#### PS Possible Origins for Low Thermal Maturity, High-Nitrogen Natural Gases\*

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#### **Abstract**

Some areas in the western USA have high-nitrogen natural gases in settings with low thermal maturity, such as western Kansas, southeast New Mexico, and southeast Utah. Published models for high-nitrogen gas generation require high thermal maturity. This presentation evaluates sources and mechanisms for forming high-nitrogen natural gas at relatively low thermal maturity. Both organic and inorganic components of sediment contain nitrogen. During early diagenesis, organic matter may generate microbial gases with up to about 20% N<sub>2</sub>. Planktonic organic matter N/C drops precipitously during diagenesis (possible N<sub>2</sub> generation) but remains stable during late diagenesis and catagenesis (no N<sub>2</sub> generation). Sedimentary rocks typically contain about 0.1 to 1 mg N/g rk after removal of organic matter. Much of this nitrogen is ammonium in clays. Ammonium in clays comes from organic matter during early diagenesis and catagenesis. Clays can generate N<sub>2</sub> where ammonium is released from clays and oxidizes in the pore water. Ammonium in illite increases with depth, so smectite illitization is not likely to generate N<sub>2</sub>. However, kaolinization or chloritization of smectite could generate N<sub>2</sub>. A nitrogen-rich gas phase will form at shallow depth after minor N<sub>2</sub> generation. For example, pure N<sub>2</sub> gas is formed after generation of only 0.01 mg N/g rk in rocks with 5% porosity saturated with 200,000 ppm NaCl pore water at 1 km depth. Low pressure, high salinity, and low porosity favor gas-phase formation. A dispersed, lean, nitrogen source could therefore form high N2 gas at shallow burial. A lean nitrogen source rock can generate large quantities of high N<sub>2</sub> gas where N<sub>2</sub> source rock volume is large. For example, release of 10% of the nitrogen in a rock with 1 mg N<sub>2</sub>/g rk releases about 70 BCF N<sub>2</sub> gas from a rock unit 100 m thick over the area the size of a USA township (36 mi<sup>2</sup>; 94 km<sup>2</sup>).

Nitrogen generation is dwarfed by methane generation from thermally mature petroleum source rocks. High-nitrogen gases are expected only where hydrocarbon gases cannot dilute the nitrogen. Many of the western USA high-nitrogen gases are associated with high salinity, low porosity, and low thermal maturity consistent with a lean nitrogen source. An inorganic nitrogen source is more probable due to low organic carbon, but a late diagenetic organic source is possible where planktonic organic carbon is abundant.

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# Possible Origins for Low Thermal Maturity, High-Nitrogen Natural Gases

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#### **Synopsis**

- Nitrogen in many cratonic gas accumulations is not sourced by currently recognized, late catagenetic and basement nitrogen sources. Nitrogen is probably sourced from surrounding late diagenetic to early catagenetic sediments.
- · Organic matter is not likely to be a direct source for early nitrogen gas. Kerogen and coal do not release significant nitrogen during late diagenesis and early catagenesis.
- · Ammonium in clays is the most probable source for nitrogen in gas accumulations in late diagenetic and early catagenetic sediment. Ammonium was probably released by interaction with brines. Dissolved ammonium is oxidized to nitrogen gas.
- Water interaction with gas controls nitrogen concentration. - Nitrogen is released into pore water. Lower porosity increases
- the nitrogen concentration in pore water. - The higher the nitrogen concentration in water, the higher the
- nitrogen in gas in water-dominated systems. The greater the volume of hydrocarbons, the lower the
- nitrogen in hydrocarbon-dominated systems. Nitrogen source rock is lean and dispersed. Nitrogen concentrations in sedimentary rocks are low. Less than a quarter
- of the nitrogen is released. Source-rock volumes must be quite large to compensate for low amount of released nitrogen. However, the required source volumes for even the largest nitrogen accumulations are small
- Very high nitrogen gases form from direct gas exsolution from water. Exsolution is favored by high clay content, high salinity, low porosity, and shallow depth.

fugacity divided by the higher total pressure. Where

total pressure is high, the percent atmospheric

nitrogen is low (Figure 1). Trace concentrations of

nitrogen related to air-saturated water a

commonly reported in noble gas studies (Ballentine

Atmospheric nitrogen concentrations in aquifer

waters may be up to 50% greater than the

atmospheric equilibrium nitrogen concentration

("Excess air"; see Kipfer et al. 2002). However, high-

nitrogen gases in the deeper subsurface would

require a partial pressure hundreds of times that of

nitrogen in the atmosphere. No natural high-nitrogen

subsurface gas with geochemical characteristics of

predominantly atmospheric nitrogen has been

al. 2002; Prinzhofer 2013).

relative to the volume of rock that interacts with migrating gas.

#### Introduction and Problem

Nitrogen is a common trace to major component of many natural gases (see Figure 9A). Despite the common occurrence of nitrogen in natural gases, relatively little research has focused on the origin of these natural gases. The recognized sources for nitrogen in gas (below) are all associated with high thermal maturity or are ineffective.

High-nitrogen natural gases in cratonic settings are far from potential high-maturity sources. Nitrogen in these gases has no currently recognized source. It is the origin of these types of nitrogen gas that will be investigated here. Nitrogen lacks a "smoking gun" geochemical indicator for its source. Therefore, source must be determined from setting, potential source rock concentrations, potential source rock volumes, and consequences of rock-water-gas interaction. It is difficult to prove a source by this approach, but it is possible to disprove some sources and identify probable nitrogen sources.

#### General Strategy

- (1) Briefly review recognized mechanisms for generation of high-nitrogen gases. (Below) (2) Describe abundance and general setting for nitrogen-bearing gases. Show examples of high-nitrogen gases from the midcontinent area (USA) where basement and late catagenetic sources are unlikely to essentially impossible. (Right and Panel 2)
- (3) Evaluate potential nitrogen source rocks. (Panel 2) - Use nitrogen concentrations and N/C to demonstrate that kerogen is not likely to be a
- direct source for nitrogen during late diagenesis and early catagenesis - Use a large dataset of nitrogen sediment analyses to evaluate controls on sediment
- nitrogen concentration. Mathematically remove nitrogen associated with kerogen to demonstrate that non-kerogen storage is associated with clay. - Use literature data to estimate the amount of nitrogen likely to be released from
- sediment during late diagenesis and early catagenesis. (4) Evaluate rock - water - gas interaction to determine how lean nitrogen source rocks can form high-nitrogen gases. (Panel 3)
- (5) Evaluate how much nitrogen source rock or nitrogen-bearing water is needed to form high-nitrogen accumulations. Use these estimates to determine if sufficient nitrogen source rock is available. (Panel 3)

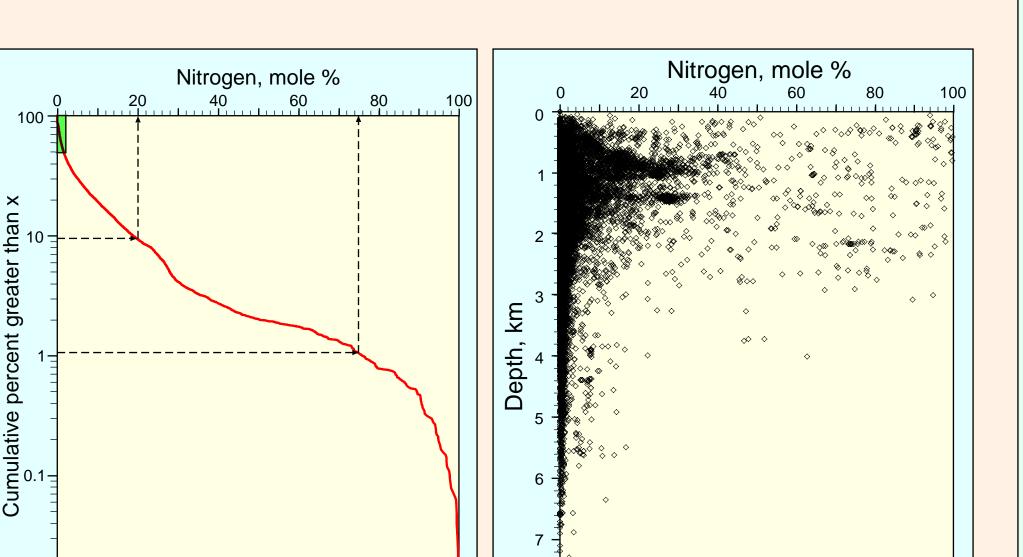
#### Setting for North American High-Nitrogen Gases

Gas analysis databases such as the USGS gas database have many high-nitrogen gases. About half of the samples have less than 2 % nitrogen (green box, Figure 9A). Approximately 9.3% of the analyses have greater than 20% N<sub>2</sub> and 1% of analyses exceed 75% N<sub>2</sub> (Figure 9A).

Most gases with nitrogen exceeding 20% occur at depths shallower than about 2.7 km with greatest number of analyses between 0.7 and 1.5 km (Figure 9B). Most of the highnitrogen gases samples are from the midcontinent area. Some midcontinent gases are near Cenozoic volcanics, but most wells are far from deep-buried coals, recently active metamorphic belts, deep crust-scale faults, etc.

The midcontinent would seem to be ar unsuitable setting for high-nitrogen gases if they are only sourced from basement and deep catagenesis. Two examples of high-nitrogen gas will be described to demonstrate why nitrogen is not likely to be late catagenetic or basement sourced. One area is the Yates Formation (Permian) along the northern shelf of the Delaware basin. The other is the Panhandle-Hugoton gas field of Texas, Oklahoma, and

Current Models for High-Nitrogen Natural Gas are Ineffective or Require High Thermal Maturity



- Figure 9 (A) Cumulative percent of nitrogen concentrations in "good quality" samples from the USGS natural gas database. Most gases have low (<2%) nitrogen concentration (green box), but about 9.3% of samples have >20% nitrogen, and about 1 % of the samples have very high-nitrogen (>75%). (B) Nitrogen concentration vs. top of producing depth. High-nitrogen gases occur mainly at
- Data are from the USGS gas database. Only analyses that summed between 96% to 104% were used. Samples with greater than 4 % oxygen were also omitted because of contamination issues. Nitrogen and argon in the remaining ("good quality") analyses were corrected for atmospheric contamination using oxygen. The analysis was then renormalized to 100 %.

### Example 1: Yates Gas, West Texas - New Mexico: High-Nitrogen Gas Surrounded by Low Nitrogen Petroleum

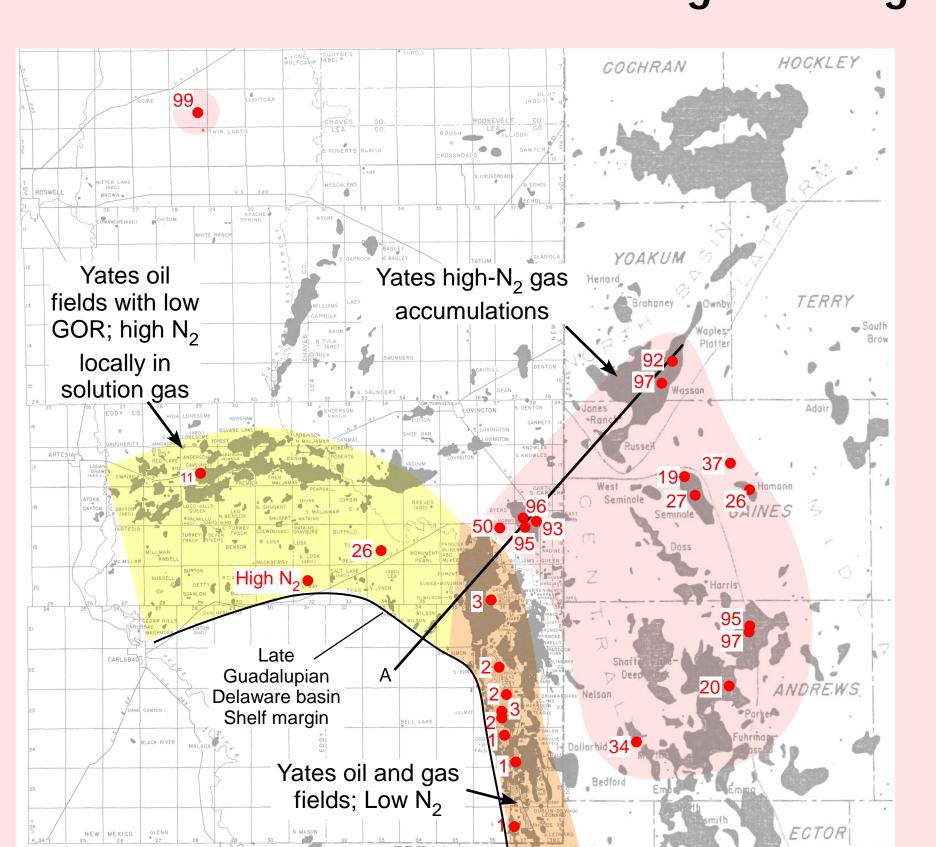
High-nitrogen gases have accumulated in Artesia Group (Permian; Late Guadalupian) reservoirs on some of the larger structural traps on the northern shelf and northern Central Basin Platform (Figure 10). Discussion focuses on gases in the Yates Formation, because more public-domain data are available for these gases.

The Yates formation is the shallowest horizon that produces either oil or gas. Most Yates accumulations in southeast New Mexico trap undersaturated oil (yellow area on Figure 10). Along the western side of the Central Basin Platform close to the Delaware Basin, Yates reservoirs contain nearly saturated oil or oil with gas caps (orange area, Figure 10). Gas nitrogen content is low, typically less than 4% (Figure 18). Nitrogen concentration in Yates gases increases farther from the Delaware basin shelf margin (red area, Figure 10). Gas accumulations closer to the shelf margin have intermediate (10 to 60%) nitrogen, whereas those farther from the shelf margin approach 100% nitrogen.

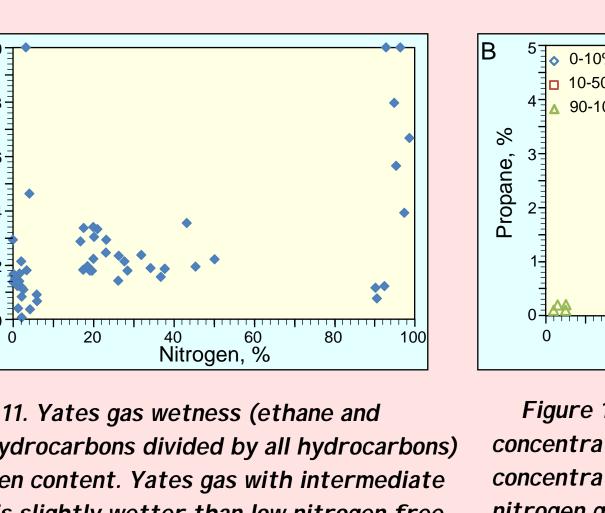
Only routine gas geochemical data are available. The wetness of low (<10%) and intermediate (10% to 60%) nitrogen Yates gases are similar to Yates oil solution gases (Figure 11). The propane content relative to ethane is a bit lower in intermediate nitrogen gases (Figure 12). This may indicate a small amount of gas biodegradation. Some of the very high-nitrogen gases (>90% N<sub>2</sub>) are exceptionally wet. Helium concentration and He/N<sub>2</sub> in Yates high-nitrogen gases are low (Figure 13). There is no correlation between helium and nitrogen concentration; He/N<sub>2</sub> decreases with increasing nitrogen content.

Geochemical data indicate that intermediate nitrogen gases form by dilution of hydrocarbon gases by nitrogen. Hydrocarbons in the high-nitrogen (>90%) gases are different from those in gases with lower nitrogen indicating a different source. Helium is a minor contaminant in both hydrocarbon and nitrogen gases. He/N2 ratios are much lower than those of the Panhandle-Hugoton field (see next panel).

Many of the units underlying the Yates Formation are also productive. Of special interest is oil in San Andres (Permian) reservoirs. San Andres oil reservoirs underlie Yates high- and intermediate-nitrogen gas accumulations. San Andres oil was undersaturated time of discovery. Solution gases in San Andres oil have low nitrogen concentration



Permian Artesia Group. Most fields to the west are oil fields with low gas-oil ratio (GOR; yellow area). Free gases with low nitrogen (orange area) lie near the Delaware basin on the western Central Basin Platform. Area with high-nitrogen gases (red) are farther from the shelf margin near and beyond the transition into evaporite facies.



may be evidence for biodegradation of the petroleum in intermediate nitrogen gases

Data from USBM dataset

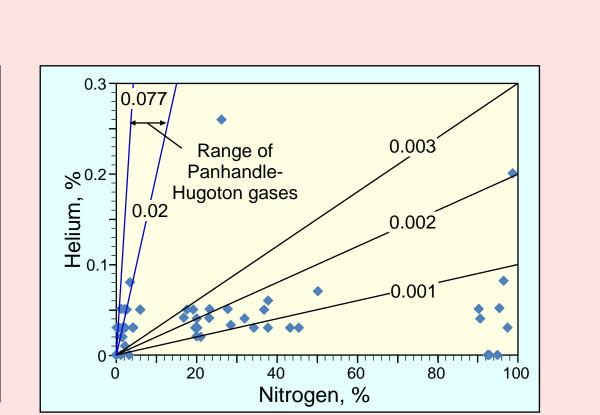
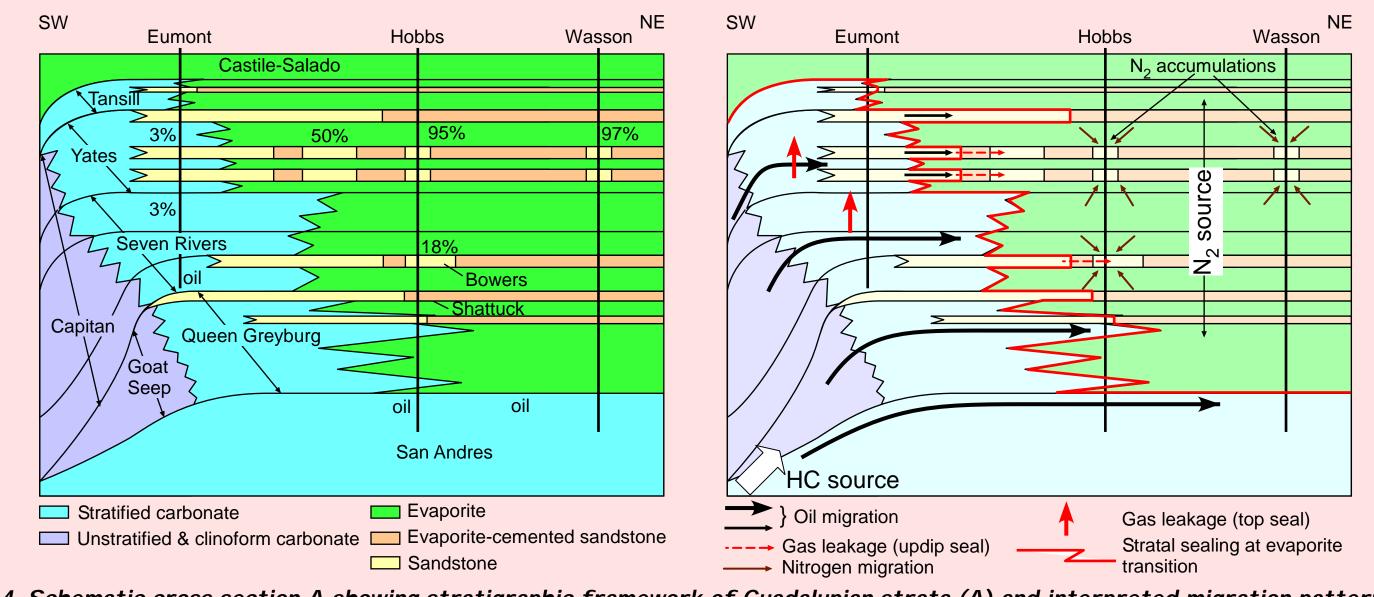


Figure 13. Helium concentration in Yates gases. Helium (symbols) and He/N2 (lines) are low. Low nitrogen gases have He/N<sub>2</sub> similar to those of the Panhandle-Hugoton field (blue lines), but higher nitrogen gas He/N2 is much lower. Data from USBM

#### Charge Scenarios and Origin of Nitrogen

The stratigraphic framework (Figure 14A) controls petroleum migration patterns (Figure 14B). Oil generated deep in the Delaware basin charges Permian reservoirs through the shelf-margin massive carbonate and clinoform system. Oil not trapped in structural closures is trapped against the regional sealing interface near the carbonate-evaporite transition (red line, Figure 14B). Topseals in the carbonate shelf-margin system are weak. Gas selectively leaked upwards until it reached the evaporite top seal above the Yates Formation where it was trapped. Regional updip petroleum migration in Yates sandstones terminates where the sandstone is cemented by evaporites near the regional carbonate-evaporite transition. Updip leakage of hydrocarbon gas through partially cemented sandstone mixed the hydrocarbons with nitrogen near the evaporite transition. Where cemented sandstones in the evaporite facies more completely isolated porous sandstone bodies, gases are predominantly nitrogen because hydrocarbons could not migrate to the trap.

High-nitrogen accumulations are completely isolated from any potential high maturity or basement nitrogen source by petroleum-bearing units low in nitrogen. There are no nearby intrusives. There are no major faults extending from deep strata into the Artesia Group. Nitrogen accumulations overlie undersaturated San Andres oil accumulations with low-nitrogen solution gas. Any nitrogen migrating from the basement along faults or fractures would have to bypass the underlying oil accumulations without mixing or carrying hydrocarbon components to the nitrogen reservoirs. This is highly unlikely. High-nitrogen gases are updip from oil and gas accumulations with low nitrogen contents in the same stratigraphic units. Any high-maturity gases migrating from the deep Delaware basin along the Yates Formation would saturate oil and be diluted before reaching the highnitrogen accumulations. Therefore, stratal nitrogen charge from the deep Delaware basin along the Yates Formation is also highly unlikely. The High-nitrogen accumulations are partially to completely isolated from petroleum accumulations to the south by evaporite cementation of the carrier bed systems. Overall, nitrogen charge from high-maturity sediments or basement is



Source rocks are thickest and thermally mature in the Delaware basin, which is the source kitchen for petroleum around the Delaware basin. Petroleum charge is up the shelf margin section along clinoforms and through massive carbonate lacking seals. Petroleum is trapped where reservoirs are interbedded with evaporite or evaporitic dolomite seals. The Late Guadalupian carbonates facies change from carbonate to evaporite acts an an updip seal relatively close to the shelf margin. Yates and other sandstones retain porosity farther updip until petroleum is trapped against evaporite-cemented sandstone. Porous sandstone near the evaporite transition may receive partial petroleum charge through leaky stratal seals. Porous sandstones far from the shelf margin are almost completely isolated from petroleum charge. Nitrogen is interpreted to be charged from thermally immature strata surrounding the updip sandstone. San Andres carbonate extends far from the shelf margin, allowing charge to structural traps far from the shelf margin, where petroleum is trapped under tight Greyburg evaporitic carbonate top seals.

#### Conclusion: Yates Gases

Nitrogen is constrained to come from surrounding strata: evaporites, evaporitic dolomites, and argillaceous to dilution by the much greater petroleum charge.

#### Volcanic and Mantle: Mostly Ineffective Source

**Atmosphere: Ineffective Source** Atmospheric nitrogen in subsurface gases can be Nitrogen concentrations in the mantle are low, but the large mantle volume makes it a identified by nitrogen isotopes, nitrogen/argon ratio potential source for nitrogen in natural gases. Mantle nitrogen has a relatively homogeneous Argon isotopes, and neon isotopes (e.g., Littke et al  $\delta^{15}$ N relative to atmosphere ( $\delta^{15}$ N<sub>atm</sub>) near -5 ± 2‰ (Sano et al. 2001). Mantle molar N<sub>2</sub>/<sup>3</sup>He 1995, Ballentine et al. 2002). Atmospheric nitrogen ratio is approximately 8.9x10<sup>5</sup> in melts (Sano et al. 2001). Nitrogen is less soluble in basalt enters the subsurface as gas dissolved in water melts than is helium (Sano 2001); therefore,  $N_2/^3$ He increases in volatiles equilibrated to Nitrogen fugacity in water in water equilibrated to mantle melts by a factor of about 10. atmosphere is about 0.7 atmospheres. Water retains The fraction of mantle nitrogen in total nitrogen can be estimated from a plot of  $\delta^{15} N_{atm}$  vs. this fugacity with burial, and the mole fraction of  $N_2/^3$ He (Sano et al. 2001). Two sets of mixing curves are shown, one for melt source and or atmospheric nitrogen in subsurface gases is i

> About 1 and 10% of the nitrogen in island arc hydrothermal and volcanic gases was derived from the mantle if melt equilibration is assumed. This is about a third of the mantle N<sub>2</sub> fraction estimated from  $N_2/^{36}Ar$  ratios and  $N_2$  isotopes (Sano et al. 2001). The similarity of mantle and sediment N<sub>2</sub>/<sup>36</sup>Ar ratios and the wide range of sedimentary nitrogen isotopic

ratios make estimates of mantle contribution based on  $N_2/^{36}Ar$  ratios uncertain.

for volatiles equilibrated to basalt melts (Figure 2). Glass samples in backarc basins and

oceanic islands show high fractions of mantle nitrogen. No natural gas has such high mantle

The Jenden et al. (1988) natural gas samples from the California Great Valley overlaps Sano's volcanic volatiles (Figure 2). Jenden's volcanic end member (V) lies within the range of island arc hydrothermal fluids reported by Sano et al. (2001). Based on  $N_2/^3$ He, only about 0.1 to 3% of the nitrogen in Jenden's samples was derived from the mantle. If Sano's analyses are representative of all volcanic gases, Jenden's volcanic end-member is indeed volcanic in origin. The endmember has about 17% nitrogen.

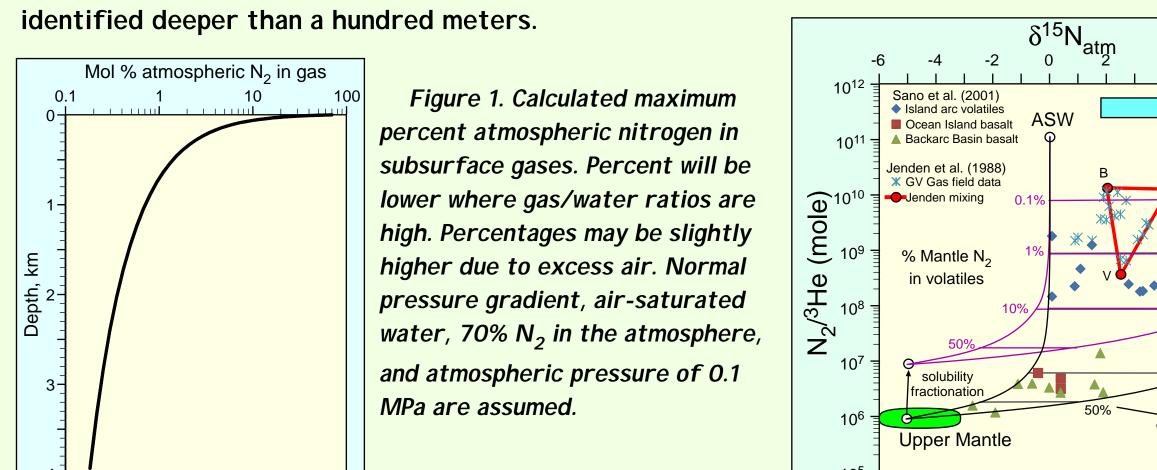


Figure 2. Mixing of mantle with near-surface nitrogen as indicated by  $N_2/^3$ He molar ratios and nitrogen isotopes. Mixing curves assume either mantle basalt melt (black lines) or volatiles equilibrated with mantle basalt melt (magenta lines). Nitrogen in backarc basin (green triangles) and ocean island basalt (red squares) glasses has significant mantle nitrogen (data from Sano et al. 2001). I sland arc hydrothermal and volcanic gases (blue diamonds) have elevated  $N_2/^3$ He ratios due to mixing with shallow  $N_2$ . Only about 0.1 to 3% of the nitrogen in California Great Valley natural gases (Jenden et al. 1988) is mantle derived if mixing with melt-equilibrated volatiles is assumed. ASW = air-saturated water. B, S, V are basement, sedimentary,

and volcanic end members of Jenden et al. (1988).

# Basement: High Thermal Maturity Source

Metamorphic basement has low to intermediate nitrogen concentrations (~10 to 1000 wt ppm; Bebou and Fogel 1992; Haendel et al. 1986; Palya et al. 2011). Much of this nitrogen is ammonium substituting for potassium in micas.

Nitrogen is lost with increasing metamorphic grade (Bebout and Fogel 1992; Haendel et al. 1986; Paly et al. 2011). As nitrogen concentration decreases, its isotopic ratio becomes heavier, with  $\delta^{15}N$  increasin from about 2 to as much as 17 %  $\delta^{15} N_{
m atm}$  in highly nitrogen-depleted samples (Figure 3). Nitrogen bearing volatiles released during metamorphism must be isotopically lighter than the source nitrogen to balance isotopes. Fits of data using Rayleigh fractionation models show nitrogen isotope to bulk nitroge fractionation factors between 0.9983 and 0.9985. Released nitrogen has a calculated  $\delta^{15} N_{atm}$  between about 0% and 4% at lower metamorphic grade where most nitrogen is lost (Figure 3). The correlation between nitrogen loss and metamorphic grade indicates that the metamorphic source is only active during metamorphism. Burial of exhumed, old metamorphic belts are not likely to release nitrogen to strata above the nonconformity, because the metamorphic rocks were devolatilized long before reburial

basement in origin based on proximity to the metasedimentary basement and association with heavycarbon methane (Jenden et al. 1988; "B" end member on Figure 2). The  $\delta^{15} N_{atm}$  of the California highnitrogen gases range from 1.9 to 2.7 % (Figure 5). This is consistent with a metamorphic origin. The Great Valley has young basement (Cretaceous Franciscan Series) and Late Cenozoic exhumation of the eastern side of the Great Valley. The basement may still be releasing volatiles due to their young age Exhumation might cause exsolution of nitrogen from water in the basement and its weathering products.

Nitrogen in high-nitrogen gases in the California Great Valley was interpreted as metasedimentary

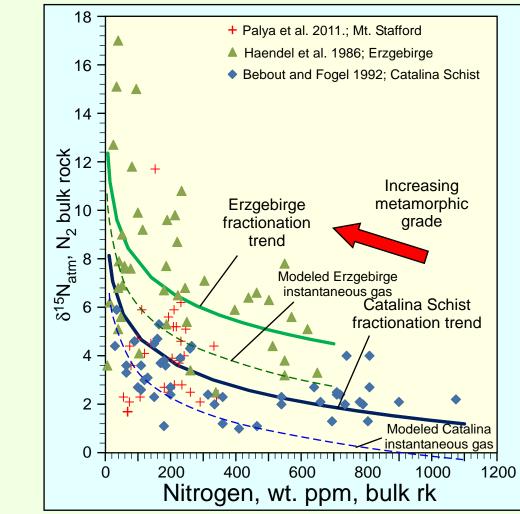
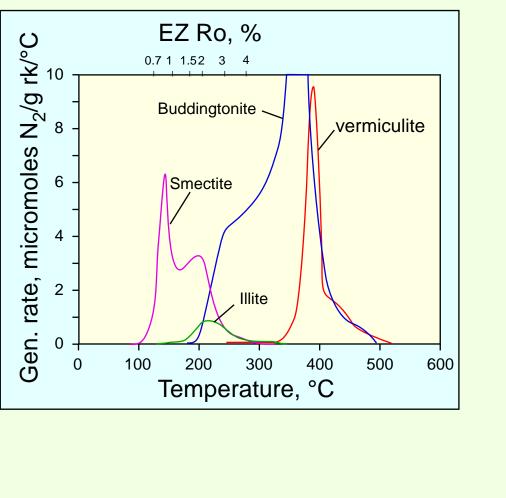


Figure 3. Nitrogen in metamorphic rocks. Bulk nitrogen decreases with increasing metamorphic grade, and nitrogen becomes heavier with decreasing nitrogen content. Erzgebirge and Catalina Schist data were fit with Rayleigh models using fractionation factors of 0.9983 and 0.9985 respectively and different initial nitrogen isotopic and bulk compositions. Modeled instantaneous evolved nitrogen gas has  $\delta^{15}N_{atm}$  between about -1 and +6 % over most metamorphic grades, with the lighter nitrogen (0 to +4 %  $\delta^{15}N_{atm}$ ) at lower metamorphic where most nitrogen is lost. Model predicts relatively uniform  $\delta^{15}N_{atm}$  at a given location and

#### Clay Ammonium: High Thermal Maturity Source Ammonium may also be released from phyllosilicate minerals during late catagenesis and early metagenesis (Everlien and Hoffmann 1991). They

measured ammonium released during laboratory pyrolysis, and extrapolated generation rates to geological heating rates (Figure 4). They proposed that ammonium would be lost from illite under late catagenetic conditions whereas buddingtonite and vermiculite release nitrogen under metamorphic conditions. Once it is released from clays, ammonium converts to nitrogen. Mingram et al. (2005) propose that nitrogen is released from clays during late catagenesis and early metagenesis due to interaction of clays with saline brines, because nitrogen concentration are anomalously low where

Figure 4. Total nitrogen release rate from ammonium-saturated silicates at geological heating rates as estimated by Everlien and Hoffman (1991). Heating rate is 6.3 C/My. Samples (except for buddingtonite were artificially saturated with ammonium. Much of the nitrogen loss was as ammonium. Kinetics were poorly constrained for most samples. EZRo vitrinite reflectance was calculated for their heating rate. Nitrogen loss from smectite is probably due to dehydration and breakdown during



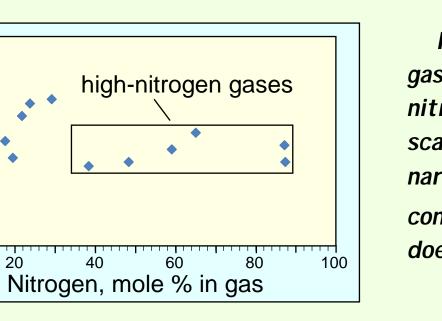


Figure 5. Nitrogen in Great Valley, California gases analyzed by Jenden et al. (1988). Low nitrogen gases show moderate nitrogen isotopic scatter, but high-nitrogen gases fall within a narrow range of 1.9 to 2.7 %  $\delta^{15}N_{atm}$ . This range is consistent with a metasedimentary source bu does not exclude a sedimentary source.

#### Organic Nitrogen: High Thermal Maturity Source Both nitrogen concentration trends and pyrolysis experiments demonstrate the

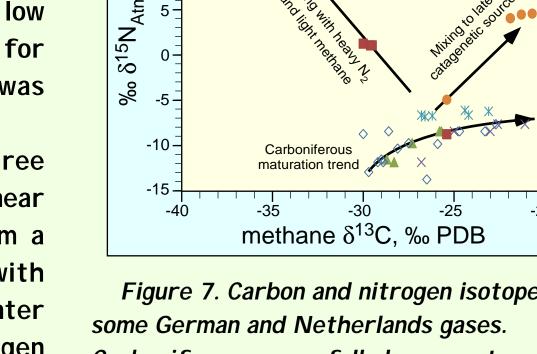
nitrogen in humic kerogen and coal is released at high thermal maturity after the main phase of methane generation (Littke et al. 1995; Krooss et al. 1995; see also Figure 22). Nitrogen concentration in incremental-generated gas is about 30% at about 245°C (~3.2% random vitrinite reflectance, VRo), based on kinetic models at geological heating rates (Littke et al. 1995). Gases with nitrogen concentrations approaching 100% are generated at temperatures exceeding 350°C (Krooss et al.

Rotliegend and Triassic Buntsandstein reservoirs in north Germany and northern Netherlands. The areas with nitrogen concentrations in gas exceeding 50% roughly vitrinite reflectance (Krooss et al. 1995). At such high thermal maturity, coals release sufficient nitrogen to account for the nitrogen in gases. However, no direct geochemical indicator for organic nitrogen has been substantiated.

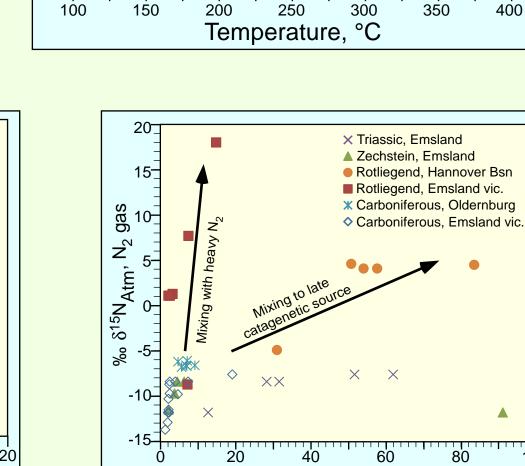
Only incremental, high-maturity coal-generated gases have high nitrogen (Krooss et al. 1995). Traps that capture and retain all gas are likely to have moderate to low nitrogen concentrations. The predominance of high-nitrogen gases is evidence for late gas trapping in Germany. Only about 1 % of the total generated gas was trapped in areas with high (>50%) nitrogen (Krooss et al. 1995)

Nitrogen isotopic ratios in North Germany high-nitrogen gases indicate three possible nitrogen sources (Figure 7, 8). In the Emsland and Oldenburg areas near the German-Netherlands border, Carboniferous-reservoired gases form a maturation trend where nitrogen is isotopically light but becomes heavier with maturity (Figure 7). The source is probably high-maturity coals. Triassic Bunter and Zechstein gases fall along the same trend, but have much higher nitroger concentrations. Rotliegend gases near the Ems Estuary mix with heavy nitrogen from the unidentified Groningen source. Light carbon methane indicates mature source. Hannover basin Rotliegend gases are a mixture of high maturity Carboniferous-sourced gases with a gas containing heavier, more abundant nitro (Figures 7 and 8). The nitrogen in this gas has isotopic ratios similar to metamorphic values and may be late catagenetic or early metagenetic nitrogenetic

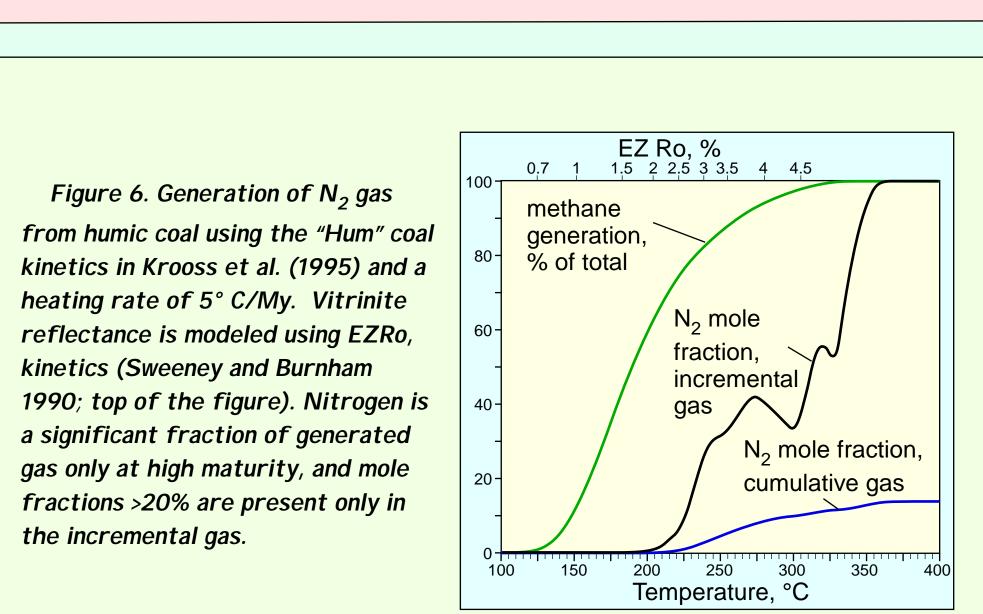
# fractions >20% are present only in the incremental gas.

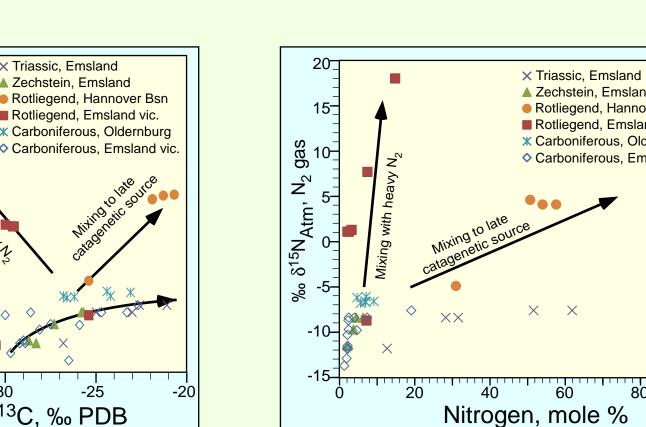


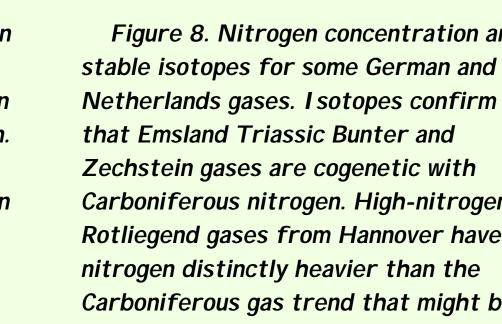
Hannover gases mix with a high-nitrogen gas with heavier nitrogen and heavy-carbon methane that is probably of high maturity by exceptionally heavy nitrogen and lighter carbon methane possibly indicating lower thermal maturity gas. Most data are from Stahl et al. (1977).

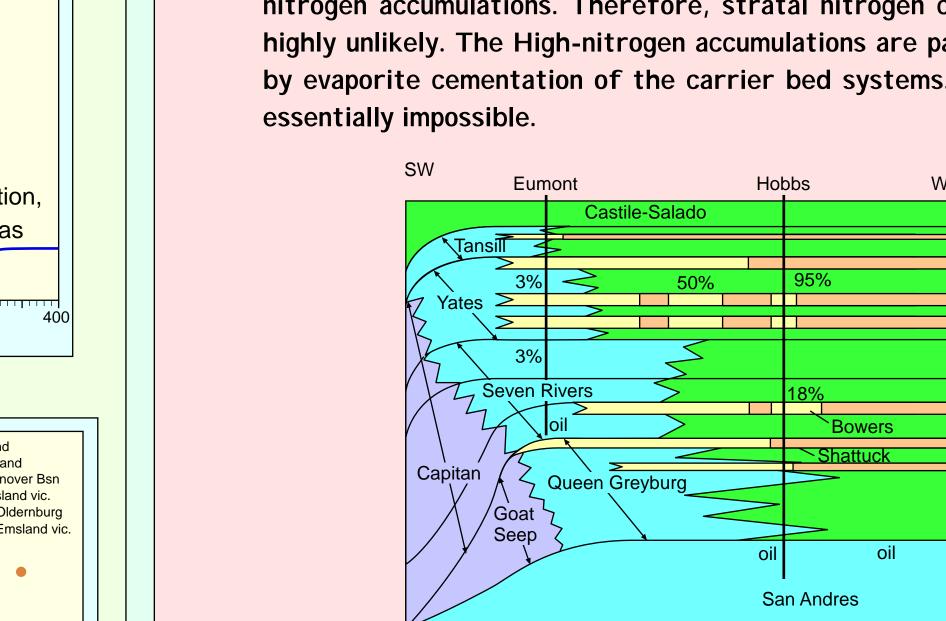


stable isotopes for some German and Netherlands gases. I sotopes confirm that Emsland Triassic Bunter and Zechstein gases are cogenetic with Carboniferous nitrogen. High-nitroge Rotliegend gases from Hannover have nitrogen distinctly heavier than the Carboniferous gas trend that might be derived from clays or much higher thermal maturity organic source.



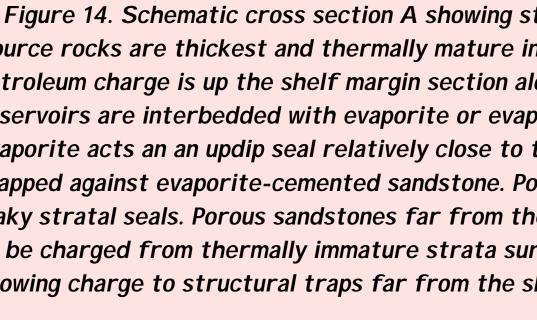


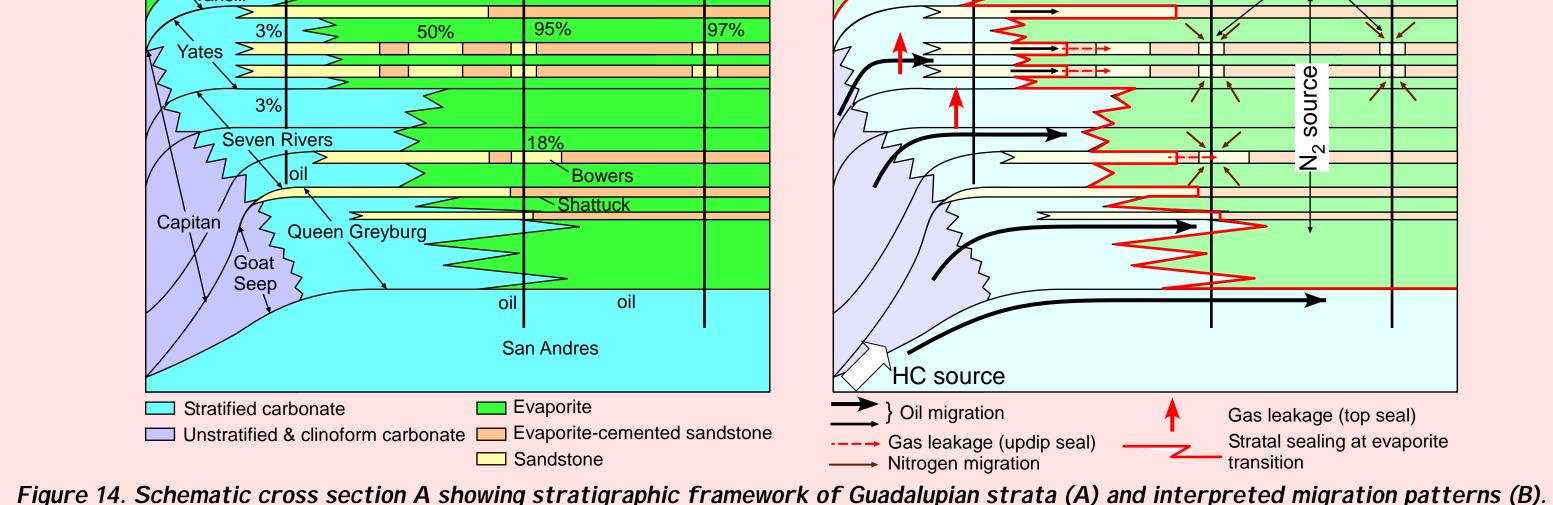




derived from previously devolatilized bitumer

the reservoir. Data from USBM dataset





sandstones. These strata are thermally immature for oil generation. Nitrogen may also be sourced from shelf-margin strata. High-and intermediate-nitrogen accumulations may be absent near the shelf margin due

# Possible Origins for Low Thermal Maturity, High-Nitrogen Natural Gases

Sedimentary nitrogen may be stored in the organic (kerogen) or

## Example 2: Panhandle-Hugoton Field: Mixing Patterns and Trace Gases Indicate Sedimentary Source

The Panhandle-Hugoton field of Texas, Oklahoma, and Kansas is one of the largest nitrogen-hydrocarbon accumulations in the world (Figure 15). Origin of helium and nitrogen in the field remain controversial.

Ballentine and Sherwood Lollar (2002) identified three nitrogen endmembers (1) Mantle nitrogen forms a minor endmember (<1.5% of the in-place nitrogen) not discussed further here. (2) Light (-3 %  $\delta^{15}N_{atm}$ ) nitrogen endmember has <sup>4</sup>He/N<sub>2</sub> of 0.077 and elevated <sup>20</sup>Ne. Ballentine and Sherwood Lollar (2002) interpret a low-grade metamorphic source with transport to the field dissolved in groundwater. (3) Relatively heavy (+13 %  $\delta^{15}N_{atm}$ ) nitrogen endmember has no <sup>20</sup>Ne or <sup>4</sup>He. Ballentine and Sherwood Lollar (2002) interpret a relatively mature marine source rock in the Anadarko basin, with charge predating filling by hydrocarbons.

Brown (2010) integrated the field charge history reported by Sorenson (2005) with additional geochemical data (USBM gas database and Jenden and Kaplan 1989). Two high-nitrogen and one low-nitrogen endmembers with different He/N<sub>2</sub> ratios were identified (red diamonds, Figure 16A). Both high-nitrogen end members were exsolved from water flowing beneath the field, which was originally charged with the low nitrogen gas end member. Water flowed from two sources (Palo Duro basin and area west of Hugoton field). The different He/N<sub>2</sub> and the dominance of two-component mixing trends are explained by mixing of initial gas charge with gases dissolved in the two aquifers. Helium and nitrogen were interpreted to be generated from the sedimentary rocks and possibly shallow, fractured basement.

The two models can be compared by integrating bulk gas composition with other datasets. The Ballentine and Sherwood Lollar (BSL) endmembers are ratios that plot as lines on He-N<sub>2</sub> plots; therefore, unique end member contributions to each gas sample cannot be determined (Figure 16B). The BSL model does not explain the absence of gases with He/N<sub>2</sub> ratios less than about 0.02 or why gases with high He/N<sub>2</sub> do not contain more than 2% He (Figure 16A). Most Anadarko basin gases have low nitrogen and helium (grey field), inconsistent with the high nitrogen, zero He endmember proposed by Ballentine and Sherwood Lollar (2002). Almost all Panhandle-Hugoton gas analyses can be explained by mixing between the Brown (2010) endmembers (Figure 16A). Gas compositions from different parts of the field form different linear trends indicating predominantly two-component mixing of the two high He, high  $N_2$  endmembers with the low helium endmember. SE Colorado gases show mixing between Hugoton gases and higher He gases of the Las Animas Arch area.

Nitrogen isotopic compositions of almost all gas samples are also explained by the three endmembers on Figure 16A The Hugoton Embayment endmember has  $\delta^{15}N_{atm}$  of +10.7%, whereas the Redcave and Palo Duro endmembers have  $\delta^{15}N_{atm}$  of +2% (Figure 17). The BSL model fails to explain the greater range of He/N<sub>2</sub> in light-nitrogen samples, the nitrogen isotopic data from Jenden et al. (1989), or the absence of gases with  $\delta^{15}N_{atm}$  near their proposed endmember

The quantity of nitrogen is large, approximately 460 billion m<sup>3</sup>. Of >75 TCF OGIP in Panhandle-Hugoton field, about 16 TCF is N<sub>2</sub>. Because nitrogen correlates to helium, determining the source of helium indicates likely source of nitrogen. For example, if insufficient helium could be generated in sediments near the field, a larger source volume such as the crust must be considered for both nitrogen and helium. Contrary to conclusions by Ballentine and Lollar (2002) and in agreement with Pierce et al. (1966), sufficient sedimentary rock is available to generate all helium in the Panhandle-Hugoton field (Figure 18). The aquifers supplying helium and nitrogen extend into the Dalhart basin, eastern New Mexico and across the northern part of the Las Animas Arch. Source area for dissolved helium and nitrogen could be significantly larger than modeled on Figure 18, because N<sub>2</sub> and He were transported as dissolved components in hydrodynamic water If N<sub>2</sub> and He are co-sourced, nitrogen could have been generated in the sediment column. An average of 0.0025 mg N<sub>2</sub>/g rock (25 wt. ppm) must be released from the total rock volume if the modeled sediment volume is the nitrogen source.

#### Trace Gas Geochemistry

Trace argon and neon concentrations follow the three-component mixing trends evident in the nitrogen-helium data (Figure 19A, 19B). Neon isotopic ratios do not show major systematic variation with nitrogen concentration (Figure 19C) <sup>20</sup>Ne/<sup>21</sup>Ne are lower than atmosphere, indicating <sup>21</sup>Ne generation and relatively old water. Together, these data indicate that trace gas concentrations differ by dilution and mixing between gases with approximately the same <sup>20</sup>Ne/<sup>21</sup>Ne age.

I sotopic ratios of the radiogenic gas components can be used to assess the duration of helium generation. Radiogenic <sup>20</sup>Ne and <sup>21</sup>Ne generation are mainly controlled by the concentrations of U, Th, and oxygen with smaller contribution from Mg and Na (Ballentine and Burnard 2002). Because oxygen concentration is relatively constant in rocks, the generation rates of these two isotopes are proportional to the rate of helium generation. <sup>20</sup>Ne/<sup>4</sup>He, <sup>21</sup>Ne/<sup>4</sup>He, and <sup>20</sup>Ne/<sup>21</sup>Ne all change systematically with age due to mixing of atmospheric neon and radiogenic production of helium and neon. If porosity, temperature and pressure of gas equilibrium with water can be estimated and if all He and Ne goes into the water and gas phases, the helium and neon concentrations in gas equilibrated with the water will change systematically with duration of generation.

Models using conditions in Palo Duro basin (for generation) and Panhandle Hugoton field (for exsolution) show that the neon forms a dilution trend extrapolating to an helium generation duration between about 180 and 300 My (Figure 20). Gas <sup>20</sup>Ne/<sup>21</sup>Ne are consistent with source in sediment with generation duration over about 150 to 420 My, depending or assumptions (Figure 21). The  $^{20}$ Ne/ $^{21}$ Ne is well below that of the atmosphere (338) but far greater than those of metamorphic fluid inclusions (e.g., 14 - 26; Kendrick and Burnard 2013).

#### Conclusions

Major gas components indicate mixing of three sources, two of which are associated with aquifers. The source volume needed to generate helium (and nitrogen) is consistent with the volume of sediments in the Palo Duro and western Hugoton embayment. Both neon/helium ratios and neon isotopic ratios point towards a generation duration of about 200 to 300 million years, the expected duration of sedimentary generation prior to Cenozoic hydrodynamics. <sup>20</sup>Ne/<sup>21</sup>Ne exclude both a young water age and a basement origin.

Neither major nor trace gas components provide evidence for gas origin in the basement. Trace gases provide <u>strong evidence for a helium and nitrogen source in the sediments, and neon isotopes eliminate a basement origin. A</u> sedimentary nitrogen and helium origin is consistent with the geological and hydrodynamic setting of Panhandle <u>Hugoton field.</u>

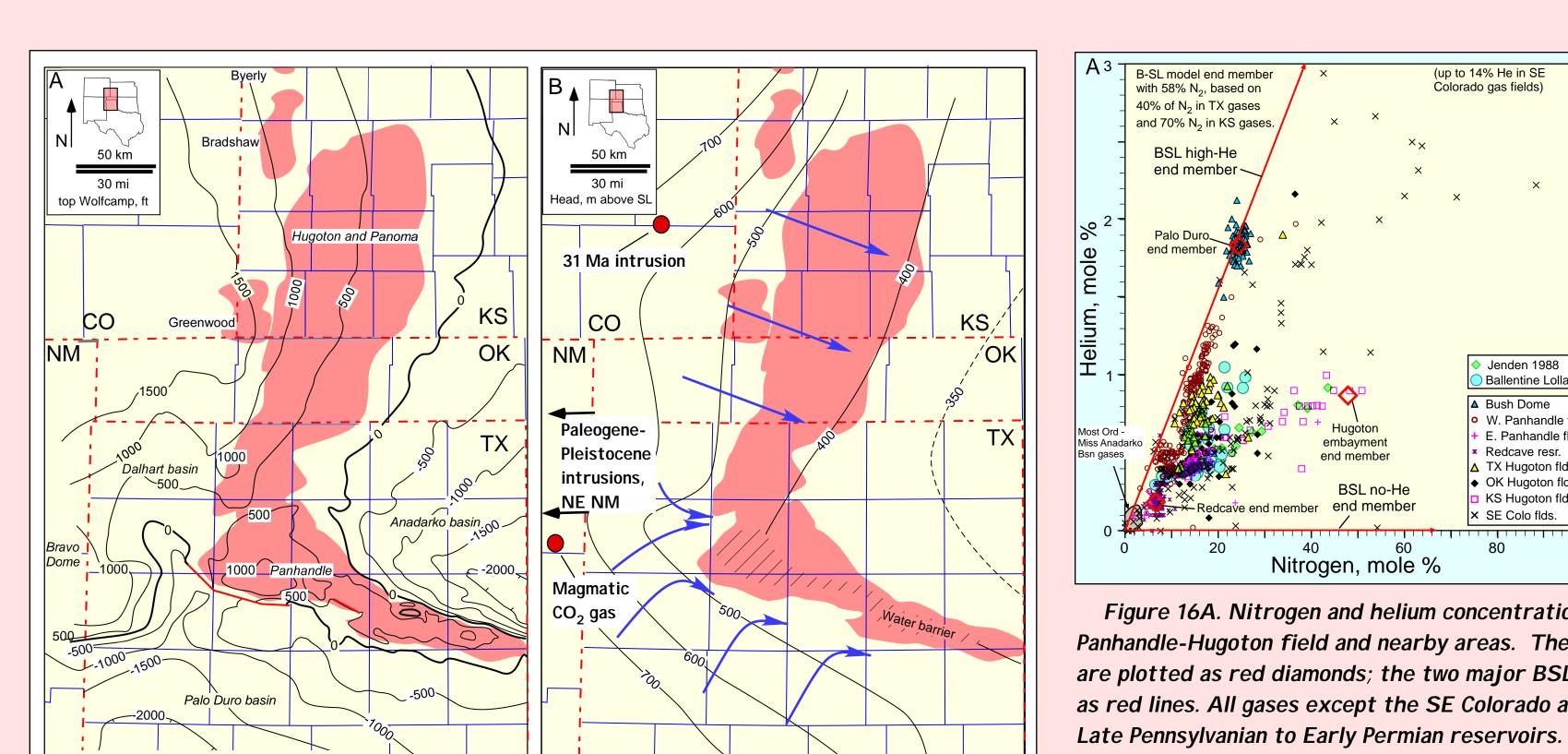


Figure 15. Panhandle-Hugoton field area. (A) Structure on top of Wolfcampian. (I Potentiometric surface of Wolfcampian-Virgilian aguifer. Inferred flow directions (blue arrows) wrap around Panhandle field due to basement blocking water flow (hatch). Potential sources of magmatic gas contamination are identified (red dots). Field locations in red

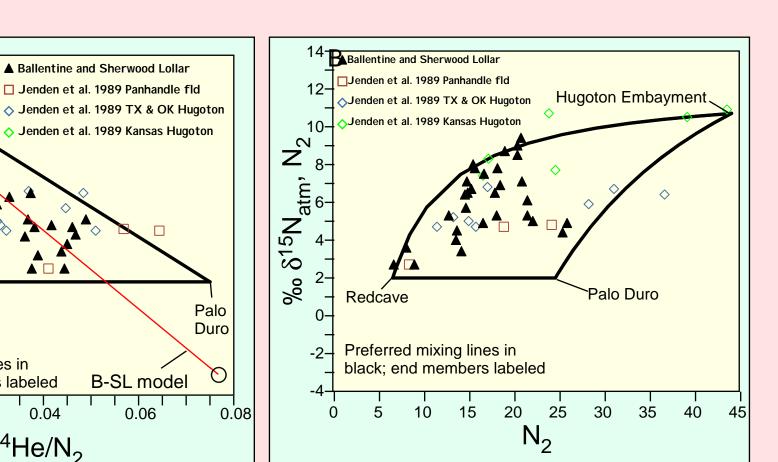
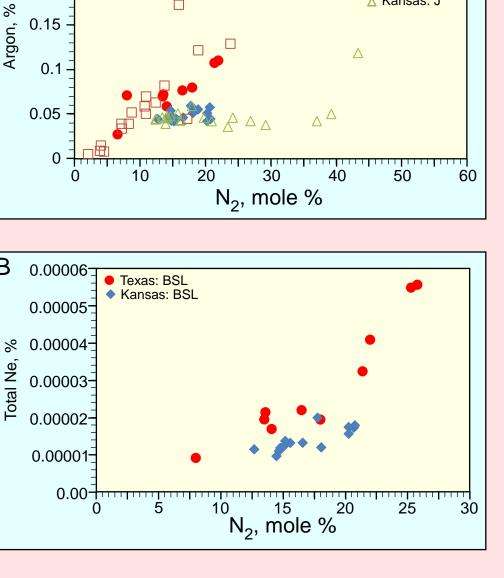
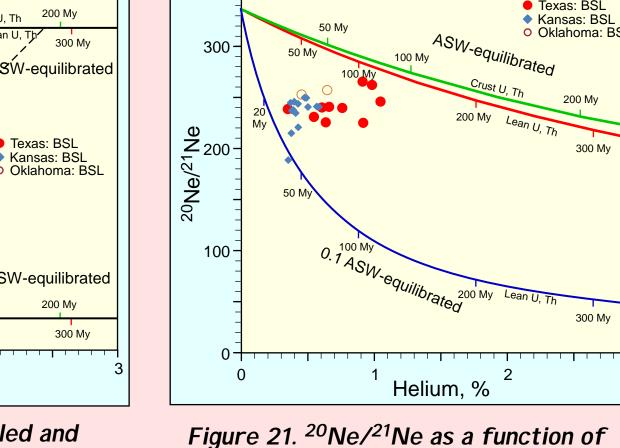


Figure 17. Nitrogen isotopes in Panhandle-Hugoton gases as a function of He/N<sub>2</sub> ratio (A) and nitrogen content (B). Mixing models preferred here (black lines) encompass most data plotted against ratios and nitrogen content. The BSL model does not explain light nitrogen isotopes in Panhandle high He/N2 gases (Jenden et al., 1989) or absence of samples with nitrogen isotopic ratios less than +2%. BSL ratio mixing cannot be plotted on nitrogen isotope vs. nitrogen plot.

Figure 19. Trace gas concentrations vs. N<sub>2</sub>, Panhandle-Hugoton field. (A) Argon; (B) Neon; (C)  $^{20}$ Ne/ $^{21}$ Ne. Argon and neon show similar mixing patterns with nitrogen as helium (see Figure 16). Neon isotopic ratio  $(^{20}\text{Ne}/^{21}\text{Ne})$  is significantly below atmospheric value (338) and significantly greater than basement ratios (14 25). Together, these data indicate mixing of components similar to N<sub>2</sub> He patterns, significant time since atmospheric gas entrapment, and lack of basement contamination. Data from Ballentine and Sherwood



• 3 6 5



Data from Ballentine and Sherwood Lollar

# Figure 16B. Ratios are unsuitable for mixing ndmembers without addition onstraints because analyses cannot be uniquely unmixed. T mponent (red dot) and three

can be mixed to form the same

are plotted as red diamonds; the two major BSL nitrogen endmembers are plotted as red lines. All gases except the SE Colorado and Anadarko Basin gases are from

Figure 18. Helium generated in the Palo Duro basin (green), western Hugoton embayment (blue), and total area (brown and red) as a function of generation time and assumed U and Th concentrations. Two U and Th concentrations are modeled crust average (2.8 and 10.7 wt ppm, respectively) and low model based on analyses in Pierce et al. (1966; 2.5 and 5 wt ppm, respectively). Assumed areas: Palo Duro basin: 41,000 km<sup>2</sup>: western Hugoton embayment: 44,000 km<sup>2</sup>. Both have about 1 km average pre-salt sediment thickness The amount of helium generated since deposition of the seal exceeds that in the

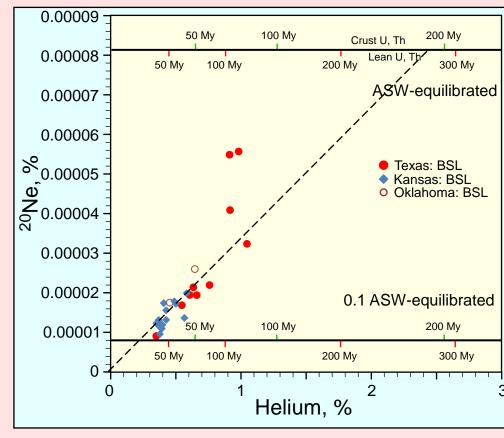
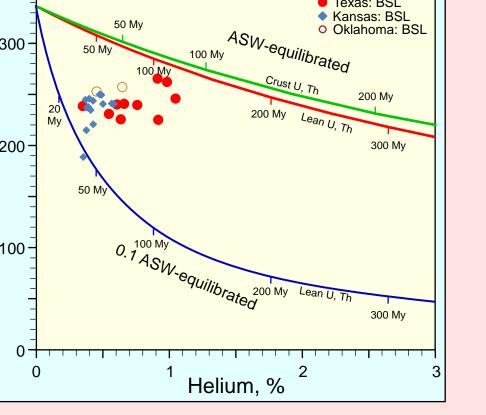


Figure 20. Comparison of modeled and gas exsolved from 100,000 ppm NaCl water at 3 MPa and 35°C, the approximate reservoir conditions in Panhandle-Hugoton field. Radiogenic <sup>20</sup>Neon is generated so slowly that it remains at that of airsaturated water (ASW) as helium concentration increases with generation. Data fall on a dilution (mixing) line with gases generated from water either partially (90%, lower horizontal line) or completely purged of air components. Assuming mixing, ASW-end member has a He generation age near 200 to 300 My depending on assumed average U and Th concentration. The hydrocarbon endmember migrated through water 20 to 50 My after its deposition.



helium generation from rocks with different U and Th concentrations and with different ratios of ASW. Crust (green line) and low (red line) models are mixes with ASW for seawater at 25°C. A model with 0.1 ASW and lean radioactivity represents gas diluted by prolific hydrocarbon generation (blue line). Lower ASW (or porosity) causes significantly lower <sup>20</sup>Ne/<sup>21</sup>Ne due to lower initial atmospheric Ne content. <sup>20</sup>Ne/<sup>21</sup>Ne age (assuming ASW and 8% porosity) ranges from 150 to 420 My depending on the assumed U, Th model. Concentration of gas phase is calculated based on 8% rock porosity, 2.7 g/cc grain density, and exsolution at 35°C and 3 MPa, the discovery Panhandle-Hugoton reservoir conditions. Data from Ballentine and Sherwood Lollar (2002).

# Potential Sedimentary Source Rocks

(A). Hydrogen and oxygen concentrations of

sedimentary organic matter as shown on the van

precursor plankton to modern marine organic matter

near the sea floor to kerogen are diagenetic changes

kerogen types. Figured kerogens are late diagenetic

with some early catagenetic kerogens in the Toarcian

For most groups, N/C is relatively uniform over the

range of O/C. Average marine kerogen is about 0.025

(Scotchman 1991); Toarcian: Paris basin outcrops and

cores (Durand et al. 1972); Cretaceous black shale

Cameroon (Durand and Espitalie 1976); Green River

Ruble and Philp 1998): modern marine OM and moder

terrigenous OM: piston core samples of Quaternary

deep sea sediments in settings with predominantly

marine and terrestrial organic matter, respectivel

terrigenous organic matter: reconstructed average

organic matter prior to degradation (Pelet 1983).

elemental composition of pure marine and terrigenous

(Tissot and Pelet 1981); average planktonic and

eastern North Atlantic boreholes, DSDP leg 75

(Deroo et al. 1978); Logbaba: Douala basin cores

but it varies between sample groups. Data:

Kimmeridge: England shallow cores and outcrops

(B) The N/C vs. O/C of the same kerogen samples

Krevelen diagram. Decreasing O/C and H/C from

inorganic parts of the rock. The nitrogen source potential for diagenetic and early catagenetic kerogen and coal will be evaluated from elemental C and N trends. Decreasing N or N/C indicates nitrogen release and possible nitrogen gas source. Variations between different lithologies in ancient rocks will be analyzed using the large Trask and Patnode (1942) database. Kerogen nitrogen storage will be identified from TOC. Kerogen nitrogen will be mathematically removed using N/C ratios. Correlations between lithology type and remaining (non-kerogen) nitrogen will be used to identify probable inorganic nitrogen storage mechanisms. The dominant storage site (as ammonium in clay) will be confirmed using

amount of nitrogen stored in components other than kerogen. Trask and Patnode (1942) used a relatively reliable modified Kjeldahl method for nitrogen analysis with probable error of 3% to 5% of the reported value. However, more recent studies report incomplete recovery of nitrogen for some Kjeldahl extraction procedures (Holloway and Dahlgren, 2002). Carbon analyses are less accurate and precise. Probable error based on duplicate analyses is on the order of 11% of the reported carbon content in clastic analyses are averages of duplicate analyses and the probable error is less than that calculated from the difference between duplicate analyses. Assuming most uncertainty is in the carbon analysis and its probable error, the probable error of N/C in siliciclastic rocks is also on the order of 10% of the reported value (i.e., an N/C of 0.05 would be 0.045 to 0.055). See Trask and Patnode (1942) for discussion of the analytical methods and the probable analysis errors.

more recent studies of fewer samples that directly measure the

#### Coal: Increasing Nitrogen with Maturity

Nitrogen concentration in coals was evaluated using the USGS COALQUAL dataset. Reported elemental concentrations were renormalized to an ash-free, dry basis. Weight percent carbon on a dry, ash-free (DAF) basis is used as a maturity index data following van Krevelen (1961). Average nitrogen concentration in coals (diamonds) and N/C molar ratio (blue lines) increase through diagenesis and early catagenesis (Figure 22; see also Boudou et al. 1984 and Burchill and Welch 1989). Coal nitrogen content drops precipitously during late catagenesis and metagenesis

The rapidly decreasing nitrogen content of high-rank coals is consistent with nitrogen gas generation at high thermal maturity. In contrast, increasing nitrogen with rank during diagenesis and early catagenesis is inconsistent with significant loss of nitrogen from coals. Increasing nitrogen concentration during diagenesis may be due to the loss of oxygen and carbon weight as CO<sub>2</sub>.

The average N/C of lignites and subbituminous coals are similar to those of wood and leaves (Figure 22). This indicates that there is not a significant nitrogen loss near the sediment floor in coal depositional

The low overall nitrogen concentration in vitrinitic kerogen, the similar nitrogen content of lignites, wood, and leaves, and the increasing nitrogen concentration during diagenesis are all consistent with coal as an ineffective source for early maturity nitrogen gases. However, detrital terrestrial material delivered to the ocean has higher nitrogen content than average plant material. Dispersed type III kerogen in marine sediments may have minor nitrogen generation potential.

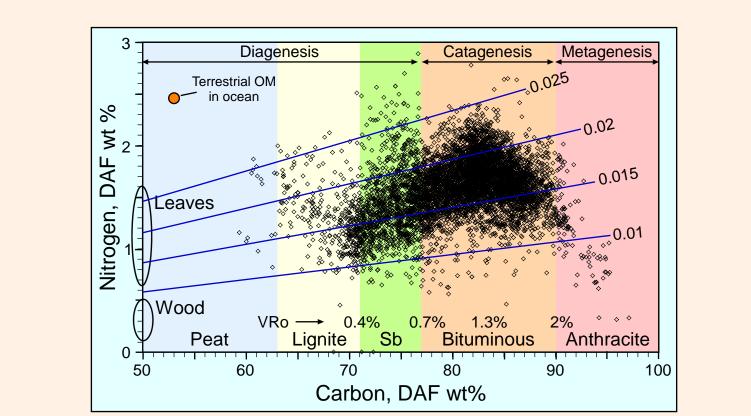


Figure 22. Nitrogen concentration in dry, ash-free (DAF) coals. Average nitrogen concentration increases through the diagenesis and early catagenesis stage. (0.4 to 1.3% VRo equivalent). Nitrogen decreases during late catagenesis and metagenesis. (1.3% to 5% VRo). Nitrogen concentrations of lignites are similar to those in living plants (leaves and wood). Increasing nitrogen in coal with increasing rank argues against substantial release of nitrogen from coally kerogen during the diagenesis and early catagenesis stages. Blue lines are molar N/C ratios. Data from USGS COALQUALdatabase. Average terrestrial organic matter delivered to ocean (orange circle) is from Pelet (1982).

## Dispersed Kerogen: Stable Nitrogen

Nitrogen in dispersed kerogen is indexed to total organic carbon (TOC) because total nitrogen in the sediment varies with TOC. The organic nitrogen in a sediment can be characterized by TOC and N/C ratio.

Series of kerogens extracted from different formations and basins are shown in Figure 23. Only kerogens from diagenetic and early catagenetic stages of evolution are plotted. At early stages of kerogen evolution, oxygen and O/C decrease with burial and maturation much more than hydrogen and H/C (Durand and Monin 1980; Figure 23A). Where N/C decreases with decreasing O/C, nitrogen is released from kerogen; stable or increasing N/C with decreasing O/C indicates little or no nitrogen release.

Molar N/C of dispersed kerogen ranges from about 0.008 to 0.05 (Durand and Monin 1980). The wide range of Kerogen N/C reported by Durand and Monin is caused by considering kerogen from different basins, formations, and thermal maturity. N/C is relatively constant within each kerogen group during late diagenesis and early catagenesis (Figure 23B). The only plotted kerogen showing decreasing nitrogen with maturity is the eastern North Atlantic Cretaceous kerogen, and its decrease is not very systematic (Figure 23B). Highest N/C are in algal-lacustrine kerogens (For example, Green River, Figure 23B). Most oil-prone marine kerogen N/C range from about 0.016 to 0.026, but the eastern North Atlantic Cretaceous shale is somewhat higher (Figure 23B). Gas-prone kerogen in marine sediment (Logbaba samples, Figure 23B) has higher N/C and greater scatter than most oil-prone kerogens and coals with similar H/C and O/C.

The N/C of marine organic matter drops significantly during early diagenesis prior to its conversion to kerogen. The greatest N/C decrease in deep-sea sediments is from plankton to seafloor organic matter derived from that plankton (upper red arrow, Figure 24). N/C decreases with increasing water depth and exposure time on the sea floor (Robinson et al. 2012). N/C in kerogen decreases further during the change from seafloor organic matter to keroger (lower red arrow, Figure 24). In the modern deep ocean, most of this change is relatively shallow, but decrease continues over kilometer below the surface (e.g., Simoneit and Mazurek, 1981 Once kerogen forms, the N/C of each marine kerogen group relatively stable during late diagenesis and early catagenesis.

Terrigenous organic matter delivered to the ocean has lowe initial N/C than planktonic organic matter, but less nitrogen is lost in the water column and on the sea floor (Figure 24). N/C seafloor organic matter derived from terrigenous material i slightly less than the source, and N/C of buried terrigenou kerogen in marine sediment is similar to that of seafloor terrigenous organic matter (Figure 24).

These changes indicate that the main time for nitrogen release from organic matter is early diagenesis prior to and during the formation of kerogen from organic matter. The main potentia nitrogen source is planktonic-derived ("marine") organic matter which shows the greatest overall nitrogen loss. Terrestrial organi matter in marine sediments has less early diagenetic nitrogen loss Once kerogen is formed, its nitrogen content appears relatively stable during late diagenesis and catagenesis

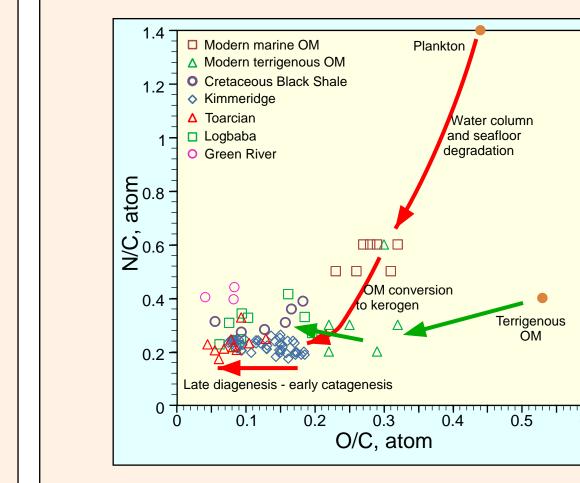


Figure 24. The N/C vs. O/C of the kerogen samples and their precursors shown on Figure 23. Marine organic matter shows significant loss of nitrogen and oxygen between the precursor plankton and the sea floor (upper red arrow). Nitrogen continues to decrease as the seafloor organic matter changes to kerogen during early diagenesis (middle red arrow). Once kerogen is formed, nitrogen concentration stabilizes, indicating little loss of nitrogen during late diagenesis and early catagenesis. Terrigenous kerogen in marine sediments has higher N/C than that of coals. Less nitrogen is lost in the water column and during conversion of sea-floor organic matter to kerogen (Green arrows). The N/C difference used by oceanographers to identify organic matter origin is lost during conversion of organic matter to kerogen.

#### Conclusion: Kerogen and Coal are Ineffective Late Diagenetic Nitrogen Sources The potential for releasing nitrogen directly from kerogen during late diagenesis and early catagenesis is low, because kerogen concentrations do not decrease and coal nitrogen concentration increases.

# Nitrogen in Sedimentary Rocks: Nitrogen Stored in Kerogen and Clay

#### Nitrogen Concentration Nitrogen weight percent is lognormally distributed with a mean 0.098 wt% N and a median near 0.075 wt % N (Figure 25A). Carbon is also lognormally distributed (Figure 25B). Highest nitrogen concentration measured was 1.54% in a coal sample. Nitrogen concentration appears to increase with clay content (Figure 26). Claystones have highest nitrogen concentrations, and nitrogen decreases through shale and siltstone to sandstone (Figure 26A). Limestones have higher nitrogen than dolomites, evaporites, a cherts; however, limestone nitrogen concentration (median o 0.02%) is much lower than nitrogen in shale (median of 0.095% Figure 26). Evaporites, even where mixed with shales and

#### Nitrogen/Carbon Ratio

mudrocks, have some of the lowest nitrogen concentrations.

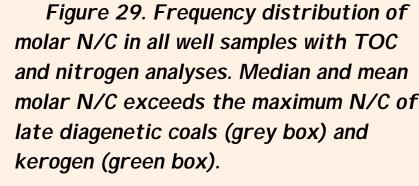
carbon (TOC; Figure 27). This correlation is only apparent in high samples lie in a narrow range near 0.05 (Figure 28). Molar N/C scatter increases as TOC decreases. There is little or no correlation between nitrogen and TOC for samples with less than 2 % TOC. Over 75% of Trask and Patnode (1942) samples have les

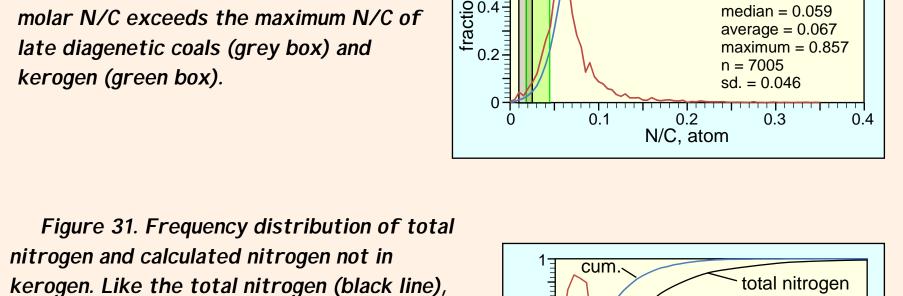
Molar N/C ratios greatly exceed those of kerogen and coa especially at low TOC (shaded rectangles, Figure 28, 29). Many samples have almost no organic carbon but have moderate nitroger concentration. The presence of nitrogen in samples lacking organic carbon and the elevated N/C of samples with organic carbon indicate nitrogen storage in some other material besides kerogen Mudrocks (shales, claystones) have higher N/C than limestones dolomites, and sandstones (Figure 30). Clay is therefore the most probable site for the excess nitrogen storage.

#### Non-Kerogen Nitrogen Storage

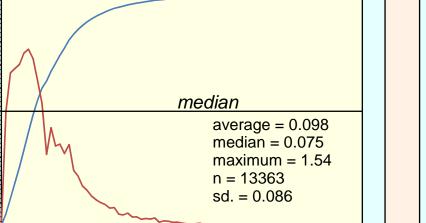
To better characterize nitrogen not stored in keroger nitrogen in kerogen was subtracted from the total nitrogen k multiplying the average kerogen weight N/C by TOC and subtracting from sample nitrogen. An average molar N/C kerogen of 0.025 was assumed. Nitrogen not in kerogen has a lognormal distribution, with an average near 0.057 wt % N and median near 0.044 wt % N (Figure 31). Nitrogen not in keroger comprises between half and two thirds of the total nitrogen o most samples (Figure 31).

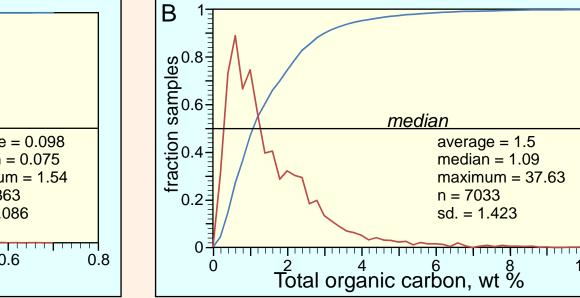
In shales, the concentration of nitrogen not in kerogen st correlates with TOC (Figure 32). In sandstone, the nitrogen not kerogen does not correlate to TOC and it has the same approximate average as that of shales with low TOC. Non-keroger nitrogen storage depends on two factors: a storage site (clay) and a potential source (nitrogen released from early diagenetic organic matter). Where both are present, non-kerogen nitrogen concentrations are high. Where clay is present without kerogen or where clay concentration is low, little non-kerogen nitrogen is stored in the rock.



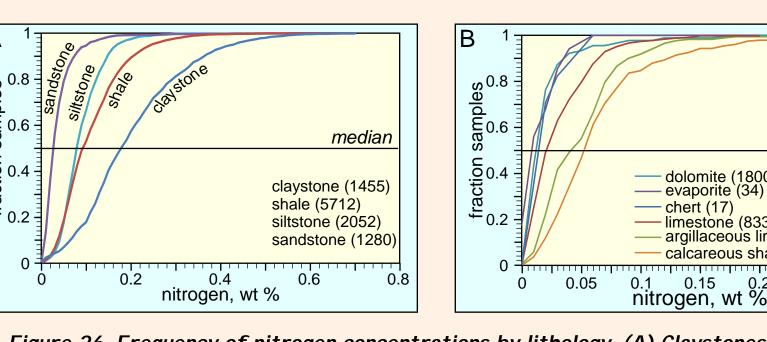


kerogen. Like the total nitrogen (black line) the cumulative distribution of nitrogen not in kerogen (blue line) forms a lognormal distribution. Spread of the non-kerogen incremental nitrogen concentration curve (red) is less than that of total nitrogen (Figure 25). The difference between the curves is the nitrogen in kerogen. On average, less than half of the total nitrogen is stored





analyses. Relatively high median TOC is due to selective analysis of samples with evidence for high organic carbon. Data from Trask and Patnode (1942).



aystone and siltstone samples are from California; shales and sandstones represent all areas and ages. (B) Carbonates and evaporites have lower nitrogen concentration than shales and om). Increasing nitrogen concentration from limestone to argillaceous limestone to calcareous hale demonstrates importance of clay for nitrogen storage. Numbers of analyses for each lithology is given in parentheses. Data from Trask and Patnode (1942).

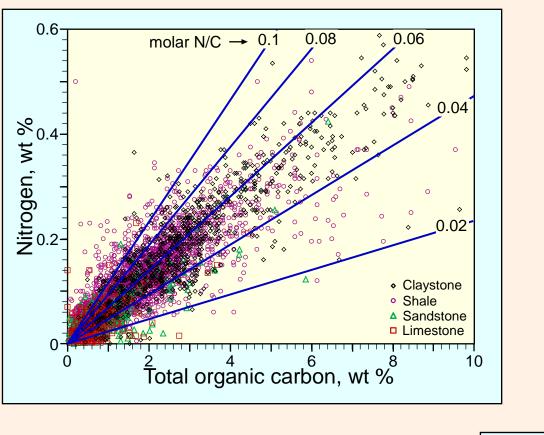
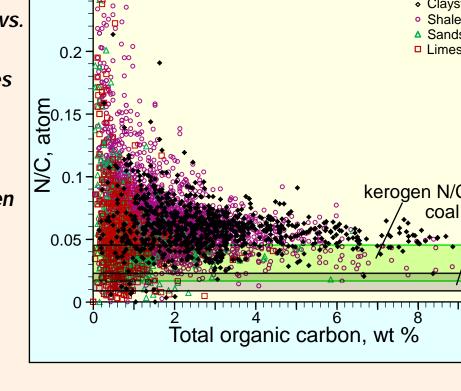
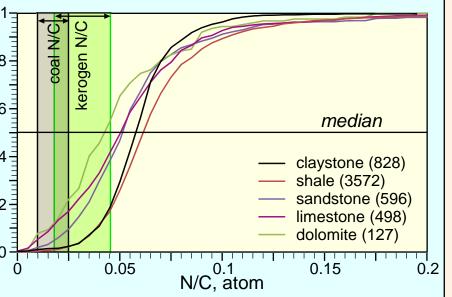


Figure 27. Nitrogen vs. TOC weight percent for selected lithologies. Data cloud shows correlation between nitroge and TOC. Most samples have molar N/ About 75% of the analyses have less the 2% TOC. Correlation of nitrogen to organic carbon is poor below 2% TOC. Data from Trask and Patnode (1942)

Figure 28. molar nitrogen to carbon ratio vs. DC weight percent for same lithologies and samples as in Figure 27. Shales and claystones show increasing scatter with decreasing TOC. N/C of late diagenetic coals and kerogen re the grey and green rectangles,



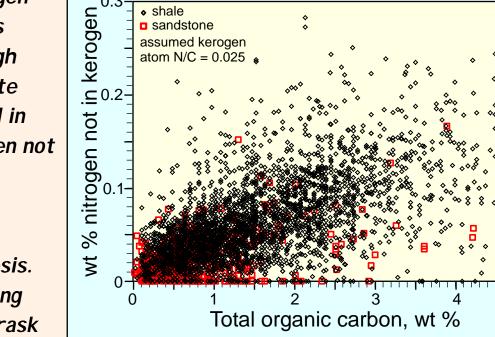


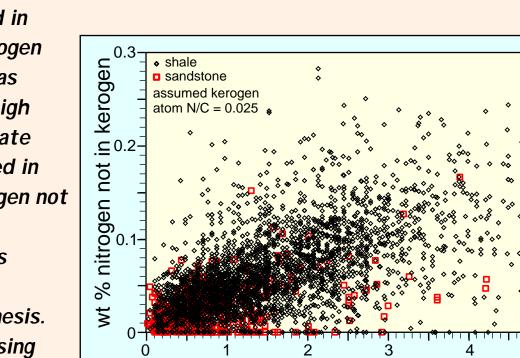
of molar N/C for different lithologie Only dolomite has median N/C in the range of kerogen. Shale and claystone have highest average and median N/ Number of analyses are given in parentheses. Data from Trask and

Figure 30. Frequency distribution

Figure 32. Nitrogen that is not stored in kerogen as a function of TOC. Shale nitrogen not in kerogen correlates to TOC, whereas sandstone nitrogen does not. Relatively high nitrogen concentrations at low TOC indicate that a lower fraction of nitrogen is stored in kerogen at low TOC. Correlation of nitrogen no in kerogen to TOC is probably caused by storage of nitrogen in clay minerals. Clays provide the storage and organic matter provides the nitrogen during early diagenesis Nitrogen not in kerogen was calculated using kerogen molar N/C of 0.025. Data from Trask

and Patnode (1942).





# Possible Origins for Low Thermal Maturity, High-Nitrogen Natural Gases

## Most Late Diagenetic Nitrogen Not in Kerogen is Ammonium in Clays

Ammonium starts to accumulate on clays near the sea floor. Most late diagenetic sediment stores nitrogen either in kerogen or as fixed ammonium in clay. Average ammonium in clay increases with thermal maturity.

In sediment near the sea floor, sorption of ammonium, amino acids, and other nitrogen-bearing organic compounds onto clays is responsible for elevated N/C in bulk sediment (e.g., Muller 1976). Ammonium is the ultimate breakdown product of nitrogen-bearing organic molecules (Baxby et al. 1994). Most ammonium in older sediments is fixed (i.e., non-exchangeable) into clays (e.g., Stevenson 1962).

Tagouchi et al. (1986) tracked nitrogen speciation in shallow-buried Cenozoic strata in Japan. Total nitrogen concentration increased with depth from about 500 ppm to 1200 ppm whereas nitrogen in kerogen remains low and relatively constant at 300 ppm due to low kerogen content. Source of increasing nitrogen is not clear and may be an early diagenetic soluble nitrogen-bearing species. Exchangeable ammonium decreases, and fixed ammonium increases with depth.

Williams et al. (1995) finds that fixed nitrogen comprises an average of 60% of the total nitrogen in Louisiana late diagenetic mudstones with TOC greater than 0.5%. The fraction of fixed nitrogen increases with decreasing nitrogen content. At the low TOC of their sediments, total nitrogen does not correlate to TOC. N/C ratios and nitrogen concentrations are in the same range as documented by the

Trask data. Total ammonium in the sediment strongly correlates with clay content. Nitrogen undergoes a significant storage change during catagenesis. Fixed nitrogen increases with the illite-smectite ratio (Williams and Ferrel 1991; Schroeder and McLain 2001). Illitization occurs near the temperatures of oil generation; therefore, any ammonium released during catagenesis was captured by illite as it transformed from smectite. Illite ammonium occurs as separate layers of tobelite (ammonium illite; Drits et al. 1997), which is quite stable. Apparently little of the fixed nitrogen is lost from well-ordered clays until late catagenesis and metagenesis (Everlien and Hoffmann 1991).

# Potential Late Diagenetic N<sub>2</sub> Sources

- The most likely late diagenetic to early catagenetic sedimentary source for nitrogen is ammonium in clays. When ammonium is released, it oxidizes to nitrogen (N<sub>2</sub>) by reaction with mineral oxidants such as hematite.
- Ammonium is most likely released from clays by exchange with other cations during exposure to subsurface brines. Ammonium in smectite is mostly exchangeable (Steffans and Sparks 1999). High-salinity brine can strip exchangeable ammonium from clays. Even the supposedly non-exchangeable fixed ammonium can be released from illite and vermiculite after longer exposure to hydrogen-, sodium-, and calcium-saturated cation exchange resins (e.g., Steffans and Sparks 1999). Continued release of ammonium is aided by ammonium decomposition to nitrogen in pore water.

Ammonium is not released from clays by increasing thermal maturity alone (see also Mingram et al. 2005). Both exchangeable and fixed ammonium increase with depth in the North Sea (Lindgreen 1994). The Trask dataset shows no systematic change in total nitrogen or nitrogen/carbon with increasing depth in any area. On the other hand, nitrogen concentration in evaporitic shales and mudstones is low compared to that of non-evaporitic shales with similar low TOC (Trask and Patnode 1942). This demonstrates that exposure to brines decreases rock nitrogen concentrations.

- Nitrogen source rocks are likely to be lean and dispersed rather than rich and concentrated as in oil source rocks. Nitrogen concentrations in sedimentary rocks are typically low (average less than 0.1%). Exposure to brine releases nitrogen from clays but not from kerogen. Only part of the nitrogen in clays is released by brine interaction. At least 4% of the ammonium is exchangeable in diagenetic and early catagenetic sediments (Lindgreen 1994). About a quarter of the nonexchangeable ammonium and essentially all of the recently fixed ammonium is released from illite upon longer exposure (Steffans and Sparks 1999).
- As a rough approximation, about 17% of the total nitrogen in typical clay-bearing sediment is likely to be released during exposure to brine. About 60% of the total nitrogen in claybearing sediment is ammonium nitrogen. Of that, about 30% of the ammonium nitrogen is released. Given a median nitrogen concentration of 0.1 wt % in shale, median nitrogen released from shale upon interaction with concentrated brines is expected to be about 0.017 wt % (170 ppm).

In a water-dominated system, the nitrogen concentration in the gas is controlled by its concentration in the water phase and the total pressure. The nitrogen concentration in pore water is controlled by the amount of nitrogen released from the rock, its grain density, and the rock porosity.

#### Gas Concentration vs. Water Concentration

The fugacity of nitrogen in the water and gas phase must be equal at equilibrium. The fugacity is approximately equal to the partial pressure, the mole fraction of nitrogen in the gas multiplied by the total gas pressure. The mole fraction of nitrogen in water can be related to fugacity by an extended Henry's law of

is the total pressure,  $f_{N2}$  is the mole fraction of nitrogen in the gas, and H<sub>a</sub> is the apparent Henry's constant for appropriate total pressure, pore-water salinity, and temperature. Henry's constants for nitrogen at subsurface conditions are quite large; therefore, the amount of nitrogen dissolved in water is quite small (Figure 33). Less than 100 wt. ppm dissolved nitrogen in pore water equilibrates with a 20 % nitrogen gas where porewater salinity is high. A pure nitrogen gas phase is in equilibrium with less that about 500 wt. ppm dissolved nitrogen in brines.

#### Porosity as a Concentration Multiplier

Prior to interaction with a gas phase, the nitrogen concentration in pore water is the sum of the small amount o atmospheric nitrogen (see Figure 1) plus the nitrogen released from the rock. Nitrogen concentration in the water is essentially the nitrogen released from the rock adjusted for the difference in rock and water volumes (porosity). The lower the porosity, the greater the volume of rock that releases nitrogen and the less the volume of water that receives the nitrogen. This increases the concentration of nitrogen in pore water over that released from

 $C_w$  is the weight nitrogen concentration in water,  $C_r$  is the weight nitrogen concentration released from the rock,  $\phi$  is fractional porosity, and  $\rho_{\alpha}$  and  $\rho_{w}$  are the grain and water

The porosity and density differences greatly enhance porewater nitrogen concentration relative to that released from the rock (Figure 34). For example, a rock with a grain density of 2.7 g/cc and 50% porosity that released 10 ppm nitrogen will charge the water with 27 ppm nitrogen weight concentration. At respectively. 10 percent porosity, the water concentration is 243 ppm, whereas at 1 % porosity, the water concentration is 2,673 ppm. Pore water in low porosity rocks are much more likely to have high nitrogen

# From Dissolved Nitrogen To Gas

Where x is the mole fraction of dissolved nitrogen in water, P

#### $C_w = C_r^*(1-\phi)/\phi^*\rho_q/\rho_w$

densities, respectively

Wt. ppm N in porewater @ 20% saturation

Figure 33. Nitrogen concentration in water

that is in equilibrium with a gas containing 20%

 $N_2$  as a function of pore-water salinity and

depth. Multiply by 5 to get concentrations in

equilibrium with 100% nitrogen gas. Model

assumes a normal pressure gradient, a surfac

temperature of 20°C, and thermal gradient of

50 100 150 200

Figure 34. Weight of nitrogen in water relative to weight nitrogen released from the rock as a function of porosity. Grain and water densities are assumed to be 2.7 and 1.0 g/cc,

0 10 20 30 40

porosity, %

#### Formation of High-Nitrogen Gases

#### Migrating Gas Extracts Nitrogen from Water

As gas migrates through water-saturated rock, it interacts with the water. Nitrogen dissolved in pore water will be partitioned into the gas phase so that fugacities are equal. In the absence of diffusion, gas will quickly deplete the nitrogen in the water so that only the gas that first interacted with the water will have elevated nitrogen concentrations (see Brown 2014). Most nitrogen will be concentrated near the leading edge of the migrating gas. Gas that later migrates on the same pathway will not have elevated nitrogen. Gas accumulations near the edges of petroleum systems are from the leading edge of the migration gas. These gases are more likely to have the elevated nitrogen concentrations.

Like other inert gases, nitrogen readily diffuses through water-saturated rock. Diffusive length is on the order of hundreds of meters over time periods on the order of millions of years. Diffusion equilibrates pore-water nitrogen concentrations. Gas migrating through carrier beds captures the dissolved nitrogen surrounding the carrier bed, because nitrogen fugacity nitrogen gas (Figure 35). However, given enough gas, the nitrogen in this larger volume of water will also be depleted.

Low amounts of nitrogen released from rocks must be compensated by large rock volumes to form significant nitrogen accumulations (Figure 36). This is typically not a problem Migrating gas interacts with a surprisingly large rock volume. For example, one TCF gas with 10% nitrogen (100 BCF N<sub>2</sub>) requires a source volume of 29 km<sup>3</sup> where rock releases 50 wt. ppm N (Figure 37). If source rock is 100 m thick, the nitrogen source rock covers an area of 290 km<sup>2</sup>, approximately the area of three standard US townships. Drainage areas for the large traps in Midcontinent settings easily accommodates such large nitrogen source volumes. The Panhandle-Hugoton field contains about 16 TCF nitrogen and requires a source volume of about 4000 km<sup>3</sup> of source rock that released 50 ppm N. If a 100 m thick source is assumed, the source area is 40,000 km<sup>2</sup>. This is only twice the five million acres of productive area in the Panhandle-Hugoton field reported by Pippin (1970).

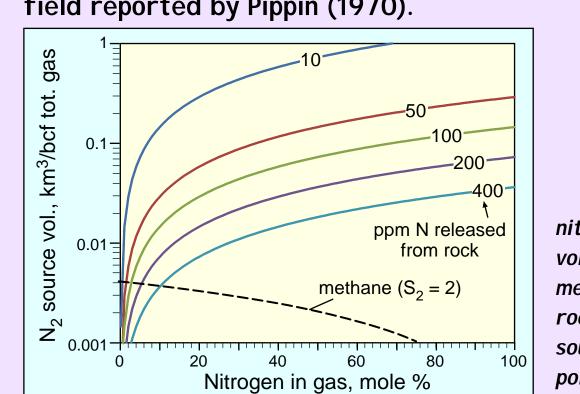


Figure 37. Nitrogen source volume (cubic kilometers/BCF total gas) as a function nitrogen content of the gas and nitrogen released from the rock. The nitrogen sourc volumes are much greater than those for methane with source potential of 2 mg methane/g rock and the same nitrogen concentration (dashed line). 2 mg methane/g rock is near the lower limit for a methane source rock. Volumes of richer methane source rocks would be considerably less than shown here. Nitrogen model assumes 10%

# Trapped Gas Extracts Nitrogen from Moving Groundwater

it from groundwater moving through the transition zone and below the gas-water contact (Figure 38). Most nitrogen is lost at the up-flow end of the accumulation, because nitrogen strongly partitions into the gas phase. The moving water must have nitrogen fugacity higher than that of the gas in the reservoir. An example is the Panhandle-Hugoton field.

Figure 39. The volume of water needed to dilute a BCF of of dissolved nitrogen concentration in the water.

Figure 35. Interaction of migrating gas with surrounding water. Shale (grey) with high nitrogen release and low porosity interbedded with sandstone (yellow) with low water, creating a concentration (fugacity) gradient for nitrogen diffusion towards the migrating gas. The migrating gas therefore "sees" a larger rock and water volume the

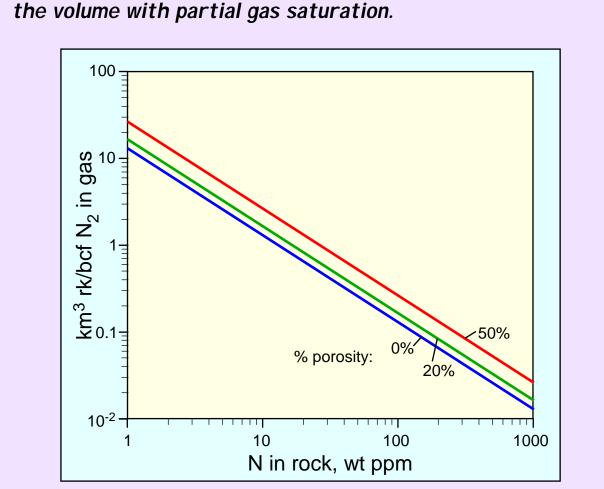


Figure 36. Volume of rock required to releas enough nitrogen to form one billion standard cubi feet of gas (28 million m<sup>3</sup>) as a function of amount o nitrogen released from the rock and porosity. A grain density of 2.7 g/cc is assumed.

porosity and 2.7 g/cc grain density.

A pre-existing low-nitrogen gas accumulation can acquire nitrogen by extracting

The amount of water needed to supply nitrogen depends on the concentration of nitrogen in the water and the amount of nitrogen needed. Figure 39 shows the water volume in cubic kilometers required to supply the nitrogen to a bcf of gas with a specified nitrogen content. Only about 0.035 km<sup>3</sup> water with 100 ppm dissolved nitrogen is needed to form a BCF of gas with 10% nitrogen. However, significant water volumes are needed to form large, high-nitrogen gas accumulations.

For example, the 16 TCF nitrogen in the Panhandle-Hugoton field requires about 4900 km<sup>3</sup> water with 100 ppm dissolved nitrogen (Figure 39). Using the average specific discharge estimated by Senger and Fogg (1987) of 5.4E-5m/d, the modern aguifer could supply the necessary water in about 7.7 million years, assuming that all nitrogen from water within 100 m below the gas goes into the gas. The relatively short time needed to deliver such massive amounts of water is due to the great length of the Panhandle-Hugoton field normal to regional water flow. Of course, actual dissolved nitrogen concentration in pore water is not known, so time estimates are speculative.

total gas to the specified nitrogen concentration as a function

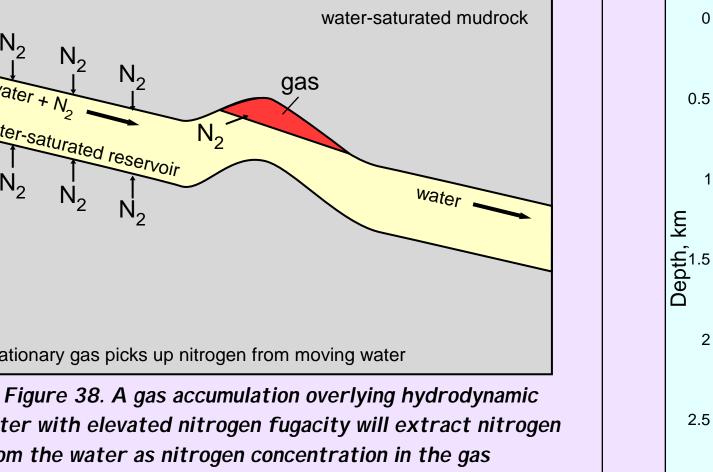
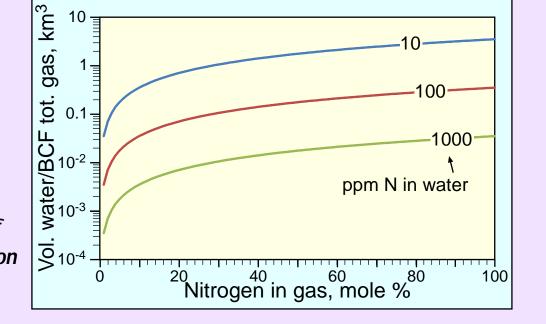


Figure 38. A gas accumulation overlying hydrodynamic water with elevated nitrogen fugacity will extract nitrogen from the water as nitrogen concentration in the gas increases. Nitrogen diffuses from surrounding mudrocks into the hydrodynamic aquifer.



# Exsolution of N<sub>2</sub> Gas from Groundwater

water-saturated mudroc

Nitrogen fugacity

Figure 40. Where pore water becomes supersaturated

different porosity and nitrogen release. Where shale

(grey) nitrogen release exceeds saturation, a nitrogen

sedimentary section only saturates a small fraction of

Even minor amounts of nitrogen generation in shallowburied rocks can saturate the pore water (Figure 33). A gas phase can form at saturation. Once the nitrogen gas phase forms, other sparingly soluble components such as helium and methane will partition from water into the gas. If gas can migrate, it may migrate to traps to form accumulations with predominantly nitrogen gas (Figure 40). However, gas must reach some minimum saturation before it can migrate. This is referred to as the critical gas saturation. Critical gas saturation is typically only a few percent of the pore

Normally, a gas phase would form in any available porosity once nitrogen reached saturation. Nitrogen solubility in nitrogen will be sourced from mudrocks. Nitrogen must water is so low that the volume of gas formed from diffuse to carrier beds. Sufficiently high gas saturation supersaturated pore water is likely to be less than the must form in the carrier bed for gas to migrate. Only critical saturation. With no migration, nitrogen migrating gas may form high-nitrogen gas accumulations. accumulations do not form even if pore waters are

The small pores in mudrocks restrict formation of a gas phase. Such small pores are filled with bound water. Gas must displace bound water to form. Because the water is bound, it is difficult for the gas to displace the water from the pores. Dissolved nitrogen therefore diffuses to nearby units with larger pores (carrier beds). Gas can exsolve more readily in larger pores with predominantly unbound water (Figure 41). Because gas phase forms in only a limited part of the section, the gas saturation in that part of the section will be higher.

This concept is illustrated with an example (Figure 42). A shale-dominated section has 10% thin sandstone beds. The shale has 5% porosity filled with bound water and generates either 10, 50, or 100 ppm nitrogen. The sandstone has higher porosity (20%) and low nitrogen generation. Water is assumed to be fresh. Average porewater nitrogen concentration is high due to low shale porosity (5%) and high fraction of shale. At shallow depths, even small amounts of released nitrogen will supersaturate the pore water (Figure 42A). With larger amounts of gas phase should form in the shale. However, the small released nitrogen, porewater is supersaturated at all pore size and large fraction of bound water prevents ga phase formation. Nitrogen diffuses towards beds with modeled depths. Because gas only forms in the thin larger pores (sandstone, yellow) where a gas phase can sandstone, gas saturation is relatively high within sandstone form (green). Because nitrogen released over a thick despite its higher porosity (Figure 42B). Gas saturations are high enough to exceed critical gas saturation at shallow and the gas can migrate. This mechanism can form an depth and at greater depth where nitrogen release is high. Gas will migrate where gas saturation exceeds critical saturation. Migrating gas can form high-nitrogen gas

# Gas saturation in ss, fractional $\square$ N<sub>2</sub> released

Figure 42. Model showing effects of interbedded lithology on saturation. (A). Average nitrogen concentration vs. depth for shale sections with 10 sandstone where shales releasing 10, 50, and 100 wt ppm from the rock. Black line is nitrogen concentration in nitrogen-saturated fresh water. Higher concentrations form gas. Sandstone has 20% porosity and releases 1 ppm N from the rock. Shale has 5% porosity and releases either 10, 50, or 100 ppm nitrogen from the rock. At shallow depth, even 10 ppm released from shale is sufficient to saturate pore water and form a gas phase. With greater nitrogen release, a gas phase can form at all depths. (B) Gas saturation in sandstone assuming that all nitrogen gas exsolves in sandstone beds. Because a thick section of shale contributes to the sandstone nitrogen, gas saturations are relatively high and likely to exceed critical gas saturation. Where gas saturation exceeds critical, it can migrate to form accumulations of nearly pure nitrogen.

#### Quick Summary

- An unrecognized, late diagenetic to early catagenetic source for nitrogen in gas must exist. Some high-nitrogen gas accumulations cannot be explained by currently accepted basement and late catagenetic source models. There is strong evidence for source from surrounding late diagenetic to early catagenetic sediments.
- The most likely source for nitrogen gas in late diagenetic and early catagenetic sediment is ammonium released by clay interaction with brine. Dissolved ammonium is oxidized to nitrogen gas. Only about 17% of the total nitrogen in argillaceous sediment is released during interaction with brine. Typical shale therefore releases about 170 ppm N, with a probable range from about 10 ppm to several hundred ppm.
- Low porosity concentrates the small amount of nitrogen released from rock into a small volume of porewater. The lower the porosity, the greater the porewater nitrogen
- Gas interacting with water will extract almost all nitrogen from the water. The higher the nitrogen concentration in water, the higher the nitrogen in gas in water-dominated
- The concentration of nitrogen in migrating gas is the balance between amounts of migrating hydrocarbons and nitrogen in water exposed to the migrating gas. Typically, the huge amounts of thermogenic methane swamp the nitrogen contributed from water.
- · Where moving water supplies nitrogen to a gas accumulation, final nitrogen concentration in gas depends on the water flow rate, nitrogen concentration in the water, and duration
- Very high nitrogen gases probably form by direct exsolution of a gas phase from water. Exsolution is most likely where argillaceous nitrogen sources with low porosity and high bound-water content are interbedded with potential carrier beds with large pores at relatively shallow depth.
- Nitrogen source-rock volumes must be large to offset the low nitrogen release from sediment. The required source rock volume is still less than the volume of rock with which migrating gas interacts during migration. Even the largest nitrogen accumulations can be explained by a relatively low volume of nitrogen source rock.

#### **Detailed Conclusions**

The setting and physical isolation of many high-nitrogen gas accumulations in the USA midcontinent area indicate that nitrogen associated with these accumulations was derived from thermally immature sedimentary rocks and not from basement or high-maturity sedimentary rock. Average nitrogen concentration in older sedimentary rocks is about 0.1 wt. %. Concentrations have a lognormal distribution with a median of 0.078 wt. % with 99% of samples less than 0.4 wt % nitrogen. Higher nitrogen content is correlated to organic carbon content and clay content, indicating two sites of storage: kerogen and clay.

Nitrogen in dispersed kerogen does not decrease and the nitrogen in coals increases with maturation during late diagenesis and early catagenesis. Therefore, kerogen and coals do not release significant quantities of nitrogen during late diagenesis or early catagenesis.

An estimated 60% of the non-kerogen nitrogen in late diagenetic, clay-rich sedimentary rocks is stored in clays, based on correlations to clay content in large datasets. Previous studies of smaller sample sets indicate that this nitrogen is stored as ammonium in clay. Average nitrogen concentration in clay-rich rocks increases with burial; therefore, nitrogen is not normally released by burial alone. Clay-rich rocks associated with evaporites have low nitrogen concentration. This indicates that buried clays release ammonium where clays interact with

Nitrogen typically remains in solution until it interacts with a gas phase. Based on previous lab studies, about 30% of the inorganic nitrogen is released upon interaction with brines. Typical argillaceous nitrogen source rocks therefore release on the order of 17% of the total nitrogen upon interaction with brine. This gives a median of 170 wt. ppm nitrogen released from shale with a range from about ten to a few hundred ppm. Late diagenetic - early catagenetic nitrogen sources are therefore dilute and dispersed.

The amount of nitrogen in a gas is controlled by the nitrogen concentration in pore water and by the amount of water. The nitrogen concentration in water depends upon the nitrogen released from the rock and the porosity. The lower the porosity, the greater the nitrogen pore-water concentration. For example, the weight concentration of nitrogen in pore water is about 50 times greater than that released from a rock with 5% porosity. In water-dominated systems, gas interacting with water develops a nitrogen concentration proportional to the dissolved nitrogen concentration. Where the system is dominated by hydrocarbon gases, almost all nitrogen is extracted from water and the final nitrogen concentration in gas is controlled by the amount of hydrocarbon gas and amount of dissolved nitrogen with which the hydrocarbon gas interacts. Nitrogen source volumes must be large to offset low nitrogen release; however, the rock volume encountered by migrating gas is typically much larger, especially during longdistance migration.

In low pressure systems, nitrogen concentration in pore water may reach saturation and form an almost pure nitrogen gas. Where shales are interbedded with carrier beds, nitrogen gas sourced in the shales exsolves in the larger pores in the carrier bed. Gas saturations become critical and the gas can migrate and form accumulations.

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