model of fault

LEAF

Figure 3. Histograms representing background and peak fixed-NH₄ values in wells across Fordoche Field. Distance from the fault increases from left to right.

Fordoche Field

Cross Section (Down the axis of the anticline)

Figure 4. Cross Section down the axis of the anticline across Fordoche Field. Approximate locations of wells sampled are indicated above each reservoir. Brine NH₄ concentrations are indicated in parentheses below the wells. Sandstone thickness is based on maximum thickness measured for each unit.

migration, except that the John Green 1 well is currently located in the water saturated area on the flank of the anticlinal structure. This reflects a possible influence of the oil/water ratio on pore fluid NH_4^+ concentrations.

There are only limited data on fixed- NH_4 isotopic compositions at this time. This data, from selected samples across the field, indicates that there is a 2-3‰ difference in isotopic composition between the mudstones and sandstones, and that there is roughly a 3‰ variation in N-isotopic composition across the W-8 reservoir with the heavier compositions represented in the southeast end of the field. These observations may be consistent with migration of the oil from the fault, toward the south-southeast. Once the data set is complete, we will be able to observe variations in N-isotopic compositions of fixed- NH_4 in all three reservoirs, and compare those trends with the N-isotopic composition of the brines, oils, and kerogen.

In conclusion, at this point, data suggest that oil migrated up the fault and toward the southeast into two anticlinal domes. The more volatile phases migrated farthest to the southeast into the structurally highest portion of the trap. The gas well, El Plant 7, intersects the W-8 and W-12 reservoir sandstones at the top of the dome located in the southeastern portion of the field. The fact that the highest fixed- NH_4 anomalies are associated with this gas well, suggests that NH_4^+ was initially concentrated with the volatiles. It is feasible that the present day brines do not show high NH_4^+ concentrations in the domes because exploitation of the oil has altered the pore fluid NH_4^+ concentrations. If this proves to be the case it will confirm our contention that fixed- NH_4 concentrations are a record of past geochemical conditions, that are unaffected by current geochemical fluctuations.

Monterey Formation

A comparative study was made of cuttings from a well in the Lost Hills Field, in the Miocene Monterey Fm, San Joaquin Basin, California. The results of this study were presented at the Annual Geological Society of America Meeting last fall (Williams et al., 1991). The samples were chosen because the Monterey Fm represents a high-N source rock. Oilfields in the Monterey Fm are atypical in that oil is generally produced from fractured reservoirs in a very siliceous siltstone. Petroleum is thought to be generated essentially in situ, at relatively low temperatures, forming an asphaltene rich oil high in NSO compounds (Compton et al., 1992). The results from this study show clear fixed- NH_4 anomalies within the oil horizon of the well, but show no change in isotopic composition of the fixed- NH_4 . The isotopic compositions remain around 6‰ in both

productive and non-productive intervals of the sediment. The isotopic composition of the kerogen and oil from this unit was approximately 3‰ higher. It is concluded that the migration distance was apparently insufficient to have caused a significant difference in the fixed-NH₄ isotopic composition in the reservoir versus the enclosing sediments. Where migration distances are negligible, there is apparently no significant change in N-isotopic composition.

GOALS FOR THE NEXT REPORTING PERIOD

Sampling and sample preparation for Fordoche Field is complete, therefore the next reporting period will be dominated by completing geochemical analyses and gathering data from the various collaborators. The mineralogy and microbiology are underway at Louisiana State University. If all goes well the geochemical results for Fordoche Field will be complete by the end of the year. Work next year will concentrate on the integration of data, and publication of results. Remaining geochemical work to be done includes, 1) analysis of fixed-NH₄ and extraction of N from clay mineral separates, 2) testing of the isotopic extraction to be certain that isotopic variation is not induced by the extraction procedure, 3) extraction of kerogen and bitumen from the Fordoche Field samples for isotopic analysis and gas chromatography, 4) Fourier Transform Infrared (FT-IR) analysis of selected samples will be done in order to develop this analytical technique as a rapid method of examining fixed-NH₄ in the subsurface. As data is collected the final interpretation of organic/inorganic interactions of nitrogen in Fordoche Field will be made.

One more trip is planned to the Nebo-Hemphill Field in northern Louisiana to collect oil, brine and core samples for a comparative study. Approximately two dozen samples will be collected and processed as described for the Fordoche Field. Examination of N-isotopic ratios from the oil, brine and fixed-NH₄ in sediments from this field will test the model proposed by Sassen (1990) that indicates long range (100km) migration of crude oils in the Wilcox Fm. An oil that has migrated this distance should be significantly heavier in isotopic composition than near its source, and this should be reflected in the sediments as well as the oil. At the conclusion of the next reporting period, a very extensive data set will have been generated that should allow us to determine the role of nitrogen in fluid/rock interactions on a small regional scale as well as the larger interbasinal scale. This should help determine whether or not fixed-NH₄ is a valid geochemical indicator of hydrocarbon migration.

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