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Organic/Inorganic Interactions of Nitrogen in Oil Fields

Part 1. Geochemistry

Final Report

Sept. 15, 1991-March 15, 1994

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March 1994

**PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG02-91ER14218**

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MASTER

Abstract

This research examines the nitrogen isotopic composition of fixed-NH₄ in order to test the hypothesis that NH₄⁺ is released from organic matter during hydrocarbon generation and can be incorporated in diagenetic clay minerals along migration conduits. Anomalously high levels of NH₄-substitution recognized in hydrocarbon bearing sandstones may indicate paths of hydrocarbon migration long after the hydrocarbons have moved on toward a trap. This is important because most of remaining oil reserves in the U.S. are thought to be in stratigraphic traps, and recognition of migration conduits may help to locate compartments of by-passed oil. Examination of NH₄⁺ in diagenetic clay minerals is intended to aid our understanding of reservoir heterogeneity and make enhanced recovery projects more successful.

More than 200 $\delta^{15}\text{N}$ measurements were made of kerogen, bitumen, oil, formation water, and fixed-NH₄ extracted from mudstones, non-productive sandstones, and productive sandstones from two stratigraphically related regions in the Gulf Coast Basin (USA). Results show that $\delta^{15}\text{N}$ of kerogen does not vary from shallow lignite deposits (at 60°C) to deep sedimentary kerogen in source rocks ($\approx 125^\circ\text{C}$), however bitumen becomes ¹⁴N depleted with depth. The $\delta^{15}\text{N}$ of oil near the source area correlates with bitumen, but becomes depleted in ¹⁴N with increasing distance from the source area. Formation water becomes similarly depleted in ¹⁴N indicating equilibrium between the oil and water (90–125°C). Changes in fluid $\delta^{15}\text{N}$ may result from preferential stripping of ¹⁴N-compounds by clay minerals. Authigenic illite can record the $\delta^{15}\text{N}$ of migrated fluids depending on the timing of illitization relative to migration, and fixed-NH₄ quantities (relative to %illite) can indicate horizons within sandstones through which hydrocarbons have travelled. The $\delta^{15}\text{N}$ of fixed-NH₄ falls on a mixing curve between $\delta^{15}\text{N}$ of the oil and water depending on the oil/water ratio. The relative timing of migration may be deduced from N-isotopic relationships between the organic and inorganic phases. Where authigenic illite formation is minimal ($T \leq 60^\circ\text{C}$), fixed-NH₄ may only represent N inherited from detrital sources or local organic matter. Fixed-NH₄ anomalies are not found associated with petroleum occurrences in the shallow basin sediments examined.

Introduction

Ammonium (NH_4^+) is present in pore fluids from the breakdown of organic compounds. "Fixed- NH_4 " refers to NH_4^+ that substitutes for K^+ in the interlayer sites of clay minerals. Once NH_4^+ is fixed in a mineral structure it is not released until the structural framework of the mineral is altered. Field and laboratory experiments performed under the initial grant (DE-FG05-87ER-13748) led to recognition of the relationship between fixed- NH_4 quantities and hydrocarbons in oil fields. The amount and type of organic-N molecules present in organic matter varies, however field investigations showed an increase in the quantity of fixed- NH_4 as maturity levels reach the catagenetic (oil producing) stage (Williams et al., 1989; Williams and Ferrell, 1991; Compton et al., 1992). In the Gulf Coast Basin, fixed- NH_4 concentrations in mudstones increase up to depths of ~4km. The increase may be a consequence of the degree of illitization and a redistribution of N-containing species rather than a net increase in the concentration of NH_4^+ . The more authigenic illite formed, the higher the fixed- NH_4 concentration (Williams and Ferrell, 1991). Documentation of this led to the normalization the fixed- NH_4 concentrations measured on whole samples to the amount of host mineral (in this case illite/smectite) in the rock. When fixed- NH_4 was normalized in this manner, anomalous fixed- NH_4 values were found within hydrocarbon producing intervals of cores from the Eocene Wilcox Fm (Gulf Coast Region)(Williams et al., 1992a,b) and from the Miocene Monterey Fm. (San Joaquin Basin, Calif.)(Compton et al., 1992). These data are significant because they establish a correlation between high NH_4 -substitution and the presence of hydrocarbons.

This research project (DE-FG02-91ER14218) was a field test of the use of fixed- NH_4 as an indicator of hydrocarbon migration paths within a basin. Examination of the concentration and isotopic composition of nitrogen in organic and inorganic phases provided data suggesting correlations that indicate the source of N incorporated into clay minerals, and how $\delta^{15}\text{N}$ changes during hydrocarbon migration.

A detailed analysis was made of nitrogen variations in two typical oil fields in the Eocene Wilcox Group of the Gulf Coast Basin (Fig. 1). One is a multi-reservoir field in south-central

Louisiana (Fordoche Field) at a depth of 4 km and one is located updip in the same strata at a depth of 2 km (Bee Brake Field). The mineralogy, N-content and N-isotopic composition of more than 200 samples was determined. A comparison of the two areas allows examination of the effect of burial temperature (and possible microbial activity) on the N-geochemistry of organic and inorganic phases. Furthermore, the two fields were chosen to test a proposal based on organic geochemical evidence that oils in the updip Wilcox reservoirs have migrated from source areas in the downdip Wilcox (Sassen, 1990). If this is the case, then significant changes in $\delta^{15}\text{N}$ due to migration may be expected (Stahl, 1977). The results of this project allow examination of diagenetic interactions of organic and inorganic-N on a local and regional scale. Mineralogy and Microbiology were examined in Part II of this project (R.E. Ferrell and M.M. Walsh).

Objectives

1. To provide a field test of the use of fixed- NH_4 as an indicator of hydrocarbon migration paths
2. To examine nitrogen isotopic compositions of organic and inorganic phases in order to establish the source of nitrogen in clays
3. To determine how diagenetic factors (temperature, mineralogy, microbiology) affect nitrogen fixation.

FORDOCHE FIELD

Summary of Results

The reservoirs in this oil field are divided by a normal growth fault which separates the productive intervals by ~2000 vertical feet (610m). This allows examination of diagenetic differences due to a temperature differential of ~30°C which spans the interval of maximum hydrocarbon generation during catagenesis (90-120°C). Details of the geology are summarized in the manuscript appended (Williams et al., 1994, in review). A discussion of the results is also in this paper, so a brief summary is presented here.

Figure 1. Location map (above) and cross section (below) showing location of oil fields studied.

The $\delta^{15}\text{N}$ of kerogen extracted from mudstones at depths of 11,500 ft. (3505m) to 14,300 ft. (4360m) average +3‰. The bitumen (soluble organic matter) extracted from the same samples is +3 to +5‰; increasing with depth. Oil in the deeper reservoir ($T \sim 120^\circ\text{C}$) has an average $\delta^{15}\text{N}$ of +5‰ corresponding to that of the bitumen in the source area (deep Wilcox mudstones). However, in the upper reservoir ($T \sim 90^\circ\text{C}$) oils have an average $\delta^{15}\text{N}$ of +11‰. Similarly brines in the deep reservoir are isotopically light (avg -2.2‰), but in the upper reservoir they average +4‰. Fluids (oil and water) apparently become enriched in ^{15}N during migration into the upper reservoir.

Inorganic-N extracted from clays in deep reservoir sandstones ($T > 100^\circ\text{C}$) have isotopic ratios similar to the oil (+3 to +5‰), while non-productive sandstones have distinctly low $\delta^{15}\text{N}$ values (+1 to -3‰), similar to the formation water. N extracted from mudstones corresponds isotopically with the bitumen (+3 to +5‰). At temperatures $< 100^\circ\text{C}$ clay minerals do not have isotopic compositions comparable to the co-existing oil. This suggests that authigenic clay minerals formed prior to the introduction of the present fluids. Authigenic illite incorporates NH_4^+ isotopically proportional to that of the fluid dominating the environment at the time of illitization. It is not isotopically reset during later fluid migration, unless recrystallization occurs.

Discussion

A model was formulated based on the data from Fordoche Field, which explains the changes in N-geochemistry and N-isotopic ratios observed. It integrates the observations into a broad scheme relating N-sources, burial diagenetic changes, and the evolution of N-isotopic ratios during the generation, expulsion and migration of oil.

N-containing organic materials of terrestrial and marine origin were deposited with smectite-rich clays in fluvial and coastal environments during the late Eocene. As they subsided and were exposed to increasing temperatures during burial, the organic matter matured and the smectite altered to illite. With increasing maturity, organic-N in mudstones decreases due to

changes occurring in certain organic compounds, possibly associated with terrestrial components of the whole rock kerogen. Organo-nitrogen compounds generated by the kerogen was incorporated in bitumen, oil, and clay minerals in the mudstones with little isotopic fractionation.

When buried to depths of ~15,000 ft. (~4500 m) and exposed to temperatures near 140°C, the Wilcox mudstones became effective source rocks for oil and the expelled hydrocarbons migrated a relatively short distance to accumulate in the deepest (Wilcox) reservoirs. Some of the N from the oil was released and equilibrated isotopically with the formation water ($\Delta_{\text{oil-water}} \approx -7\text{‰}$). The N-isotopic ratio of reservoir oil nearest to the source zone retained a $\delta^{15}\text{N}$ value corresponding to that of the bitumen in the source rock. With further migration (vertically ~2000 ft.) to the Sparta Fm reservoirs, the N in the oil and formation water became enriched in ^{15}N by $\approx 6\text{‰}$. Migration results in a loss of ^{14}N as the N-compounds in oil degrade, or are adsorbed by clay minerals.

Deep reservoir clay minerals develop N-isotopic ratios intermediate between the formation water and the crude oil while shallower reservoir clay minerals have N-isotope ratios that are more ^{15}N depleted than the associated waters and oils. The differences in the clay mineral N-isotope ratios occur because the deeper clay minerals are recrystallizing and equilibrating with the newly introduced fluids, while clay minerals at shallower depths preserve a N-isotopic ratio produced by earlier fluids.

BEE BRAKE FIELD

Results

The depositional environment of the sandstones in the updip Wilcox is somewhat different from downdip Wilcox sandstones. The sedimentological interpretation and kerogen petrography indicate deposition on the lower delta plain. The field encompasses a distributary channel, interdistributary bay deposits and intersects several lignite intervals representing swamp and marsh deposits (Goddard and Echols, 1993). One core (Angelina 1) was sampled in which oil is present in two thin sandstones at 6745 ft. (~2056m) and 6760 ft. (~2060m) that are part of the "Minter Interval". This is a well defined productive

horizon in Louisiana which is widely recognized in electric log correlations. We also sampled the Minter Interval at 14,300 ft. (~4360m) in the downdip Wilcox (Livonia Field; Kimball 1 core).

Organic Carbon and Fixed-NH₄

The geochemical results and facies interpretations for the Angelina 1 core are summarized in Table 1. The stratigraphy has been interpreted by Goddard and Echols (1993). Lignites are interbedded throughout the 500 ft (152m) core (Fig. 2; Table 1). Four lignites deposited in a lower delta plain marsh (Goddard and Echols, 1993) were sampled and have total organic carbon (TOC) values between 35 and 60%. The fixed-NH₄ concentrations for the lignites are ~500ppm which is similar to the concentrations observed in mudstones where TOC contents are only ~1% (Fig. 3). This indicates that the amount of organic matter present locally does not determine the amount of NH₄-fixation. Fixed-NH₄ concentrations in the oil producing interval of this core (6755-6757 ft) average ~150ppm (Fig. 3; Table 1), and in non-productive units such as the interdistributary bay deposits, the fixed-NH₄ concentrations are highly variable (from <100 to >500 ppm). The clay mineral content of each sample is the dominant control on the amount of fixed-NH₄. Clay rich samples contain >300 ppm fixed-NH₄. Fixed-NH₄ concentrations from these relatively immature sediments are similar to those found in Fordoche Field, which seems contrary to earlier results (Williams et al., 1989,1992) indicating that fixed-NH₄ increases with depth of burial (maturity). However, in this case we are looking predominately at fixed-NH₄ in sandstones, which represent an open system, whereas before we considered only shales which more closely represent closed system geochemical interactions.

Nitrogen Isotopes

The isotopic compositions of fixed-NH₄ in the Angelina 1 core (Table 1; Fig. 4) range from +0.2 to 6.2‰ which is not greatly different from values reported in the downdip Wilcox, but is more ¹⁵N enriched than the Sparta Fm samples. The kerogen (lignite interbedded with distributary channel and bay fill sandstones) has an isotopic ratio of +3.1±0.2‰ (n=4), which is similar to the kerogen isolated from mudstones in the Fordoche Field. This implies that most N-

Figure 2. Stratigraphy and electric log data for the cored interval (6367 - 6872 ft.). The blackened intervals on the SP log indicate lignites and mudstones. Arrows indicate sample locations. Oil is found at 6755-6757 ft.

Table 1. Angelina 1 Core Geochemical and Lithologic Data									
Depth (ft.)	Facies	Lithology	Perm. md	TOC %	Tmax °C	HI	OI	Fixed-NH4 ppm	$\delta^{15}\text{N}$
6384	Interdistrib. Bay	mudstone	25	0.89	430	92	188	433	0.75
6386	Interdistrib. Bay	mudstone	25	0.91	430	120	220	544	1.91
6400.5	Distributary Channel	sandstone	100					114	3.89
6407.5	Distributary Channel	sandstone	250					94	0.22
6442.5	Distributary Channel	sandstone	350					87	5.46
6455.3	Interdistributary Bay	laminated ms/ss	10	3.04	428	223	127	543	5.06
6457	Interdistributary Bay	laminated ms/ss	10					119	4.07
6458.5	Interdistributary Bay	laminated ms/ss	10					246	4.22
6458.8	Interdistributary Bay	laminated ms/ss	10					444	6.15
6459.5	Interdistributary Bay	laminated ms/ss	10	0.76	435	134	213	401	5.04
6587	L. Delta Plain Swamp	lignite	25	60.59	416	388	6	515	4.48
6619	L. Delta Plain Swamp	lignite	25	60.84	419	466	9		3.29
6742.5	L. Delta Plain Swamp	lignite	50	35.06	418	301	7		2.87
6742.8	L. Delta Plain Swamp	lignite	50					328	2.98
6744.5	Overbank Bay Fill	oil sandstone	100					200	3.12
6747	Overbank Bay Fill	oil sandstone	100					231	3.21
6749.9	Overbank Bay Fill	silty mudstone	50					174	0.98
6751	Overbank Bay Fill	silty mudstone	50	0.62	431	15	347	455	0.65
6755.8	Overbank Bay Fill	oil sandstone	200					121	3.01
6756	Overbank Bay Fill	oil sandstone	200					161	3.31
6757.9	Overbank Bay Fill	sandstone	50					226	1.08
6758.5	L. Delta Plain Marsh	lignite	50					543	3.15
6759.5	Interdistributary Bay	mudstone	50					551	2.85

Figure 3. Fixed-NH₄ concentrations versus sample depth. Facies are indicated for intervals sampled. The samples that contain >300 ppm fixed-NH₄ are mudstones or lignites.

Figure 4. Nitrogen isotopic ratios of fixed- NH_4 in core samples. The facies interpretation is from Goddard and Echols (1994).

compounds in kerogen are stable and generally non-reactive in the temperature range examined (60-125°C). One sample of lignite, which is interpreted based on maceral contents as being deposited in a wet forest swamp (Goddard and Echols, 1993), had a slightly higher $\delta^{15}\text{N}$ of +4.5‰. The more ^{15}N -enriched (terrestrial) organic macerals may contain more reactive N-compounds (Williams et al., 1994).

The average $\delta^{15}\text{N}$ of fixed- NH_4 in the mudstones is $1.5 \pm 0.9\text{‰}$ (n=3) which is half of the average $\delta^{15}\text{N}$ value of mudstones in the downdip Wilcox. The $\delta^{15}\text{N}$ in non-productive sandstone (e.g. Wilds Distributary Channel) is as variable as the fixed- NH_4 concentrations. In general, the low permeability sandstones (<50 md) have higher $\delta^{15}\text{N}$ values (avg. $+5 \pm 0.8\text{‰}$; n = 5), while high permeability sandstones (≥ 200 md) have extremely variable $\delta^{15}\text{N}$ (+0.2 to +5.5‰). The fixed- NH_4 in the productive "Minter Interval" has an average $\delta^{15}\text{N}$ of $+3.2 \pm 0.1\text{‰}$ similar to the lignites which enclose this sandstone unit. Oil from this interval has an average $\delta^{15}\text{N}$ of $+14 \pm 1\text{‰}$ (n=3) (Coastal Science Laboratories, Austin, Tx). The present oil is therefore an unlikely source of fixed- NH_4 in these samples.

Discussion

A comparison of results from the updip Wilcox "Minter Interval" (Bee Branch Field; Angelina 1 core), to correlative units in the downdip Wilcox (Livonia Field; Kimball 1 core) allows us to observe geochemical differences that result from diagenesis and fluid migration. The modified Van Krevelen plot (Fig. 5), compares the organic matter composition of the two cores according to Rock Eval analysis, and indicates that both cores contain mixed Type II/Type III organic matter. Differences in organic matter type due to depositional setting are negligible. The downdip Wilcox samples are more mature than the updip Wilcox as a result of H and O generation during thermal maturity (Tissot and Welte, 1984). T_{max} values (Fig. 6) for the downdip Wilcox range from 435° to 445°C, indicating that those sediments are thermally mature for hydrocarbon generation. The T_{max} values in the updip Wilcox mudstones average $429 \pm 3^\circ\text{C}$ (n=16) and the lignites are even less mature (415°C). The reason for these different pyrolysis results is not known,

Figure 5. Modified Van Krevelen plot showing a comparison of organic matter compositions in correlated updip and downdip Wilcox Fm sediments (Minter Interval). The HI of lignites is anomalous due to the pyrolysis technique (Peters, 1988, p. 322).

Figure 6. A comparison of T_{max} (organic maturity) in the updip and downdip Wilcox Fm (Minter Interval).

but Peters (1986) notes that coals of higher plant origin (Type III) do not generally respond to pyrolysis in the same way as dispersed Type III organic matter. In any case, these sediments are not thermally mature for hydrocarbon generation and can be ruled out as a source of the crude oil (Goddard and Echols, 1993). Vitrinite reflectance values of 0.4% for the Angelina shales and lignite have been reported whereas the oil was expelled from mature sediments with $R_o = 0.8$ to 0.9% (Goddard and Echols, 1993). Figure 7 shows the relationship between R_o , T_{max} , and hydrocarbon generation, and indicates that T_{max} values of 445°C reported for the downdip Wilcox, are comparable to R_o values (0.8–0.9%) that generated the updip Wilcox oil.

Even though the sediments in Bee Brake are organically immature for hydrocarbon generation, the temperatures are high enough (60°C) to release nitrogen (Williams et al., 1991). With increasing temperature over a range of 50 to 80°C, we have observed a steady decline in the N/C and O/C ratios in organic matter (Fig. 8), suggesting that nitrogen is released as C–O bonds are broken (Williams et al., 1991). Released NH_4^+ may be incorporated in clay interlayers as the transformation of smectite to illite gradually occurs. The onset of illitization in Gulf Coast mudstones begins at ~60°C as the expandability of smectite begins to decrease (Eberl, 1993). Therefore the interaction of locally derived organic-N with authigenic clay minerals is possible. Fig. 9, plots $\delta^{15}N$ versus fixed- NH_4 concentration and shows that the downdip Wilcox has somewhat higher fixed- NH_4 , perhaps due to greater illite formation in mudstones at higher temperatures. The $\delta^{15}N$ values of fixed- NH_4 span a limited range, but the updip Wilcox sandstones contain somewhat higher values. The regression line for the downdip Wilcox data is significant ($r = 0.55$) indicating a relationship between the variables, however there is no significant correlation between the $\delta^{15}N$ and fixed-N in the updip samples. This lack of correlation does not preclude the possibility that fixed- NH_4 concentrations reflect diagenetic reactions, but suggests that the organo-N/mineral relationships are more complex in the shallow diagenetic environment. At temperatures experienced by the Angelina samples (~60°C), the microbial influence on N-species may be more important than at temperatures >80°C (Williams and Winters,

Figure 8. Data from the Miocene Monterey Fm siliceous mudstones indicating that N is released from organic matter at temperatures as low as 50-80°C.

Figure 9. A comparison of $\delta^{15}\text{N}$ to fixed-NH₄ concentration in the updip and downdip Wilcox Fm. (Minter Interval).

1964). The presence of nitrifying bacteria could oxidize NH_4^+ to N_2 which would not be incorporated in authigenic minerals.

The similarity of $\delta^{15}\text{N}$ in the swamp lignite to the $\delta^{15}\text{N}$ in the interdistributary bay sediments stratigraphically above (Fig. 4; Table 1), is suggestive of a genetic link. The study of fixed- NH_4 in coals (Klein and Jüntgen, 1971) suggests that N bonded in aliphatic compounds is released early in diagenesis, along with methane, whereas N in heterocyclic compounds would not be released until much higher temperatures of coalification (Juster et al., 1987). It is possible, therefore, that the lignite (sub-bituminous coal) has generated at least some N which has migrated into nearby shales to be incorporated in clay minerals (e.g. Daniels and Altaner, 1990).

The $\delta^{15}\text{N}$ of the oil from the Angelina 1 core is significantly heavier (^{15}N -enriched) than the oil in downdip Wilcox reservoirs. Oil from the downdip Wilcox in Fordoche Field averaged +5‰, while 2000 ft above these reservoirs in the Sparta Fm oil had an average $\delta^{15}\text{N}$ of +11‰. The oil from the Angelina core in the updip Wilcox gave $\delta^{15}\text{N}$ results of +14±1‰ (n=3). This ^{15}N enrichment would be expected if ^{14}N is preferentially eliminated from hydrocarbons during migration. The $\delta^{15}\text{N}$ of the formation water in the downdip reservoirs changed by roughly +6‰ over 2000 ft. (-2‰ to +4‰; Williams et al., 1994). Although water samples from the Angelina 1 core were not available, if the 6‰ $\delta^{15}\text{N}$ fractionation ($\Delta_{\text{oil-water}}$) determined for the Fordoche Field is applied, the $\delta^{15}\text{N}$ of the Bee Brake waters should be ~+8‰. In the deeper Wilcox reservoirs of Fordoche Field, the $\delta^{15}\text{N}$ of the fixed-N in sandstones falls on a mixing line between the $\delta^{15}\text{N}$ of the water and the oil, depending on the ratio of the two fluids in contact with the clays. If this held true for the updip Wilcox sediments, the $\delta^{15}\text{N}$ values of fixed-N should be much higher. Although temperature effects on the $\delta^{15}\text{N}$ fractionation between oil-water and water-clay are unknown, it is unlikely that the clay minerals in the Angelina core have incorporated any N related to the present hydrocarbons.

Organic maturity and geochemical data suggests that oil has migrated into the Fordoche reservoirs from a source region within the downdip Wilcox where T_{max} reaches 445°C (Sassen, 1990). These values are observed in the "Minter Interval" from the Kimball 1 core, at a depth of

14,300 ft. If the oil in the Bee Brake Field has come from the same source rocks as the Fordoche oils, then the oil would have to have migrated laterally (diagonally) a distance of ~60 km (37 miles) (Sassen, 1990). The $\delta^{15}\text{N}$ difference between the downdip Wilcox oil and the updip Wilcox oil is only ~10‰ which seems too little a change for such a great distance. Fordoche Field results indicate that the $\delta^{15}\text{N}$ of crude oil changed by 6‰ after migrating a vertical distance of ~2000 ft., therefore one would expect an even greater ^{15}N enrichment along a migration path 100 times greater in length! However, if the stripping of ^{14}N from migrating crude oil is dependent on the interaction with clay minerals (as suggested in Williams et al., 1994), and the migration path was confined within relatively clay poor (highly permeable) sandstone units, then a smaller change in $\delta^{15}\text{N}$ is possible. In addition, the N-stripping effect of clays diminishes as the degree of illitization decreases (toward surface), so oil migrating through sediments undergoing early diagenesis ($T < 80^\circ\text{C}$) may not exhibit as great a change in $\delta^{15}\text{N}$ due to interaction with clay minerals.

Conclusion

Results indicate that the N-isotopic composition of oil and water changes significantly during primary migration, and the incorporation of N from these fluids in diagenetic clay minerals allows the isotopic variations to be preserved. Crude oil becomes ^{15}N enriched through migration as ^{14}N is released into solution, or adsorbed by clay minerals along the migration path. Nitrogen in formation waters is apparently in equilibrium with the oil during catagenesis ($T \sim 80^\circ\text{--}140^\circ\text{C}$). The timing of the fluid migration relative to the formation of diagenetic minerals is the limiting factor in the utility of fixed- NH_4 anomalies for tracing hydrocarbon migration paths. Where illitization (or recrystallization) is active, NH_4^+ introduced into the sediment will be incorporated (replacing K^+) with an isotopic ratio that may fall along a mixing curve between that of the oil and formation water. There is no indication that fixed- NH_4 in low temperature ($\leq 60^\circ\text{C}$) environments will aid in tracing hydrocarbons. Either illitization has not advanced enough at those temperatures to incorporate N generated from oil; the supply of N from oil has been diminished; or microbial activity has altered the N-species to N_2 or NO_3 which is not incorporated in the sediments. Fixed-

NH₄ in shallow basin sediments is either inherited from detritus, or is derived from local organic matter undergoing early thermal or microbial alteration.

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