

## AMMONIUM SUBSTITUTION IN ILLITE DURING MATURATION OF ORGANIC MATTER

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**Abstract**—Pierre shale samples from a thin stratigraphic zone within the contact aureole of the lamprophyric Walsen dike record changes due to thermal effects that are not influenced by detrital differences. Analyses of fixed-NH<sub>4</sub>, mineralogy, and Rock-Eval pyrolysis indicators of organic matter maturity provide new insights on the fixation process. Fixed-NH<sub>4</sub> increases with the quantity of authigenic illite formed from illite/smectite, but the maximum fixation per unit of illite formed occurs within the “oil window” where thermal breakdown of organic matter is rapid. Extrapolation of these results to the burial diagenetic regime supports the potential use of fixed-NH<sub>4</sub> as an indicator of organic maturity and hydrocarbon migration pathways.

**Key Words**—Ammonium substitution, Fixed-ammonium, Hydrocarbon generation, Illite/smectite transformation, Organic maturation.

### INTRODUCTION

Recent literature on the geochemistry of ammonium (NH<sub>4</sub><sup>+</sup>) has focused on the potential utility of fixed-NH<sub>4</sub> as a geochemical indicator of hydrothermal ore deposits (Sterne *et al.*, 1984; Kydd and Levinson, 1986; Williams *et al.*, 1987; Ridgeway *et al.*, 1990), or as a tracer hydrocarbon migration pathways in a burial diagenetic setting (Williams *et al.*, 1989). Hydrothermal ore deposits may be accompanied by increased concentrations of fixed-NH<sub>4</sub> in host rock minerals resulting from the breakdown of organic matter. Similarly, increased quantities of fixed-NH<sub>4</sub> in mudstones reflect the thermal maturity of kerogen, while anomalous concentrations of fixed-NH<sub>4</sub> in sandstones are associated with the presence of migrated hydrocarbons. There is evidence to suggest that an accelerated release of N occurs at the onset of rapid thermal cracking of kerogen (Williams *et al.*, 1989). Throughout diagenesis, NH<sub>4</sub><sup>+</sup> may be incorporated in clay minerals by adsorption and ion exchange, but more importantly by substitution for K<sup>+</sup> in authigenic minerals such as illite, feldspar, or zeolite. Published reports of this coupled organic-inorganic geochemical process have identified temperature, fluid chemistry, mineralogy and nitrogen-producing potential of the organic matter as the chief variables influencing the magnitude of the observed NH<sub>4</sub><sup>+</sup> geochemical anomalies (Williams *et al.*, 1989; Ridgeway *et al.*, 1990; Daniels and Altaner, 1990). Fixed-NH<sub>4</sub> is structurally bound in silicates and is not easily released or exchanged under normal diagenetic conditions (Keeney and Nelson, 1982). Therefore fixed-NH<sub>4</sub> in authigenic minerals records the chemistry of the diagenetic environment long after the source of NH<sub>4</sub><sup>+</sup> (i.e., migrating hydrocarbons) has disappeared.

Cooper and Raabe (1982) provided nitrogen data from the contact aureole of a basaltic dike in Montana

that substantiated an earlier model for the distribution fixed-NH<sub>4</sub> with depth on the Texas Gulf Coast (Cooper and Abedin, 1981). Their results suggest that: (1) NH<sub>3</sub> is released from organic matter, (2) NH<sub>4</sub><sup>+</sup> containing fluids migrate over long distances, and (3) NH<sub>4</sub><sup>+</sup> is removed from the migrating fluid by incorporation into newly-formed illite layers. These studies did not report specific analyses of the clay minerals nor level of organic maturity relative to the release of N, and did not conclusively determine the source of fixed-NH<sub>4</sub>.

The effects of contact metamorphism on organic matter maturity in a Cretaceous black shale have been studied by Peters *et al.* (1983). They demonstrated that the programmed pyrolysis (Rock Eval) technique provides useful indicators of the relative level of thermal maturity of organic matter, and that the effect of high temperature over a short time caused maturation processes to occur at different rates than in burial diagenesis. Both kerogen maturation and the smectite-to-illite transformation are kinetically controlled so that temperature increases the reaction rate. In this respect Rock-Eval pyrolysis, in which samples are heated to 650°C, may more closely simulate contact metamorphism than it does burial diagenesis. Maximum enrichments of N relative to C were found 5 m above a sill and 2.5 m below. Samples closest to the sill were generally depleted in N. Their investigation did not include an evaluation of fixed-NH<sub>4</sub><sup>+</sup> in minerals and could not differentiate changes due to original sediment composition or migration of constituents during the intrusion.

A major question arising from the studies of sedimentary rocks is whether fixed-NH<sub>4</sub> in minerals is strictly a product of thermal maturation of organic matter and subsequent migration, or reflects initial depositional differences in mineralogy and organic type. Large mineralogical and chemical differences are pos-

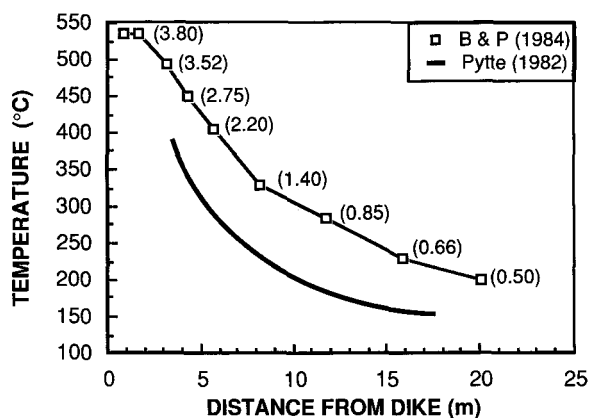


Figure 1. Maximum temperatures affecting the Pierre Shale as determined by thermal modeling (Pytte, 1982) and vitrinite reflectance ( $R_o$ ) (B&P = Bostick and Pawlewicz, 1984).  $R_o$  values indicated in parentheses beside the inferred temperature curve.

sible in the geologic environments that contain fixed- $\text{NH}_4$ , making evaluation of the anomalies equivocal. The relative importance of temperature and migration on fixed- $\text{NH}_4$  anomalies can only be evaluated if the source of N can be determined, and the effects of depositional versus diagenetic environment can be separated.

The present study reports variations in fixed- $\text{NH}_4$ , clay mineralogy, and organic matter maturity within a small (<5 cm) stratigraphic interval of a shale where the intrusion of a dike has caused a well-defined thermal gradient. The effect of sampling a single layer is to minimize the original variability of the source material (both organic and inorganic matter). In this way, changes in mineralogy and organic matter can be attributed predominantly to the thermal effects of the dike. This environment provides the opportunity to examine the thermal transformation of minerals and organic matter and to make a general comparison to variations expected with burial in a diagenetic regime. The results provide new data that can be used to aid in the interpretation of fixed- $\text{NH}_4$  during burial diagenesis in sedimentary basins.

### GEOLOGIC BACKGROUND

The Walsen Dike, Walsenburg, Colorado, is a composite lamprophyre dike of Eocene or early Oligocene age. It has intruded the Cretaceous Pierre Shale essentially perpendicular to bedding. The dike and thermally altered wallrock are well exposed in a roadcut along interstate (business) I-25 just north of Walsenburg. Johnson (1964) established three stages of intrusion, spaced closely enough in time to represent one thermal event in the country rock (Bostick and Pawlewicz, 1984). All of the igneous groundmass was analcitized, indicating some Na-metasomatism close to the dike. A

shallow burial depth has been estimated for the section, with minimal advancement of diagenetic reactions prior to dike emplacement (Bostick and Pawlewicz, 1984).

Modeling of maximum temperatures at various distances from the dike was done (Pytte, 1982; Pytte and Reynolds, 1989), according to the methods of Jaeger (1964), and using an estimated intrusive temperature of 1200°C for the 8.5 m-thick dike (Figure 1). These modeled temperatures are approximately 100°C lower than the values derived from vitrinite reflectance measurements ( $R_o$ ) by Bostick and Pawlewicz (1984). The difference in the two interpretations may be attributed to specific rock properties (conductivity and specific heat), or uncertainties in calibration of the vitrinite paleothermometer (Bostick and Pawlewicz, 1984). Subsequent references to temperature (T) will use the maximum theoretical values derived by Pytte and Reynolds (1989).

The smectite-to-illite transformation at the Walsen dike locality has been described as isochemical for the major elements (Reynolds, 1981; Pytte and Reynolds, 1989). Subsequent investigations (Figure 2) document that the complete I/S transformation takes place from ~20% illite in I/S at 15 m to 100% illite in I/S, 2 m from the dike (Pytte, 1982; Lynch, 1985; this study). Random ordering is replaced by R = 1 ordering ~8 m from the dike and a higher degree of ordering (R = 3?) is encountered in samples <5 m from the dike. Pytte and Reynolds (1989) defined the kinetics of the I/S reaction, and their modeling supports the role of kinetic factors, rather than equilibrium conditions, in controlling reaction extent. Lynch and Reynolds (1984) found that increases in %I in I/S could be explained by closed-system reactions involving the dissolution of smectite layers and other minerals with the precipitation of new illite layers. In a burial diagenetic thermal regime, progress of the smectite-to-illite reaction correlates with hydrocarbon maturation (Perry and Hower, 1970). We assume that the reactions are similar in a contact metamorphic environment, although the temperature gradient and reaction kinetics differ.

### METHODS

Samples were collected from the south side of the Walsen dike along the eastern side of the interstate I-25 (business) roadcut. They were restricted to one lithologic unit ~5 cm thick, and were taken from depths of ~30 cm to minimize the effects of surface weathering. Whole-rock mineralogy was analyzed by X-ray powder diffraction (XRD) methods utilizing randomly oriented samples (Cook *et al.*, 1975). XRD estimates of clay mineral abundances were derived from oriented aggregates of the <2- $\mu\text{m}$  fraction (e.s.d.) according to the procedures developed for the Pierre Shale by Schultz (1964). The reproducibility of these results is within 3% of the quantity reported for clay mineral concentrations >30%. Calculations of %illite layers in mixed-

layered illite/smectite (denoted %I(I/S)) were performed on 5 samples with NEWMOD (Reynolds, 1985). Results were found to be within 10% of the previously published data. We used the estimate of %I(I/S), multiplied by the quantity of I/S (%) in each sample to provide an indication of the quantity of authigenic illite (denoted [I(I/S)]).

Total-N concentrations of whole-rock samples were determined by a CHN Elemental Analyzer (Perkin-Elmer Model 240C) with a detection limit of 0.01 wt. % N. The values reported are the average of two determinations, one employing 2 mg of sample and the other using 20 mg. Triplicate analyses of samples indicate a relative standard deviation of 20% at the average concentration (0.05 wt. % N), increasing to 50% as the detection limit is approached. Whole-rock powders and clay-sized fractions were treated separately for organic matter removal (Anderson, 1963) and analyzed for fixed-NH<sub>4</sub> using Kjeldahl distillation procedures described by Keeney and Nelson (1982). Triplicate analyses indicate that the relative standard deviation for fixed-NH<sub>4</sub> values is <10% of the quantity measured for concentrations in the range 500–1000 mg/kg.

Programmed pyrolysis (Rock Eval) of each whole-rock sample provided information on the organic matter type, level of organic maturity, and the quantity of total organic carbon (TOC) (Tissot and Welte, 1984; Peters, 1986). The pyrolysis peaks represent relative quantities of free hydrocarbons (S<sub>1</sub>), potential hydrocarbons (S<sub>2</sub>), and CO<sub>2</sub> (S<sub>3</sub>) associated with the organic matter. The Hydrogen Index [HI = (S<sub>2</sub>/TOC)100], and Oxygen Index [OI = (S<sub>3</sub>/TOC)100] were used to identify the organic matter type. The Production Index [PI = S<sub>1</sub>/(S<sub>1</sub> + S<sub>2</sub>)] can indicate migration of hydrocarbons into or out of a stratigraphic interval. However, in a closed system this indicates the degradation of inherent kerogen to lighter components. The temperature at which the S<sub>2</sub> pyrolysis peak reaches a maximum is an indication of the thermal maturity of kerogen known as T<sub>max</sub>. T<sub>max</sub> parameters are only valid where TOC ≥ 0.5 and the S<sub>2</sub> pyrolysis peak is ≥0.2 (Peters, 1986).

## RESULTS

### Mineralogy

The major components of the Pierre Shale are quartz, clay minerals, plagioclase (≥Ab<sub>80</sub>), orthoclase, dolomite, and siderite, in decreasing order of abundance. In the clay-sized fraction, the dominant mineral is mixed-layered illite/smectite (I/S), with variable percentages of illite layers and type of ordering. This is followed by discrete illite, kaolinite, chlorite, and smectite. Corrensite appears in some samples near the dike, and discrete smectite (or random I/S with more than 90% S layers) is found in samples > 8 m from the dike. Our estimates of %I(I/S) are slightly higher (Figure 2)

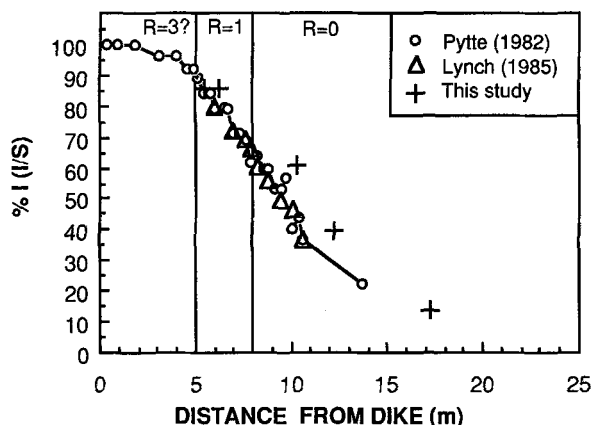


Figure 2. Percent illite in mixed-layered illite/smectite (%I(I/S)) versus distance from the dike. (R = Reichweite ordering).

than the values reported by Pytte (1982) and Lynch (1985), probably because our samples were taken from a different stratigraphic interval. The differences do not influence the interpretations significantly.

Correlation coefficients were calculated for selected variables (Table 1) and used to assess potential mineralogical reactions. Only correlation coefficients with an absolute value ≥0.60 are presented. Correlation coefficients below |0.60| can be excluded because they indicate that one variable accounts for less than 50% of the variation in the paired variable and are therefore insignificant. The data were divided into two groups representing proximal and distal segments of the contact aureole. The division at 5 m coincides with a temperature of ~300°C, where fixed-NH<sub>4</sub> concentrations sharply decrease. In distal samples, the positive correlation (r = 0.93) of fixed-NH<sub>4</sub> with authigenic illite [I(I/S)] is the most significant association. In proximal samples, fixed-NH<sub>4</sub> most strongly correlates with albite (r = 0.94). These associations suggest that the host mineral for NH<sub>4</sub><sup>+</sup> changes at T ≥ 300°C, or that NH<sub>4</sub><sup>+</sup> has simply been released from the highly ordered I/S. Negative correlation coefficients for K-feldspar, kaolinite, discrete illite, or smectite, with I/S or [I(I/S)] in both data sets indicate that their relative abundances are inversely related, and suggest that those minerals may be consumed in the illitization reaction. Other potential reactions are suggested by the negative correlation between plagioclase/carbonate, quartz/K-feldspar, and kaolinite/carbonate, but these mineralogical relationships are beyond the scope of this paper.

### Nitrogen chemistry

Figures 3a and 3b allow comparison of the trends in total-N and fixed-N in whole rock samples with increasing distance from the dike. The vertical bars in both figures indicate the relative analytical error. The mean total-N content (0.05 wt. %) is represented by the solid line and the dashed lines represent ± 1 σ (0.01

Table 1. Significant correlation coefficients between selected mineralogical and chemical variables for data sets representing proximal (&lt;5 m from dike; upper right half; n = 6) and distal samples (&gt;5 m from dike; lower left half; n = 10).

Variables	Distal						Proximal					[I(I/S)]
	NH <sub>4</sub>	carb	qtz	K-fsp	plag	clays	kaol	chl	illite	smec	I/S	
fixed-NH <sub>4</sub>		•	•	•	0.94	•	•	-0.66	•	0.68	•	•
carbonate	•		•	•	•	•	-0.74	•	•	•	•	•
quartz	•	•		•	•	-0.68	•	•	•	•	•	•
K-feldspar	•	-0.62	•		•	-0.84	•	•	•	•	•	•
plagioclase	•	-0.73	•	•		•	•	•	•	0.74	•	•
clays	•	•	•	•	•		•	•	•	•	•	•
kaolinite	•	•	•	•	•	•		-0.75	•	•	•	•
chlorite	•	•	•	•	•	•	•		0.65	•	•	•
illite	•	•	•	•	•	•	•	•		-0.77	-0.98	-0.97
smectite	•	•	•	•	-0.64	•	•	•	•		0.80	0.81
I/S	•	•	•	•	0.61	•	-0.73	•	-0.6	-0.82		0.99
[I(I/S)]	0.93	•	•	•	•	•	•	•	•	•	•	

wt. %) of the mean. The total-N content of the Pierre Shale appears to vary with distance from the dike. There is a depletion of total-N in the zone within 5 m of the dike and a slight enrichment in the interval 5–10 m from the dike. Values close to the dike exhibit the most variation. The apparent trends in the distribution of total-N must be viewed with caution because the values are near the detection limit (0.01 wt. %).

The mean fixed-N content (0.030 wt. %) of the whole rock samples is represented by the solid line in Figure 3b and dashed lines represent  $\pm 1 \sigma$  (0.005 wt. %) from the mean. Fixed-N comprises 50–90% of the total-N value, and the trend parallels total-N trends. Measurements of exchangeable-N were found to be insignificant ( $\leq 0.005$  wt. %) so the difference between total-N and fixed-N is an indication of organic-N content.

Figure 4 compares the fixed-NH<sub>4</sub> concentrations of the clay-sized fraction to %I(I/S). Fixed-NH<sub>4</sub> concentrations in the clay-sized fractions are ~500 mg/kg higher than comparable concentrations in whole-rock powders, and the trends are sympathetic indicating that most of the NH<sub>4</sub><sup>+</sup> resides in the clay-sized fractions. Background levels of fixed-NH<sub>4</sub> in the most distal shale samples average 700 mg/kg (clay-sized fraction), with concentrations reaching 1050 mg/kg ~6 m from the dike. A sharp drop in fixed-NH<sub>4</sub> concentration occurs within 5 m of the dike, where concentrations average 580 mg/kg. The increase in fixed-NH<sub>4</sub> concentration coincides with increases in degree of illitization up to about 8 m from the dike where maximum temperatures reached ~250°C.

#### Organic matter

Figure 3c shows the variation in TOC content of the shale with distance from the dike, for comparison with total-N and fixed-N values (Figures 3a and 3b). The solid line represents the mean value (0.56 wt. %) and the dashed lines represent  $\pm 1 \sigma$  (0.13 wt. %) from the mean. TOC values close to the dike are generally lower than the mean value and increase with distance from

the dike. The maximum TOC content occurs between 10–22 m from the dike, while total-N and fixed-N reach a maximum between 5–10 m.

All samples contain type III (terrestrial source) organic matter, based on Hydrogen Index (HI) and Oxygen Index (OI) data. Therefore, there are no major differences in organic chemistry that might influence organic maturation reactions. Figure 5 shows that the HI is essentially constant with respect to distance from the dike, whereas OI shows a significant decrease as the dike is approached. These trends reflect an increase in thermal maturity towards the dike (minimum OI = maximum maturity) in agreement with maturation paths predicted by Van Krevelen plots for type III organic matter (Tissot and Welte, 1984). By these parameters, thermal maturity of the organic matter with regard to oil generation is attained at approximately 17 m from the dike. The relationship of the data in Figures 5 and 6 to the “oil window” will be discussed in the following section.

Maximum quantities of generated hydrocarbons (S<sub>1</sub>) occur between 8–17 m from the dike (Figure 6) and maximum hydrocarbon potential (S<sub>2</sub>) exists between 10–26 m from the dike. The interval between 10–22 m from the dike contains the maximum total potential (S<sub>1</sub> + S<sub>2</sub>) for hydrocarbon production. Vitrinite reflectance values in this interval range from ~0.5% to a little more than 1.0% (Bostick and Pawlewicz, 1984). T<sub>max</sub> thermal maturity data are limited to four samples that provided sufficient TOC and S<sub>2</sub> for validity. The data are presented in Table 2, along with vitrinite reflectance values (R<sub>v</sub>) and Production Indices. These values generally increase toward the dike. Production Index values become variable within 8 m of the dike (Figure 7).

## DISCUSSION

#### Organic maturation

In order to examine the relationship between hydrocarbon generation and NH<sub>4</sub>-fixation, it is important

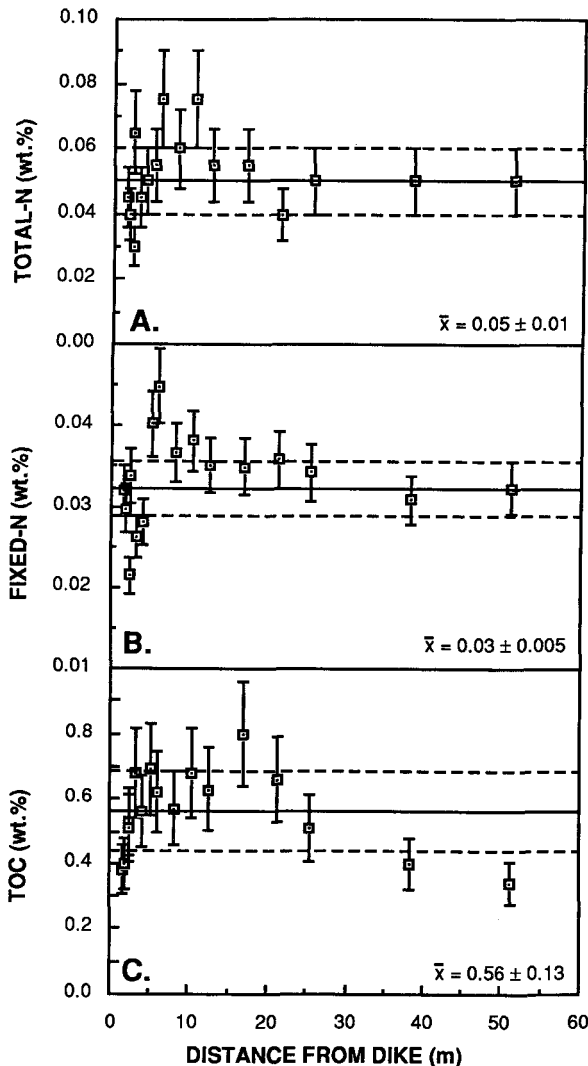


Figure 3. Variations in a) Total-N, b) Fixed-N and c) TOC concentrations in the shale with increasing distance from the dike.

to identify the "oil window." In a burial diagenetic environment, the "oil window" occurs where thermal maturity indices indicate the onset of crude oil generation and migration ( $R_o \sim 0.55\%$ ;  $T_{max} \sim 430^\circ\text{C}$ ), and extends to the onset of rapid thermal cracking of crude oil to gas-condensate ( $R_o \sim 1.0\%$ ;  $T_{max} \sim 450^\circ\text{C}$ ) (Sassen and Moore, 1988). By these guidelines, the "oil window" relative to the Walsen dike samples should be between 10–22 m from the dike where  $R_o$  values are between 0.5 and 1.0% and  $T_{max}$ -values are between  $429^\circ\text{C}$  and  $434^\circ\text{C}$ . Peters *et al.* (1983) caution that  $R_o$  responds more rapidly to high temperatures imposed over a short time than it does during burial. However, in our samples  $T_{max}$ -values and other maturity indicators such as HI and OI support the placement of the "oil window" at this location. In addition, the highest

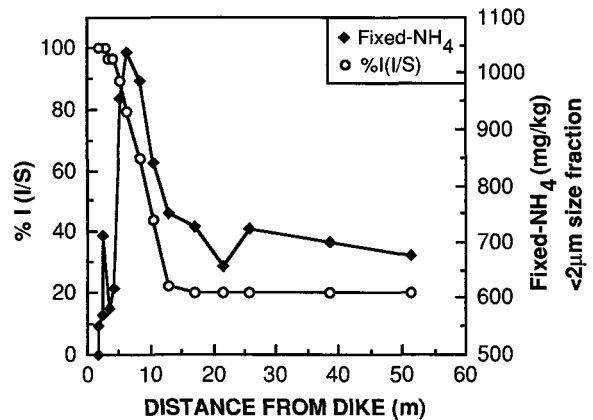


Figure 4. Fixed- $\text{NH}_4$  concentrations in clay-sized fractions, compared with %I(I/S) for samples within the contact metamorphic aureole.

total potential values ( $S_1 + S_2$ ) are found in this interval. The maximum temperatures between 10–22 m according to Pytte and Reynolds (1989) were  $150\text{--}200^\circ\text{C}$ . Temperatures above  $200^\circ\text{C}$  affected all samples taken closer to the dike. Vitrinite reflectance and  $T_{max}$ -values indicate that these samples contain overmature organic matter with respect to oil formation. All of these observations support the proposed location of the "oil window" at the indicated position.

#### Migration

The abundances of major inorganic elements in the contact aureole indicate an apparently isochemical reaction system (Reynolds, 1981; Lynch, 1985). However, the abundances of minor elements, C and N, exhibit variations that may indicate some movement of those elements during or after dike emplacement. TOC, total-N, and fixed-N abundances (Figure 3a–3c) are lowest near the dike and increase to more than one

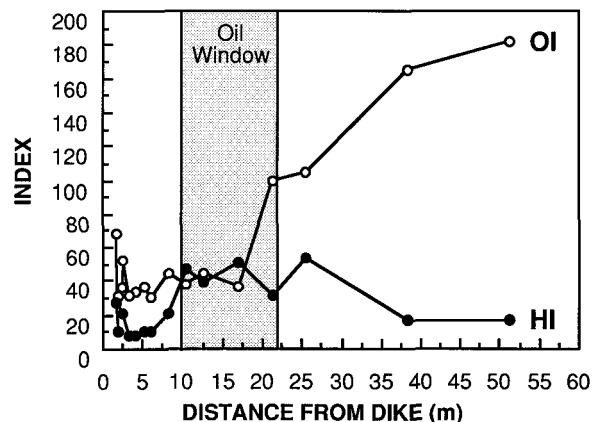


Figure 5. Hydrogen Index (HI) and Oxygen Index (OI) values versus distance from the dike, and relationship to "oil window."

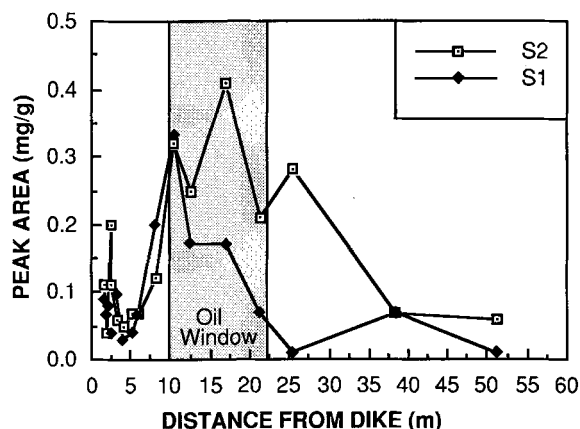


Figure 6. Area of  $S_1$  (generated hydrocarbons) and  $S_2$  (potential hydrocarbons) pyrolysis peaks versus distance from the dike.

standard deviation above the mean beyond 5 m from the dike. The variability of values near the dike suggests that the system is not closed in that interval, most likely due to transport of fluids along dike-related fractures. The quantitative evaluation of migration is difficult because of the small quantity of the elements (C, N) present and analytical uncertainties.

Rock Eval parameters ( $S_1$  relative to  $S_2$ ) also lend supporting evidence for migration of hydrocarbons away from the dike (Figure 6). The depletion of the  $S_2$  pyrolysis peaks in samples within 8 m of the dike indicates that hydrocarbons have been nearly entirely released. Since the  $S_1$  values are also low, the generated hydrocarbons must have migrated away from that interval leaving only carbon residues. The Production Index (PI) represents the ratio of distillable organic compounds to the total amount of organic compounds generated from a sample by pyrolysis [ $S_1/(S_1 + S_2)$ ]. Figure 7 shows PI values increasing toward the dike in the interval from 25 m to 8 m. Peters *et al.* (1983)

Table 2. Thermal maturity parameters, including Production Index, as an indicator of thermal degradation of organic matter. Vitrinite Reflectance ( $R_o$ ) data are from Bostick and Pawlewicz (1984).

Distance (m)	Production index	$T_{max}$ (°C)	$R_o$ (%)
2.5	0.44	523	3.5
4.2	0.37	447	2.8
5.1	0.40	*	2.54
6.2	0.50	*	2.20
8.2	0.62	*	1.40
10.4	0.52	*	1.40
12.7	0.40	434	0.85
17.1	0.29	429	0.66
21.3	0.25	*	0.50
25.6	0.04	*	*

\* Data not valid or not collected.

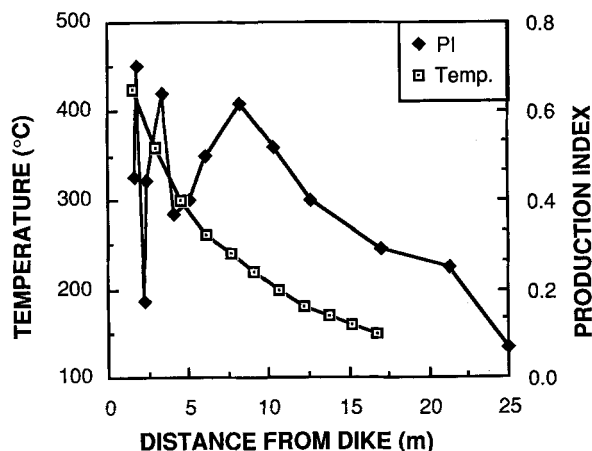


Figure 7. Variations in Production Index [ $S_1/(S_1 + S_2)$ ] in the contact aureole of the Walsen dike compared to the maximum temperature curve.

observed a similar increase in PI within Cretaceous black shales adjacent to a diabase sill. They proposed that the high temperatures imposed by the intrusive sill cracked the more labile hydrocarbon side-chains from the kerogen releasing lower molecular weight, volatile organic products such as  $CH_4$ ,  $NH_3$ ,  $H_2S$ ,  $CO_2$ , and  $H_2O$ . This results in an increased  $T_{max}$ , and since the products add to the  $S_1$  peak, the PI increases. Therefore, a progressive *in-situ* aromatization of kerogen is indicated as the dike is approached up to 8 m. Within 8 m of the dike, however, we see fluctuating PI values which can be an indication that volatiles have migrated out of the system. Thermal maturation products in this interval would migrate away from the dike primarily along fractures.

According to the maturation paths indicated by Van Krevelen diagrams, the ratio of OI/HI should approach unity with increasing thermal maturity in an ideal closed system. This ratio in Figure 8 steadily decreases toward the dike to a distance of ~10 m, indicating that a closed system may exist with regard to organic matter components in these samples. Closer to the dike there is a distinct increase in the ratio, which also suggests that migration is affecting values in this interval. This analysis is based on the assumption that the original organic type is invariant in this single bed.

The increase in total-N and fixed-N in the interval between 5–10 m from the dike (Figure 3a–3b) is difficult to interpret without knowledge of the pore fluid  $NH_4^+$  concentrations at the time of fixation. If pore fluid  $NH_4^+$  concentrations were uniform throughout the sampling interval (1–52 m from the dike), fixed-N would be expected to increase between 5–10 m because there is an increase in illitization (60–80% authigenic illite formation). On the other hand, pore fluid  $NH_4^+$  availability could have increased due to migration of N away from the dike resulting from: 1. volatilization

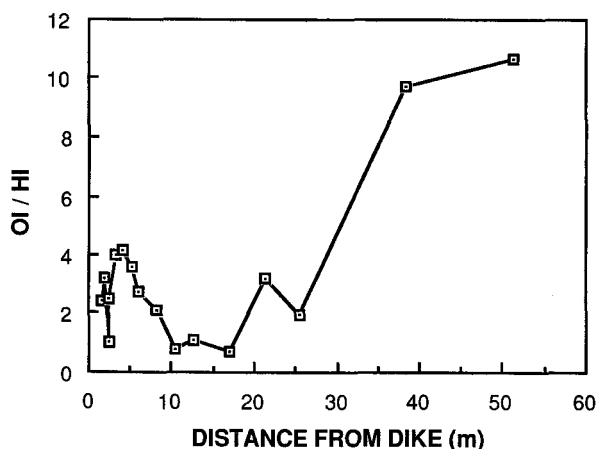


Figure 8. Ratio of Oxygen Index/Hydrogen Index in the contact aureole of the Walsen dike.

of organic matter closer to the dike, 2. introduction of  $\text{NH}_4^+$ -enriched fluids associated with the dike intrusion, or 3. release of  $\text{NH}_4^+$  from silicate minerals (discrete illite and K-feldspar) near the dike. Evidence for the last was recently discussed by Bottrell and Miller (1990). Release of fixed- $\text{NH}_4$  from illite (as  $\text{NH}_3$ ) is known to occur at pyrolysis temperatures as low as  $400^\circ\text{C}$ , with maximum release occurring at approximately  $650^\circ\text{C}$  (Voncken *et al.*, 1987). Since any of these processes could account for an increase in fixed-N and total-N, the interval between 5–10 m from the dike cannot be interpreted uniquely.

#### Fixed- $\text{NH}_4$ relative to maturation and migration

The data presented in Figure 4 show that the fixed- $\text{NH}_4$  concentration of a sample is linked to the degree of illitization. More details of this relationship can be examined in Figure 9 where concentration and substitution are compared. Levels of  $\text{NH}_4$ -substitution were estimated by normalizing fixed- $\text{NH}_4$  concentrations to the quantity of authigenic illite [ $\text{I}(\text{I}/\text{S})$ ]. The reproducibility of this ratio may be large due to errors involved in the calculation. However, trends defined by this ratio are the same within the limits of error. Maximum levels of  $\text{NH}_4$ -substitution per layer of authigenic illite occur in samples between 10–22 m, which is the interval identified as the “oil window.” The degree of illitization in this interval is between 20–35%. The coincidence of maximum  $\text{NH}_4$ -substitution within the “oil window,” despite the low degree of illitization can be explained by a number of mechanisms. However, it is important because it shows that the  $\text{NH}_4^+$  concentration of the pore fluids is reflected in the clay minerals independent of the percent illitization. This coincidence indicates a significant relationship between organic maturation and the amount of  $\text{NH}_4$ -fixation.

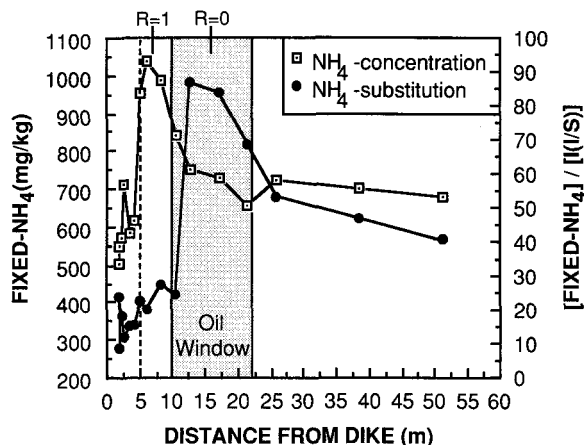


Figure 9. Fixed- $\text{NH}_4$  concentrations in clay-sized fractions and levels of  $\text{NH}_4$ -substitution,  $[\text{fixed-NH}_4]/[\text{I}(\text{I}/\text{S})]$ , versus distance from the dike.

Figure 9 indicates a low level of  $\text{NH}_4$ -substitution per unit of authigenic illite in the interval from 5–10 m where fixed-N and total-N concentrations are maximum. Apparently the illite layers formed at these locations do not contain as much fixed- $\text{NH}_4$  as those formed in the “oil window.” One explanation for this could lie in the temperature and/or redox effects on the speciation of N. Barnes (1979, p. 409) indicates the T-pH stability of aqueous  $\text{NH}_3$  and  $\text{NH}_4^+$ , showing that temperatures in excess of  $200^\circ\text{C}$  ( $\text{pH} \geq 6$ ) favor  $\text{NH}_3$  over  $\text{NH}_4^+$ . The speciation of nitrogen was recently discussed by Bottrell and Miller (1990) who examined the geochemical behavior of N compounds at high temperature and pressure ( $325^\circ\text{C}$ ; 1.8 kbar) in a hydrothermal gold deposit. They suggest that at temperatures similar to those encountered within 8 m of the Walsen dike,  $\text{NH}_3$  is likely to react with graphite to form  $\text{CH}_4$  and  $\text{N}_2$ . Although some  $\text{NH}_4^+$  obviously existed under these conditions, the bulk of the nitrogen may have been  $\text{NH}_3$  or  $\text{N}_2$ , which would not substitute for  $\text{K}^+$  due to its nonionic nature. Where temperatures drop below  $200^\circ\text{C}$  (at  $\sim 8$  m) the dominant form of nitrogen would be  $\text{NH}_4^+$ .

Competition or ion selectivity of the clay minerals may also have an effect on the amount of  $\text{NH}_4$ -fixation. It is possible that the amount of  $\text{NH}_4$ -fixation between 5–10 m is related to the  $\text{K}^+/\text{NH}_4^+$  ratio in the pore fluids at the time of intrusion. The dissolution of both K-feldspar and discrete illite near the dike may have increased this ratio enough to reduce the degree of  $\text{NH}_4^+$ -substitution. Juster *et al.* (1987) proposed that there is more solid solution between the K- $\text{NH}_4$  end members of illite at low temperatures than exists at high temperatures. Therefore, mineralogical constraints may account for the lower levels of  $\text{NH}_4$ -substitution at the temperatures encountered between 5–10 m from the dike.

Burial diagenetic studies show that the zone of maximum hydrocarbon generation generally coincides with  $R = 1$  ordering and 60–80% illitization of smectite (e.g., Perry and Hower, 1970). Within the contact aureole of the Walsen dike, there is a clear separation of the “oil window” from the zone of  $R = 1$  illitization (Figure 9). This may result from high temperatures imposed over a short period of time in the contact aureole. The short duration of the thermal event has probably influenced the rates of the organic maturation and illitization reactions causing a separation in time and space from the  $R = 1$  ordering of illite. Previous work indicated that fixed- $\text{NH}_4$  concentrations are related to increased maturity (Williams *et al.*, 1989), but the effects of increased  $\text{NH}_4^+$  generation due to organic breakdown could not be separated from increased illitization. In the Walsen dike samples, both processes are clearly separated. Ammonium fixation is dependent on both concentration of  $\text{NH}_4^+$  and the degree of illitization. Therefore, where migration is involved, the rate of release of N from organic matter (as  $\text{NH}_4^+_{\text{aq}}$ ) will compete with the rate of illitization to influence fixed- $\text{NH}_4$  concentrations.

In future studies of fixed- $\text{NH}_4$  it is important to differentiate between the fixed- $\text{NH}_4$  concentration of a sample and the level of  $\text{NH}_4$ -substitution within a host mineral. The implication for burial diagenesis is that one cannot compare fixed- $\text{NH}_4$  concentrations in a sample with 80% I(I/S) to one with only 20% I(I/S) without normalizing the fixed- $\text{NH}_4$  concentration to the amount of host mineral. By comparing the levels of  $\text{NH}_4$ -substitution per unit of authigenic illite one can establish where fixed- $\text{NH}_4$  anomalies are independent of the mineralogy. The anomalous  $\text{NH}_4$ -substitution observed within the “oil window” of this study is most probably caused by an increase in  $\text{NH}_4^+$ -availability within the oil window due to the rapid thermal degradation of kerogen. The release of  $\text{NH}_3$  from organic matter is associated predominantly with the decomposition of aliphatic, alicyclic and heterocyclic compounds (Klein and Jüntgen, 1971). The temperature of  $\text{NH}_3$  release therefore depends on the composition of the organic matter. Other variables such as ion selectivity, N-speciation, and reaction rate must also be considered to influence the level of  $\text{NH}_4$ -substitution in a mineral.

### SUMMARY

The results of this study clearly establish the link between organic matter maturation and  $\text{NH}_4$ -fixation in authigenic illite. The highest levels of  $\text{NH}_4$ -substitution occur within the “oil window.” High fixed- $\text{NH}_4$  concentrations outside the “oil window” may be influenced by: (1) migration of N into the system, (2) reactions dependent on N-speciation, and (3) the extent (or rate) of illitization. The evidence for this is the following: Nitrogen is fixed in  $\text{NH}_4^+$  in authigenic illite

of the Upper Cretaceous Pierre Shale and within the contact aureole of a large lamprophyre dike near Walsenburg, Colorado. Increases in fixed- $\text{NH}_4$  concentrations parallel increases in authigenic illite and increased breakdown of organic matter approaching the dike. Where maximum temperatures were  $\geq 300^\circ\text{C}$ , the association of fixed- $\text{NH}_4$  with authigenic illite ends, and concentrations decrease. Variations in total-N, OI/HI ratio and PI indicate that migration of C and N away from the dike may have occurred within 8 m of the dike contact. Increases in  $\text{NH}_4$ -substitution per unit of authigenic illite occur between 10–22 m from the dike. This is within the “oil window,” as defined by vitrinite reflectance values between 0.5–1.0%,  $T_{\text{max}}$  between  $429^\circ\text{C}$ – $434^\circ\text{C}$ , minimum OI values, and maximum hydrocarbon generation peaks. Maximum temperatures at this distance from the dike are estimated to be  $150$ – $200^\circ\text{C}$  (Pytte and Reynolds, 1989).

The excellent correlation of fixed- $\text{NH}_4$  concentrations with the extent of smectite illitization, indicates that interpretation of fixed- $\text{NH}_4$  anomalies must consider variations in host mineralogy. Normalization of fixed- $\text{NH}_4$  concentrations to quantity of authigenic illite suggests that anomalously high  $\text{NH}_4$ -substitution reflects rapid thermal maturation related to hydrocarbon generation. Extrapolation of these results to burial diagenetic regimes in sedimentary basins supports the contention of Williams *et al.* (1989) that fixed- $\text{NH}_4$  in authigenic illite is a potential indicator of hydrocarbons or their migration pathways.

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