

Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations

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Abstract

Nitrogen (N₂) contents of natural gases in Rotliegend and Buntsandstein reservoirs of the North German basin regionally approach 100%. A review is given of the various hypotheses (primordial origin, volcanic or magmatic origin, radiogenic origin, atmospheric origin, organic origin, inorganic nitrogen in sedimentary rocks) presented to account for nitrogen anomalies in this area and other parts of the world. The objective of the present study was to investigate sedimentary organic matter, in particular coals, as a potential source of molecular nitrogen in the subsurface. Comparison of reservoir sizes and gas generation potentials indicates that Carboniferous coal measures, which are considered as the source of the natural gas in the North German basin, can readily account for the nitrogen quantities found in present-day reservoirs. Laboratory pyrolysis experiments were carried out to investigate the kinetics of generation of methane and molecular nitrogen from coals of different type and rank. Under experimental conditions nitrogen is formed at higher temperatures than methane supporting the concept of a 'fractional generation' of methane and nitrogen in natural systems. Based on the kinetic parameters derived from laboratory experiments methane and nitrogen generation rates from coals were calculated for geologic heating rates. Gas containing more than 50% nitrogen is generated under these conditions at temperatures in excess of 300°C. Nitrogen-rich gases are thus formed only in the final stage of gas generation after methane generation has practically ceased. It is concluded that the amounts of gas encountered in nitrogen-rich gas accumulations represent only a small fraction (possibly < 1%) of the total gas generation potential of this area while the bulk of the generated gas has escaped to the atmosphere. The present-day composition of the reservoir gases reflects the composition of only the most recently generated gas (on a geologic time scale).

1. Introduction

To the petroleum geologist the term 'natural gas' commonly implies methane with more or less significant admixtures of light hydrocarbons, carbon dioxide, hydrogen sulphide and traces of noble gases like He, Ne, Ar. In a substantial number of natural gas accumulations, however, methane constitutes only a minor percentage. In certain regions these 'anomalous' natu-

ral gases, e.g. with high CO₂, N₂ or H₂S contents, represent a serious exploration risk. These gases, though worthless from a commercial point of view, are probably a key to an improved understanding of the mechanisms of formation, longevity and compositional evolution of natural gas accumulations on the geologic time scale and therefore are valuable study objects for the geoscientist. This improved understanding is not merely a scientific challenge but will have economic consequences in the prediction of natural gas compositions and minimization of the exploration risk.

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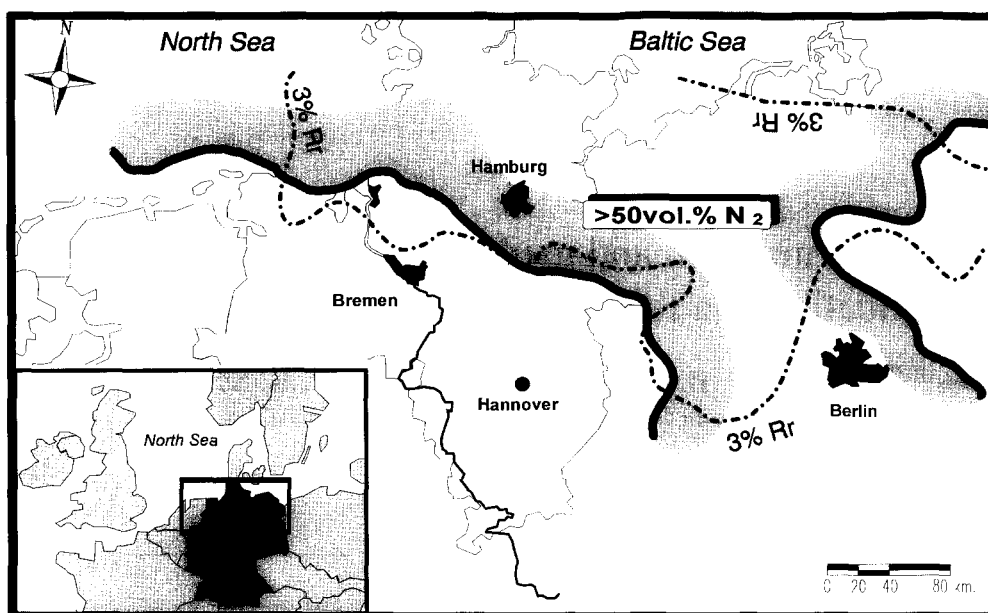


Fig. 1. North German sedimentary basin showing the regional extension of the 'Nitrogen Province'.

The North German sedimentary basin, Germany's major natural gas province (Fig. 1), is part of the North and Central European Permian basin system. It extends from the southern North Sea eastwards to the Polish border and continues into Poland. One specific feature of this area is the occurrence of nitrogen-rich natural gases in many reservoirs of the Permian Rotliegend and the Triassic Buntsandstein formations. Thus, all of the eleven gas test wells drilled in the German sector of the North Sea until 1970 produced natural gases which contained such a high proportion of nitrogen (50–90%) as to be uneconomic (Kent and Walmsley, 1970). The nitrogen problem is also encountered in onshore exploration activities in northern Germany, in particular in the East Hannover region. Gases from the Wustrow field contain more than 50% N_2 necessitating a work-up plant to reduce the nitrogen content before selling (Philipp and Reinicke, 1982). Many nitrogen-rich gas accumulations were also encountered on the territory of the former GDR (e.g. Altmark district). These were extensively studied by Müller (1980, 1981) and co-workers (Müller et al., 1973, 1976).

The regional extension of the 'nitrogen province' in northern Germany may be defined by the $>50\% N_2$ content iso-line as indicated in Fig. 1. It is interesting to note that this line roughly coincides with the 3% iso-

reflectance line of Upper Carboniferous coals also shown in this map. The iso-reflectance line is, however, only poorly documented because only a small number of exploration wells actually reached Carboniferous strata which are buried at depths in excess of 5000 m in the basin centre.

The traditional gas fairway across northern Germany extends from the giant gas accumulation of Groningen (The Netherlands) near the Dutch–German border in the west to east of Hannover. Increasing exploration efforts off this fairway into new areas carry a higher risk and prospects need to be examined and evaluated carefully. In this context the nitrogen problem plays an important economical role and improved methods for the prediction of gas composition and the reconstruction of the accumulation history are required.

The nitrogen problem touches upon yet another fundamental scientific aspect, namely the interdependence of the processes of gas generation, migration and accumulation in the subsurface and the dynamics of natural gas accumulations on a geologic time scale. It has been pointed out earlier (Leythaeuser et al., 1982) that natural gas accumulations are dynamic features controlled by the rates of supply and loss of gas. However, substantial controversy still exists concerning the amount of gas supplied in relation to reservoir capacities, the

dismigration rates through cap rocks and the lifetime of natural gas accumulations (cf. Krooss et al., 1992a, b).

The systematic investigation of 'gas anomalies', whether compositional or isotopic, will provide further insight into the sources and fluxes of natural gas in the subsurface and help to unravel the remaining mysteries.

2. World-wide occurrence of nitrogen-rich natural gases

Although the present study was triggered by a regional problem, the occurrence of nitrogen-rich natural gases constitutes a world-wide phenomenon. Thus, Beyer (1955) in one of the first comprehensive investigations on this subject reports gases with high nitrogen contents in Estonia, Sweden, Texas, Kansas and Colorado. Maksimow et al. (1973) present compositional data on natural gases of the Ural–Volga basin which show nitrogen contents between 85 and 100%. Jenden et al. (1988) studied nitrogen-rich gases and their potential origin in the Great Valley of California. Table 1 lists a selection of reservoir locations and gas compositions of nitrogen-rich gas accumulations reported in the literature.

3. Sources of molecular nitrogen in natural gases

Nitrogen in the subsurface of sedimentary basins can, in principle, either be primordial, i.e. derived immediately from the deep crust and mantle, or 'recycled' in the sense that it passed through the atmosphere and was re-incorporated into the lithosphere either directly, e.g. dissolved in meteoric water, or through the biosphere, i.e. via organic matter input into sedimentary layers. Fig. 2 gives a schematic overview of potential sources of molecular nitrogen in the subsurface proposed in the literature. A similar though more general scheme was published by Maksimow et al. (1973, 1975).

The main hypotheses for the origin of nitrogen-rich natural gas accumulations are briefly discussed in the following paragraphs.

3.1. Primordial nitrogen

According to current understanding accretion of the earth occurred about 4.5 billion years ago. The accretion phase was followed by an outgassing period of the mantle which resulted in the formation of a palaeo-atmosphere and proceeded almost completely (99%) within about 50 Ma (Allègre et al., 1987). It is difficult to estimate to which extent outgassing of nitrogen from the mantle is still going on and what are the present fluxes across oceanic and continental crust, respectively, but it can be assumed that the fluxes decreased continuously as a consequence of cooling of the outer mantle. Müller et al. (1973) quote the values for the quantities of nitrogen in the different geospheres given by Sokolov (1971) (Table 2). A slightly different value for atmospheric nitrogen ($4 \cdot 10^{21}$ g, corresponding to $4000 \cdot 10^{12}$ t) but a significantly lower value for crustal nitrogen ($1.7 \cdot 10^{21}$ g, corresponding to $1700 \cdot 10^{12}$ t) is given by Maksimow et al. (1973). The data in Table 2 show that the bulk of the earth's nitrogen resides in the mantle. The atmosphere, however, constitutes the reservoir with the highest nitrogen concentration of all geospheres.

A maximum value for the present-day N_2 flux from the mantle into the atmosphere can be estimated by assuming that outgassing did *not* proceed 'catastrophically' but continuously throughout the earth's history. Under these circumstances, in order to account for the total nitrogen in the present atmosphere ($5.27 \cdot 10^{21}$ g), a nitrogen (N_2) flux of 2.31 [$kg\ km^{-2}\ year^{-1}$] (approx. 2 [Std. $m^3\ km^{-2}\ year^{-1}$]) must have prevailed for 4.5 billion years. In terms of the model of Allègre et al. (1987) (99% of degassing within the first 50 Ma) the present-day N_2 flux should be lower by a factor of 100, corresponding to about 23 [$g\ km^{-2}\ year^{-1}$] (0.02 [Std. $l\ km^{-2}\ year^{-1}$]).

These estimated fluxes may be compared to the nitrogen content of an actual gas field. The Groningen gas field in The Netherlands with a closure area of $192\ km^2$ (Kent and Walmsley, 1970) and total gas reserves of $2690 \cdot 10^9$ Std. m^3 (Grunau, 1987) is Europe's largest gas accumulation. The reservoir gas consists mainly of methane with a nitrogen content around 15%. Taking the above estimate for the maximum primordial nitrogen flux and only vertical migration (drainage area = field area) a period of 1.08 billion years would be required to supply the total amount of nitrogen in

Table 1

World-wide occurrence of nitrogen-rich natural gases

Region	Location/Coordinates	Reservoir formation	N ₂ [vol. %]	Reference
Eastern Europe				
N Estonia		Lower Cambrian arcotic sandstone	98.5–99.5	Beyer (1954/55)
Tujmasa		metamorphic basement	> 80	Müller et al. (1973)
Tataria	Russian Shield	Middle Carboniferous	90–99	id.
Volga–Ural basin		Permo–Carboniferous	30–40	id.
Volga–Ural basin		P ₂	89.54	Maksimow et al. (1973)
		P ₂	95.43	id.
		C ₂	99.4	id.
		C ₂	99.1	id.
		P ₁ ^{ka}	98.52	id.
		P ₂	99.59	id.
		P ₁	98.8	id.
		C ₂	97.5	id.
		P ₁	99.9	id.
		C ₃	100	id.
		C ₂	99.9	id.
		P ₁ ^a	85.0	id.
		P ₁	91.5	id.
		P ₁ ^a	98.9	id.
		C ₁ ^{ok}	99.7	id.
Sweden				
	Dannemora	Precambrian	19.7–66.4	Beyer (1954/55)
	Ammeberg		44.8	id.
	Boliden		22.9–36.6	id.
USA				
Colorado	Model Dome		79.71	id.
Kansas	Augusta–Feld	Upper Carboniferous	85.56	id.
Texas	Westbrook	Permian	95.6	id.
Utah	Woodside	Permian	62.33	id.
Washington			98.5	id.
California	Great Valley	Cretaceous	up to 87	Jenden et al. (1988)
Germany				
East Hannover			20–90	Philipp and Reinicke (1982)
North Sea		Rotliegendes	50	Kent and Walmsley (1970)
		Rotliegendes	60	id.
		Rotliegendes	95	id.
		Rotliegendes	50	id.
Alpine Molasse	Pfullendorf	Stubenssandstone	19.5	Wollanke (1983)

the present reservoir. In order to account for this gas quantity within the estimated time since cap rock deposition (200 Ma B.P.) the drainage area must be taken as 5.4 times the closure area. With the much lower nitrogen flux rate derived from the model of Allègre et al. (1987) the time for accumulation of primordial nitrogen in the quantity encountered in the Groningen field takes the tremendous value of $108 \cdot 10^6$ yr or, alternatively, a drainage area of 103,500 km² (a square of 322 by 322 km) has to be assumed. Even though gas migration distances are considered to be potentially

large, i.e. in the range of tens to hundreds of kilometres, a drainage area of this size is totally unrealistic, especially when taking into account numerous smaller gas reservoirs with often considerable N₂ contents located in this 'drainage area'.

This estimate shows that the primordial nitrogen contribution to nitrogen-rich natural gas accumulations is probably marginal. Evidently, outgassing of primordial nitrogen cannot be expected to occur uniformly over the entire surface of the earth. It will be largely confined to zones of seismic and volcanic activity. Vol-

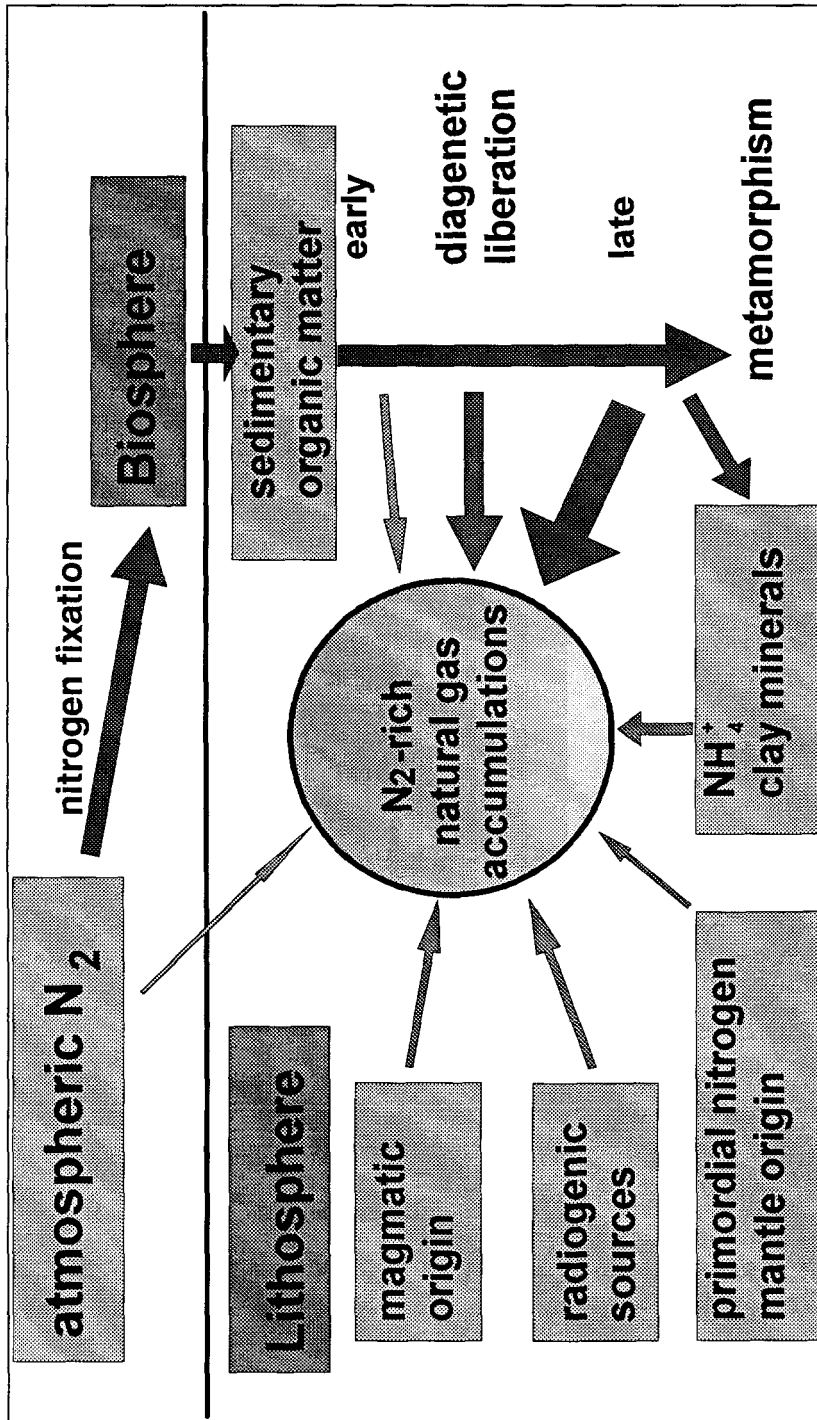


Fig. 2. Sources of molecular nitrogen in natural gases.

Table 2

Nitrogen quantities in the geospheres (Sokolov, 1971, quoted by Müller et al., 1973)

Geospheres	Total amount of nitrogen in 10^{12} t
Atmosphere	5270
Hydrosphere	16
Sediments	214
Granitic and basaltic crust	7800
Upper mantle	435,000

Table 3

Nitrogen contents of crustal rocks

Rock type	N-content (g/t) = (ppm)	Reference
Magmatic rocks	5–50	Maksimow et al. (1973)
Metamorphic rocks	18–390	Maksimow et al. (1973)
Phyllites	245–650	Haendel et al. (1986)
Mica schists	95–502	Haendel et al. (1986)
Gneisses	35–180	Haendel et al. (1986)
Orthogneisses:	18–23	Maksimow et al. (1973)
Paragneisses:	47–48	Maksimow et al. (1973)
Sedimentary rocks	170–1200	Maksimow et al. (1973)
Shales	580	Maksimow et al. (1973)
Graywackes	136	Maksimow et al. (1973)
Limestones and dolomites	70	Maksimow et al. (1973)

canism occurred in the North German basin during Permian time but has ceased during the Autunian period (260–285 Ma B.P.). Magmatic intrusions like the Vlotho and Bramsche massifs which were emplaced during Cretaceous time (Santonian–Campanian) may be taken as an indication for deep crust or mantle gas sources. On the other hand these intrusions may just have provided the heat for the liberation of nitrogen from sedimentary organic matter (see below).

High nitrogen and helium contents in natural gases have been taken as indicators for an origin from deep sources, i.e. sources below the sedimentary layer. Gold and Held (1987) infer an origin of helium, methane

and nitrogen from 'sources deeper than the basement' for Kansas and Texas natural gases, based on observed He/N₂ ratios.

Parallel trends in helium and nitrogen content of natural gases in the East Hannover region (Germany) have also been interpreted as an indication for a common deep origin of these two components (cf. Philipp and Reinicke, 1982). Although such correlations undoubtedly occur in certain regions, Beyer (1955) quotes examples where this is not the case and concludes that there does not appear to exist any global relationship between these two components in natural gases. It should also be kept in mind that natural gas compositions may be related merely indirectly, reflecting a common cause rather than a common source. Thus, it is conceivable that, as a result of a thermal anomaly, the liberation temperature of He from minerals may be reached in a certain formation while in a different formation the increased temperature level may result in the onset of nitrogen generation from sedimentary organic matter.

Mantle-derived gases are characterized by ³He/⁴He ratios greater than in air, which occur predominantly in volcanically and tectonically active regions, while geotectonically stable continental regions contain ratios less than in air. Sano et al. (1993) use this relationship in an investigation of hydrogen–nitrogen gases in northern Oman and infer an organic origin for the N₂-rich gases in this region with only a marginal contribution of magmatic N₂.

The contribution of primordial nitrogen to natural gases in sedimentary basins is associated with many open questions and remains to be studied in detail. In view of the organic nitrogen potential in sedimentary basins it is, according to our present understanding, not necessary to postulate a substantial influx of primordial nitrogen to explain the gas compositions encountered in nitrogen-rich gas accumulations.

3.2. Volcanic or magmatic origin

Igneous rocks represent the largest reservoir of crustal nitrogen ($7.8 \cdot 10^{21}$ g according to Sokolov, 1971, cf. Table 2; $14 \cdot 10^{21}$ g according to Blackburn, 1983). The nitrogen quantities in igneous rocks thus exceed the amount of nitrogen in the atmosphere. Nitrogen concentrations in magmatites, on the other hand, are among the lowest encountered in crustal rocks

Table 4
Nitrogen contents of volcanic fumarole gases (Beyer, 1955)

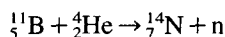
Location	Nitrogen (vol.%)
Kilauea, Hawaii	26.04 0.87–37.84 63.3%
Aetna fumaroles	79.07%
Mt. Pelée, Martinique	54.94%
Hekla crater, Iceland	81.81%

(Table 3). Presumably this residual nitrogen can be mobilized only under extreme temperature conditions, prevailing e.g. during active volcanism or igneous intrusions, whereas otherwise it will be trapped permanently in these rocks.

Volcanic exhalations are reported to contain considerable quantities of molecular nitrogen (locally >70%). Beyer (1955) quotes nitrogen contents of volcanic fumarole gases from different parts of the world (Table 4). The multiple analyses of the Kilauea gas show a high variability and suggest that, due to the inherent risk of contaminations or admixtures of atmospheric nitrogen, data on the nitrogen content of volcanic gases have to be considered with great caution. The sporadic nature of volcanic activity on a human as well as a geologic time scale renders estimates on the contribution of this process to the formation of nitrogen-rich gas accumulations practically impossible.

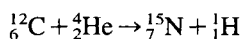
3.3. Radiogenic origin

Nitrogen can be produced by two nuclear reactions. The exoenergetic reaction of boron (${}^{11}\text{B}$) with α -particles (helium nuclei) yields the ${}^{14}\text{N}$ isotope and a neutron (n) according to:



$$\Delta E = +0.1579 \text{ MeV (exoenergetic)}$$

(Coulomb potential threshold: 2.63 MeV) whereas the ${}^{15}\text{N}$ isotope results from the endoenergetic reaction of ${}^{12}\text{C}$ with α -particles:



$$\Delta E = -4.9656 \text{ MeV}$$

(Coulomb potential threshold: 3.10 MeV)

The principal natural sources of α -particles in the earth's crust are the ${}^{232}\text{Th}$, ${}^{235}\text{U}$, and ${}^{238}\text{U}$ decay series.

Based on the present-day average concentrations of these isotopes (15, 0.03, and 4 g/t, respectively) in the earth's crust and their half-life, the amount of α -particles emitted per ton of crustal rocks since the accretion of the earth can be calculated. Taking into account the α -decays of various daughter nuclides, this yields a value of $2.37 \cdot 10^{23}$ α -decays per ton of crustal rock. The average concentrations of boron (10 g/t = $5.47 \cdot 10^{23}$ atoms/t) and carbon (870 g/t = $4.37 \cdot 10^{25}$ atoms/t) are significantly higher than the number of α -decays, so that even under the highly improbable assumption of successful reaction of each α -particle the amount of nitrogen resulting from either of these nuclear reactions is not limited by the quantities of boron or carbon but by the number of α -particles. The above assumption can be used to determine an upper limit for the amount of ${}^{14}\text{N}_2$ produced by nuclear reactions. This value is 5.52 g ${}^{14}\text{N}_2$ /t (5.52 ppm). The corresponding calculation for ${}^{15}\text{N}_2$ which takes into account only those decays producing α -particles with energies above 5 MeV, yields a value of 4.54 g ${}^{15}\text{N}_2$ /t (4.54 ppm). These values are significantly lower than the average nitrogen concentrations in crustal rocks given in Table 3. In view of the highly unrealistic assumptions with respect to the probability of the nuclear reactions it must be concluded that the nitrogen quantities generated by these mechanisms are actually lower by several orders of magnitude. Consequently, the radiogenic formation of nitrogen is considered to be of very subordinate importance in the subsurface. This result is in line with the supposition of Beyer (1955) who states that it is *not* conceivable that the masses of nitrogen found in some natural gas accumulations can be accounted for by radioactive reactions involving α -particles.

3.4. Atmospheric origin

Entrapment of atmospheric or 'fossil' atmospheric nitrogen has been proposed in several instances as an explanation for the occurrence of nitrogen-rich reservoirs (cf. Eichmann, 1969; Marty et al., 1988). One mechanism envisaged for the process of accumulation is the transport in meteoric water with subsequent exsolution at elevated temperatures. Aqueous solubility ($0.38\text{--}0.82 \cdot 10^{-3}$ mol/l, at 0–25°C) is the limiting factor for the quantities of nitrogen that can be transported by this mechanism. Marty et al. (1988) suggest

that transport of air microbubbles, which is much more effective, can account for most of the nitrogen found in the Dogger limestone reservoir of the Paris Basin. Entrapment of large quantities of atmospheric nitrogen is, however, difficult to envisage for sediments deposited in subaqueous environments.

The most compelling evidence against a direct atmospheric origin of nitrogen-rich natural gas accumulations is the very high nitrogen/argon ratio of most nitrogen-rich natural gases as compared to the atmospheric nitrogen/argon ratio (Philipp and Reinicke, 1982). Based on this argument, Beyer (1955) rules out an atmospheric origin for nitrogen-rich gases in Estonia. High N_2/Ar ratios (100 times the atmospheric ratio) were also observed by Wollanke (1983) in gas reservoirs of the northern foreland of the German Alps. Jenden et al. (1988) found nitrogen/argon ratios as high as 22,000 in natural gases from the California Great Valley as compared to $N_2/Ar \sim 40\text{--}80$ for atmospheric gas.

3.5. Organic origin

The only process of incorporation of significant amounts of atmospheric nitrogen into sediments is via the biosphere. Atmospheric nitrogen (N_2) is taken up by certain micro-organisms, especially bacteria and algae, which convert it to organic nitrogen compounds (biological fixation). The most prominent example is the *Rhizobium* bacterium which lives in symbiosis with plants of the Leguminosae family. Other nitrogen-assimilating organisms are the aerobic soil bacteria *Azotobacter*, facultatively aerobic *Klebsiella*, *Achromobacter*, *Clostridia* and all photosynthetic bacteria and blue-green algae (Lehninger, 1977; Blackburn, 1983). Proteins and nucleic acids are the main nitrogen-containing components of plants and animals. According to Maksimow et al. (1973) the nitrogen content of human tissue is 3.0%. In zoobenthos it is 10.3%, in zooplankton 11.7% and in wood 2%.

On degradation of organic matter in the soil or sediment the nitrogen-containing molecular units are transformed into simple inorganic nitrogen compounds (biological mineralization) such as urea, nitrate, and ammonium which are immediately biologically recycled. Only a minor fraction of the nitrogen from the biosphere is preserved in the sedimentary column as a constituent of the organic matter. The fate and diagenetic

pathways of organic nitrogen in the lithosphere are still poorly understood. A comprehensive overview of the present state of knowledge on nitrogen inclusion, transformation and functionality in sedimentary organic matter with focus on petroleum-forming systems is given by Baxby et al. (1994).

Within the lithosphere sedimentary rocks have the highest nitrogen contents of all rock types (Table 3). This reflects the fact that most sedimentary rocks contain at least to some extent organic matter. Metamorphic rocks like phyllites and paragneisses which are derived from organic matter-containing sediments also exhibit appreciable concentrations of nitrogen.

According to Huck and Karweil (1955) coals, the organic matter of primary interest in the present study, contain nitrogen in the range of 0.4 and 2.4%. Our own data for various coals show that values in excess of 3% occur. Coal measures of the Carboniferous Westphalian formation are considered as the main source of natural gas in the North German basin. Due to their relatively high nitrogen content as compared to other sedimentary matter, their role in the formation of nitrogen-rich gas accumulations is being investigated in this study in the first instance.

3.6. Inorganic nitrogen in sedimentary rocks

Nitrogen in sediments is overwhelmingly derived from organic matter. Significant amounts of this organic nitrogen can, apparently, be taken up by clay minerals during sedimentary diagenesis. This portion of inorganic nitrogen is commonly termed 'fixed nitrogen'. It is well known that NH_4^+ ions replace K^+ in mixed-layer clays. Thus, Cooper and Evans (1983) report that between 41 and 84% of the nitrogen in oil shale from the Green River Formation is present as ammonium fixed within silicate minerals. They propose that the nitrogen occurring as fixed NH_4^+ -N is derived from organic matter during early diagenesis under highly anoxic conditions. Scholten (1991) finds that during maturation of organic-rich shales ($R_m = 0.6\text{--}0.9$) the fixed nitrogen content (i.e. nitrogen preserved as fixed ammonium in the clay mineral lattice) increases to up to 50% of the total nitrogen content. Oh et al. (1988) report that during pyrolysis of oil shale most nitrogen is released in the generated oil and some as NH_3 . A large fraction of the NH_3 evolving from Green River shales above oil-production temper-

atures is attributed to an inorganic nitrogen source. Work performed by Whelan et al. (1988) suggests a fundamental difference in the evolution of nitrogen from organic-rich shales and coal. Clay minerals in shales can accommodate nitrogen ($\text{NH}_4^+\text{-N}$) and preserve it up to elevated maturity levels. These ammonium ions are thought to be the source of the NH_3 observed during thermogravimetry–Fourier-transform–IR spectroscopy (TG-FTIR) of marine sediments. Pyrolysis experiments performed by Everlien (1990) on ammonium clay minerals yield almost exclusively NH_3 and thus lend support to this assumption. In contrast, ammonia is not observed as a pyrolysis product of coals (Whelan et al., 1988). The clay mineral content of coals is usually low so that the diagenetical pathway of nitrogen into ammonium clays is excluded and practically all nitrogen resides in the organic matter.

The importance and the mechanisms of contribution of fixed nitrogen to the molecular nitrogen in the subsurface is not quite clear. Lutz et al. (1975) state that 'apart from coal and dispersed coaly matter, nitrogen also appears to be generated from nitrogen compounds and inclusions in clayey rocks during late diagenesis and early metamorphism'. Everlien (1990) conducted non-isothermal pyrolysis experiments with various ammonium clays and investigated the kinetics of the release of ammonia and N_2 from these compounds. These experiments had to be performed with artificial ammonium clays because ammonia yields of natural samples were too low to be detected. At heating rates of $2.5^\circ\text{C}/\text{min}$ ammonium montmorillonites released ammonia in the range of $350\text{--}650^\circ\text{C}$ with a maximum generation rate at about 500°C , while N_2 evolution occurred only to a limited extent between 700 and 1000°C . Ammonium illites produced ammonia at the same temperatures as montmorillonites but in much lower amounts (10%). No molecular nitrogen was formed at any temperature. Ammonium vermiculites produced gas at higher temperatures than ammonium smectites and illites with nitrogen instead of ammonia as the main pyrolysis product. None of the ammonia clays yielded nitrogen at temperatures in excess of 1000°C . Oh et al. (1993) studied the thermal decomposition of buddingtonite, an ammonium-bearing feldspar, and found that ammonia evolves at temperatures between 400 and 900°C . H_2 and N_2 were evolved dur-

ing these experiments at temperatures above 500°C as a consequence of NH_4 decomposition.

Applying the experimental results to geologic heating rates in northern Germany, Everlien and Hoffmann (1991) conclude that nitrogen formation from smectites and illites would occur at a depth of about 5000 m corresponding to burial depths of mostly Carboniferous strata. Gas release from ammonium vermiculites is envisaged to occur at burial depths of $10,000$ m.

Practically no information is available on the absolute amounts of naturally occurring ammonium clays in the North German sedimentary basin so that estimates on their contribution to the natural gases in this area cannot be made. Natural ammonium clays without associated organic matter appear to be rather exceptional and, in view of the large amounts of organic matter in the Carboniferous of this region are probably not an important nitrogen source on their own. The interaction between clay minerals and organic matter may influence the kinetics of nitrogen release and therefore deserves particular attention in future studies.

4. Quantities of methane and nitrogen generated from coal

Upon burial and increasing temperature sedimentary organic matter is known to generate hydrocarbon liquids and gases which eventually accumulate in reservoir structures. Type III kerogen and coals are the main producers of natural gas and are therefore of primary interest in the present context.

The assessment of the gas generation potential of coals and related organic matter is one of the fundamental problems in the investigation of the dynamics of natural gas accumulations. This problem is discussed, for instance, by Jüntgen and Karweil (1966). The amounts of hydrocarbons, in particular methane, and other components from coal during thermal maturation can be estimated in two different ways: (1) pyrolysis experiments (e.g. Hanbaba, 1967; Higgs, 1986); (2) mass balance calculations based on the elemental composition of coals at different maturity levels (e.g. Jüntgen and Karweil, 1966; Kröger and Hörtig, 1966).

Table 5
Methane yields (V0) from Carboniferous coals (Ruhr) of different rank in open-system non-isothermal pyrolysis experiments (Hanbaba, 1967)

Coal seam:	Fürst Leopold		
Cwaf	83.0%		
Ash	2.0%		
	Heating rate [K/min]		
	2.50E-03	2.60E-02	0.88
V0 [cm ³ /g (coal)]	59.4	58.9	55.8
V0 [cm ³ /g (C)]	73.0	72.4	68.6
Coal seam:	Gustav		
Cwaf	88.0%		
Ash	9.0%		
	Heating rate [K/min]		
	2.50E-03	2.60E-02	0.88
V0 [cm ³ /g (coal)]	66.6	67.5	63.4
V0 [cm ³ /g (C)]	83.2	84.3	79.2
Coal seam:	Dickebank		
Cwaf	90.0%		
ash	9.0%		
	Heating rate [K/min]		
	2.50E-03	2.60E-02	0.88
V0 [cm ³ /g (coal)]	61.5	62.1	60.9
V0 [cm ³ /g (C)]	75.1	75.8	74.4
Coal seam:	Heinrich		
Cwaf	91.0%		
Ash	5.9%		
	Heating rate [K/min]		
	2.50E-03	2.60E-02	0.88
V0 [cm ³ /g (coal)]	41.0	40.5	37.8
V0 [cm ³ /g (C)]	47.9	47.3	44.1

4.1. Pyrolysis experiments

Hanbaba (1967) performed open system non-isothermal pyrolysis experiments to assess the generation kinetics of light hydrocarbons (C1–C4) from coals at low heating rates ($2.5 \cdot 10^{-2}$ – $0.88^\circ\text{C}/\text{min}$). The methane yields from coals of different ranks (83–91% C) ranged between 38 and 68 cm³/g coal (44 and 84 cm³/g C_{org}) (Table 5). Pyrolysis experiments performed in our laboratory with different coals yielded between

22 and 57 cm³ methane per g C_{org} (Table 6). The highest yields were obtained for a humic coal ($R_r = 0.76\%$) and the lowest values for an anthracite ($R_r = 2.30\%$), reflecting the decrease in the generation potential with increasing maturity of the coal. Open-system methane yields are probably not representative for the gas generation potential of coals because they produce significant amounts of molecular hydrogen. During open-system non-isothermal pyrolysis of type II source rocks (Lias ϵ , Hils Syncline, northern Germany) performed by Lillack (1992), molecular hydrogen (H₂) was the most prominent pyrolysis gas with the major portion generated at temperatures above 550°C. Conversion of the H₂ quantities into methane equivalents increased the methane generation potential by a factor of 3–5.

Higgs (1986) used closed-vessel pyrolysis at temperatures between 200 and 450°C to determine the gas generation potential of Palaeozoic and Tertiary coals in the maturity intervals from 0.3–2.9% R_r and 0.4–3% R_r , respectively. For Palaeozoic coals from the U.S. a cumulative gas yield, expressed in methane equivalents, of 170 cm³/g organic carbon was obtained, while the Tertiary coals from Germany yielded 225 cm³/g organic carbon.

In the closed-vessel experiments of Higgs (1986) formation of molecular hydrogen was reportedly negligible.

4.2. Mass balance approach

Mass balance calculations based on the elemental composition of coals assume a limited number of products which represent only part of the vast scope of hydrocarbon and non-hydrocarbon compounds that can be generated from coals. These main products are usually CH₄, CO₂, and water. Other compounds, like H₂S or N₂, are generated in minor amounts. Their quantitative assessment is difficult due to the small absolute concentrations of the S and N and compositional inhomogeneities of the coals.

In order to take into account higher molecular weight hydrocarbons, a bulk composition of the generated hydrocarbons (CH_n) can be assumed where n may take values less than 4.

The major problem associated with mass balance calculations on coals is that the composition of the

Table 6

Quantities of methane and nitrogen generated during non-isothermal pyrolysis experiments up to 1000°C (heating rate 0.1 K/min)

Sample	Humic coal		Sapropelic coal		Anthracite		Torbanite	
% R _r	0.76		0.79		2.30		0.48	
Gas	kg/t TOC	Std. m ³ /t TOC	kg/t TOC	Std. m ³ /t TOC	kg/t TOC	Std. m ³ /t TOC	kg/t TOC	Std. m ³ /t TOC
CH ₄	38.04	56.21	32.73	48.37	14.4	21.28	21.6	31.92
N ₂	14.85	12.54	8.54	7.21	4.91	4.15	4.88	4.12

1 Std. m³/t = 1 cm³/g.

overall products is not known and that an essentially infinite number of products can be formed.

Jüntgen and Karweil (1966) performed mass balance calculations for various German coals and compared their results with those obtained by earlier workers. For the maturity range from 40 to 5% vol. mat. (0.75% R_r, high vol. bituminous coal 3.2% R_r, anthracite) the calculated cumulative yields of methane are in the range of 200 l/kg coal (200 Std. m³/t coal). Depending on the initial ash content of the coals this corresponds to about 250 Std. m³/t C_{org}.

Kröger and Hortig (1966) suggest a graphical procedure to determine the gas generation potential of Carboniferous coals on the basis of three main components (termed wax/resin, oxyhumins, and dehydrohumins complexes). For a typical vitrinite they obtain a cumulative methane yield of 193 kg CH₄/t coal (285 Std. m³/t coal; ≈ 335 Std. m³/t C_{org}) in the maturity interval 36–5% volatile matter (85–97% C).

Mass balance calculations for coals require certain assumptions concerning the product composition. This information may be inferred from calorimetric data obtained, for instance, by differential thermal analysis (DTA) (Jüntgen and Karweil, 1966) or spectroscopic data (Kröger and Hortig, 1966).

In order to assess an *upper limit* for methane and nitrogen generation potentials from coals we performed mass balance calculations using literature data on the elemental composition of coals of different maturity sequences. This upper limit was calculated without any additional assumptions on the product composition and consequently can be reached only theoretically. The scheme we used can be readily modified to take into account products other than CH₄, and the boundary conditions can be changed to produce predetermined quantities of CO₂ and H₂O in individual maturity inter-

vals. Then, however, the number of potential scenarios becomes infinite and comparison of the results is almost impossible.

Formation of water reduces the generation potential of hydrocarbons due to consumption of hydrogen, i.e. maximum hydrocarbon yields are only obtained if water generation is zero. Formation of higher molecular weight hydrocarbons increases the overall weight loss of the coal. As a consequence the calculated nitrogen yield increases because it is calculated from the final N/C ratio and the total carbon loss C/C_{initial}.

The mass balance scheme was applied to three sets of data on the elemental composition of coals. The total amounts of gases generated in the corresponding maturity intervals are listed in Table 7. The first data set was taken from Stach et al. (1982), who report elemental compositions of vitrinites in the maturity interval from 70.5 to 96% C, corresponding to vitrinite reflectances between 0.4% (sub-bituminous coal) and 5.2% (R_r) (> 6% R_{max}) (meta-anthracite). Fig. 3 shows the calculated yield curves for the three components methane, CO₂ and nitrogen as a function of maturity. The second mass balance calculation was based on compositional data of Ruhr coals in the maturity interval 40%–5% volatile matter (0.75% R_r, high vol. bituminous coal – 3.2% R_r, anthracite). The calculated yield curves for methane, carbon dioxide and nitrogen are shown in Fig. 4. For the third calculation a mass balance scenario of Carboniferous coals in the maturity interval of 36–5% volatile matter (85–97% C) presented by Kröger and Hortig (1966) was used (Fig. 5).

The values in Table 7 show that, according to mass balance calculations, the maximum generation potential for methane from coal is significantly higher than gas yields in open- and closed-system pyrolysis exper-

Table 7

Mass balance calculations for gas generation from coals

Stach et al. (1982): gas	0.4% R_r –5.2% R_r (> 6% R_{max}) kg/t initial C	Std. m ³ /t C _{org} (initial)
CH ₄	235	347
CO ₂	443	239
N ₂	9.1	7.7
Ruhr coals: gas	0.75%–3.2% R_r , kg/t initial C _{org}	Std. m ³ /t initial C
CH ₄	122	181
CO ₂	118	63
N ₂	3.1	2.6
Kröger and Hortig (1966): gas	85% C–97% C kg/t initial C _{org}	Std. m ³ /t initial C
CH ₄	209	308
CO ₂	152	82
N ₂	8.2	6.9

iments. In view of these differences some uncertainty persists, in particular with respect to the methane generation potentials of coals. Allowing for the formation of water with the corresponding consumption of hydrogen, and for certain amounts of higher molecular weight hydrocarbons, potential ultimate methane yields (PUY) of 150–200 Std. m³/t initial organic matter appear realistic for immature coals. The PUY of nitrogen can be assumed to be in the range of 7–8 Std. m³/t initial organic matter up to maturity levels of 96–

97% C(daf). It should be noted, however, that even at maturity levels where the methane generation potential is nearly zero (anthracite or meta-anthracite stage) coals retain about one half of their initial nitrogen content.

4.3. Generation potentials vs. reserves

As a first step in the quantitative treatment of gas generation and accumulation it is instructive to relate

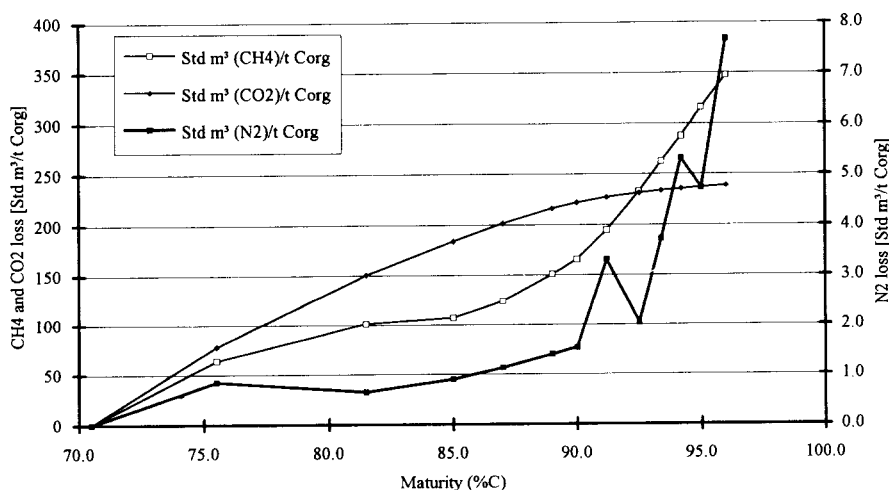


Fig. 3. Results of mass balance for vitrinites (elemental analysis data from Stach et al., 1982).

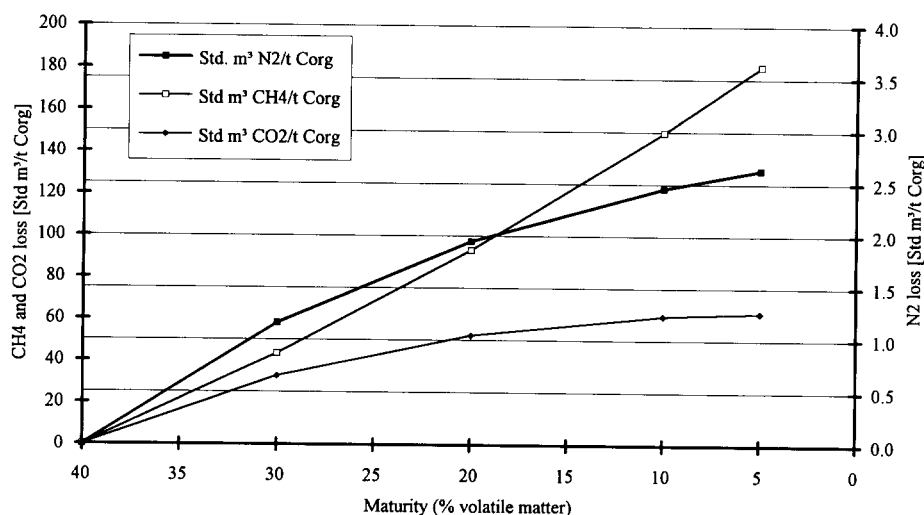


Fig. 4. Results of mass balance for Ruhr coal.

the methane and nitrogen generation potential of coals to the gas contents of actual reservoirs. Gas reserves, reservoir sizes and closure areas for deep (3500–5000 m) gas accumulations in The Netherlands and the British sector of the North Sea were taken from the literature and the following assumptions were made:

(1) Gas is supplied to the reservoirs from organic matter directly underlying the field, i.e., lateral gas flow into the reservoirs is not considered. This assumption is very conservative, because most reservoirs are filled

from a drainage area that is much more extended than the closure area

(2) The cumulative thickness of the organic matter underlying the reservoirs is 100 m and half of the nitrogen present at low levels of maturity (high volatile bituminous coal) was lost upon heating. The assumption on the thickness of the organic matter is not unrealistic in view of the fact that the reservoirs are underlain by several kilometres of coal-bearing Namurian and Westphalian strata which contain both coal seams and

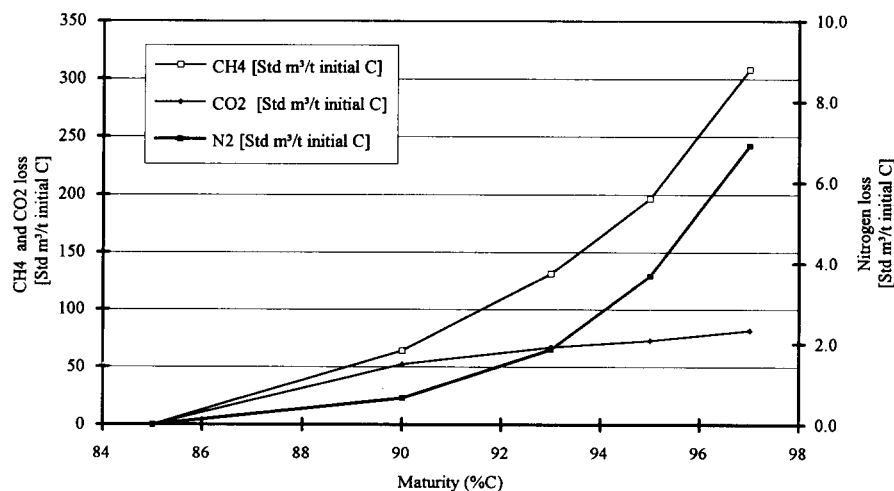


Fig. 5. Results of mass balance for Ruhr coal after Kröger and Hortig (1966) with N/C ratios from Stach et al. (1982) (CH4 Scenario; no water generated).

Table 8

Reserves, areal extent and vertical closure of commercial gas fields in NW Europe

Field	Reserves [10 ⁹ Std. m ³]	Area [km ²]	Vertical Closure [m]	Maximum CH ₄ charge [10 ⁹ Std. m ³]	Maximum N ₂ Charge [10 ⁹ Std. m ³]
Groningen (NL) ¹	2690	192	150	4992	150
Leeuwarden (NL) ²	2.5	59.5	60	1547	46
Zuidwal (NL) ²	42	76.5	90	1989	60
Harlingen (NL) ²	2.5	3.75	30	98	3
Indefatigable (GB) ³	227	128	75	3328	100
Leman (GB) ³	340	232	240	6032	181
Hewett (GB) ³	113	120	–	3120	94

After data by ¹ Grunau (1987), ² Cottençon et al. (1975), and ³ Kent and Walmsley (1970). The last column gives the total amounts of N₂ that can be derived from a cumulative thickness of 100 m of coal underlying the closure area of the reservoir. For the calculations coal density was assumed as 1.3 t/m³ and the generation potentials for methane and nitrogen 200 and 6 Std. m³/t initial organic matter, respectively.

dispersed organic matter in large amounts (Littke, 1993) and which are very probably the source rocks for both the methane and the nitrogen (Lutz et al., 1975). Furthermore, older Palaeozoic rocks may also contain significant amounts of organic matter which contributed to the gases in the reservoirs.

(3) For the calculations coal density was assumed as 1.3 t/m³ and the generation potentials for methane and nitrogen were taken as 200 and 6 Std. m³/t initial organic matter, respectively.

The results summarized in Table 8 and Fig. 6 reveal that the calculated methane charges for all reservoirs exceed by far the present-day reserves in the fields. In

three cases (Leeuwarden, Zuidwal, Harlingen) the nitrogen generation potential alone exceeds the amounts of total gas (methane + nitrogen) present in the reservoirs. In view of the fact that the calculations were performed with the conservative assumption of purely vertical migration, the quantitative importance of organic matter as source for natural gas, including molecular nitrogen, becomes obvious.

At the same time it must be noted that if the reservoirs represented a mixture of all gases generated since the earliest stages of gas generation, a uniformly high ratio of methane over nitrogen or a nitrogen percentage in the order of 3 vol% would be expected. In reality, the

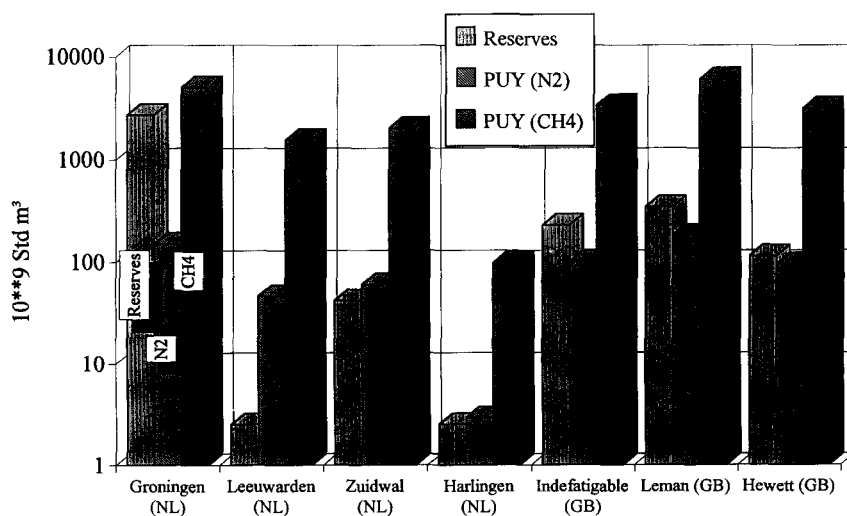


Fig. 6. Gas reserves and potential ultimate yields of gas (PUYG) from coal; (100 m cumulative thickness of underlying Carboniferous coal and vertical migration within closure area).

nitrogen percentages are highly variable and often much higher.

4.4. Mechanisms of N_2 enrichment

Generation potentials (PUY) of methane and nitrogen (see above) show clearly that, assuming simultaneous formation and accumulation, N_2 contents in natural gases derived from coals cannot exceed values of about 5 vol%. Formation of nitrogen-rich natural gas accumulations therefore requires a mechanism which results in the observed substantial enrichment of nitrogen over methane. Two hypotheses have been proposed to explain this enrichment: (i) migration-related fractionation processes resulting in a 'chromatographic' separation of methane and nitrogen, and (ii) generation of nitrogen and methane at different stages of sedimentary diagenesis, catagenesis or metamorphism.

Fractionation processes associated with migration have been suggested by Boigk and Stahl (1970), Maksimow et al. (1973), Faber et al. (1979), Lutz et al. (1975). A review of potential geochromatographic fractionation mechanisms and their relevance in petroleum migration was published by Krooss et al. (1991). Several authors refer to the experimental results of May et al. (1968), who investigated the isotopic fractionation of a N_2/CH_4 mixture on a 40 m column filled with dry molecular sieve. Besides a molecular fractionation of N_2 and CH_4 (nitrogen passed the column more rapidly than methane) an isotopic fractionation effect was reported for methane resulting in a preferential retention of the light isotope species $^{12}CH_4$ on the column as compared to the ^{13}C methane. The transfer of these results to natural systems appears problematic. Moreover, a quantification of the postulated fractionation effects has never been attempted and is virtually impossible without prior establishment of the starting and boundary conditions (migration avenues and distances, initial composition and amount of gas, partition coefficients etc.). Particularly in view of the large amounts of gas that must have flown along the migration pathways and through the reservoir structures it seems improbable that the separation efficiency of any potential chromatographic process could be sufficient to account for the enrichment of nitrogen with respect to methane observed in certain reservoirs.

Theories relating the nitrogen-rich accumulations to generation processes (either assuming *different*

sources of methane and nitrogen or generation from the *same source at different times*) appear to be more plausible. One purpose of the present study was to investigate the possibility of a 'fractional generation' (Krooss et al., 1993) of the two gases from coals (i.e. from a common source). This mechanism has been considered before. Thus Lutz et al. (1975) conclude that nitrogen percentages of the total amount of gas generated (from coal) are relatively insignificant during the main phase of methane formation but increase above FCC (fixed carbon content) 95, i.e. when methane generation is significantly reduced.

5. Experimental investigation of methane and nitrogen generation from coals

The only previous detailed systematic experimental study on the generation of molecular nitrogen from coal was performed by Klein (1971). Selected results from this work are discussed in Klein and Jüntgen (1972) and Jüntgen and Klein (1975). The kinetic parameters for the release of gases from coal were determined by non-isothermal pyrolysis experiments in an open-system packed bed reactor. This experimental method was developed and refined in the group of H. Jüntgen at the Mining Research Institute (Bergbau Forschung) Essen, Germany in the sixties. A comprehensive description of the technique, its applications and the evaluation procedures is given by Jüntgen and van Heek (1969).

During recent years it has been established that the complex reactions involved in the formation of petroleum and gas from organic matter cannot be described by just one set of kinetic parameters (activation energy and pre-exponential factor) (Braun and Burnham, 1987; Ungerer and Pelet, 1987; Burnham et al., 1988) but requires a formulation in terms of a set of parallel reactions or even more complicated reaction schemes. Otherwise the extrapolation from laboratory conditions to geologic heating rates results in unrealistically low formation temperatures (cf. Welte et al., 1988). Although the method of breaking down a 'generation complex' of gas from coals into a number of individual reactions was suggested and applied already by Hanbaba (1967) for methane and other light hydrocarbons, it was not used in the nitrogen study of Klein (1971), who represented methane and nitrogen generation from high volatile coal (Fürst Leopold) by only two indi-

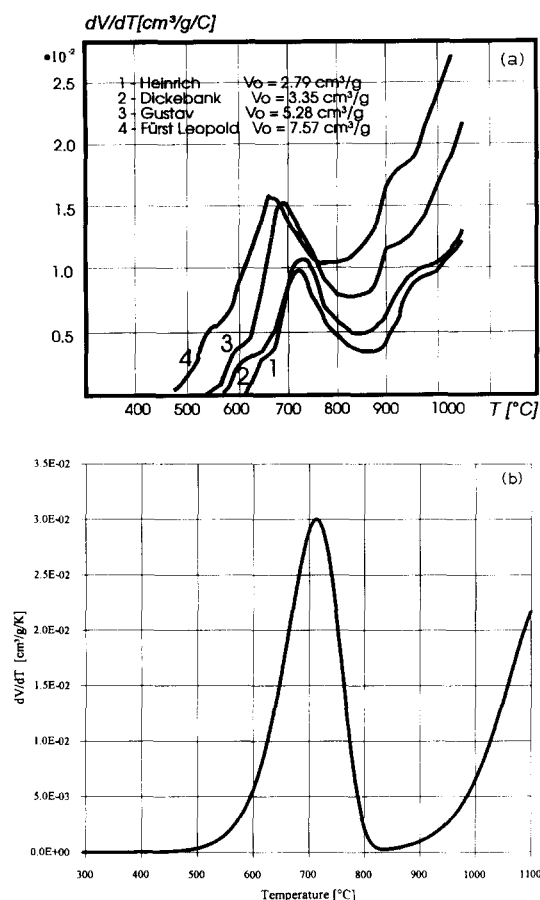


Fig. 7. Comparison of experimental and reconstructed generation curves for nitrogen from coal (Jüntgen and Klein, 1975).

vidual reactions. The measurements of Klein (1971) must be considered as a pioneering work in this field. However, the evaluation of the data is not adequate to present standards and gives only a poor representation of the experimental generation curves (Fig. 7).

In consideration of the extremely small database on the kinetics of nitrogen formation from sedimentary organic matter we have initiated a systematic study to provide the necessary information for the assessment of the quantities of molecular nitrogen and methane generated as a function of temperature history on the geologic time scale.

5.1. Experimental

The method used in this kinetic study was open-system non-isothermal pyrolysis. Fig. 8 shows a

scheme of the experimental set-up. Powdered coal samples (ca. 2 g) were heated in a quartz reactor in a He current of 48 ml/min. A detailed description of the experimental method is given by Lillack (1992). Analysis of the evolved gases was performed with a thermal conductivity detector (TCD). The experiments were carried out with a constant heating rate (usually 0.1°C/min) from room temperature to 1000°C. One sample (humic coal) was additionally heated at rates of 0.5 and 2.0°C/min. The experimental data were evaluated assuming a set of 10 to 40 first-order parallel reactions and an Arrhenius-type temperature relationship.

5.2. Samples

For a detailed study on the formation of nitrogen from organic matter a set of coals of different composition and maturity was selected. This set comprised one high volatile matter bituminous humic coal from the Ruhr district, one sapropelic coal, one anthracite and one torbanite. Vitrinite reflectances and results of the elemental analyses before and after the experiments are given in Table 9.

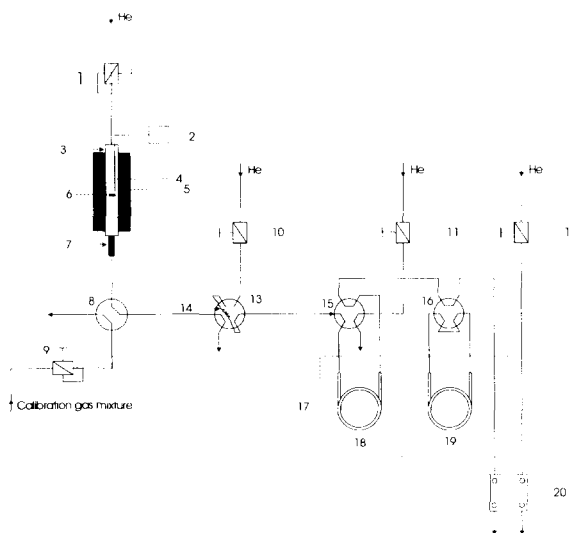


Fig. 8. Scheme of experimental system used in the present study. 1, 9 = flow regulators; 10–12 = pressure regulators; 13, 15, 16 = 6-port valves; 2 = temperature control unit; 3 = quartz glass reactor; 4 = thermocouple; 5 = pyrolysis oven; 6 = sample; 7 = tar condensor; 8 = 4-port valve; 14 = sample loop; 17 = GC oven; 18, 19 = packed columns (1 m stainless-steel, 4 mm ID, MS5A); 20 = TCD.

Table 9

Vitrinite reflectances and elemental compositions of coal samples used in open-system non-isothermal experiments

	Humic coal		Sapropelic coal		Anthracite		Torbanite	
R _r	0.76		0.79		2.3		0.48	
Component	initial (%)	final (%)	initial (%)	final (%)	initial (%)	final (%)	initial (%)	final (%)
Ash	6.30	24.70	18.00	28.00	3.00	3.50	26.78	45.71
C _{tot} (daf)	82.1	90.6	84	94.4	92.4	96.7	84	93
O (daf)	10.4	2.44	7.2	1.61	1	1.06	4.32	1.7
H (daf)	5.5	5.25	5.8	3.7	3.7	2.15	8.41	5.1
N (daf)	1.9	1.71	1.9	0.29	2.1	0.09	1.46	0.3
S (wf)	2.2	2.55	2.7	2.67	0.8	0.75	0.8	0.6

5.3. Results

The first test experiment on the generation of nitrogen from coal was performed in our laboratory in 1990 with a low-rank bituminous coal ($R_r = 0.70\%$) of the Ruhr district, Germany (Krooss et al., 1993). Fig. 9 shows the generation curves for methane and nitrogen obtained with a constant heating rate of $2^\circ\text{C}/\text{min}$ from room temperature to 1100°C . Methane generation generally starts at much lower temperatures than nitrogen generation and under these conditions reaches its maximum at about 500°C . It then decreases and ceases completely above 850°C . The onset of measurable nitrogen evolution occurs only above 700°C . The nitrogen generation curve exhibits a first maximum at 780°C . The most conspicuous feature, however, is the

strong increase in the nitrogen generation rate at extremely high temperatures. This observation is in line with the results of Klein (1971), who pyrolysed coals of different rank from the same area. Boudou (1993) performed pyrolysis experiments up to even higher temperatures and found that, with a heating rate of $30^\circ\text{C}/\text{min}$ the second nitrogen peak maximum for semi-anthracites occurred around 1200°C . These results indicate that a significant portion of the nitrogen in the coals is very refractory and will also under natural conditions require excessive temperatures to be mobilized.

Based on the experimental generation curves shown in Fig. 9 activation energy distributions for the generation of methane and nitrogen from coal were determined with a non-linear least-squares fit procedure

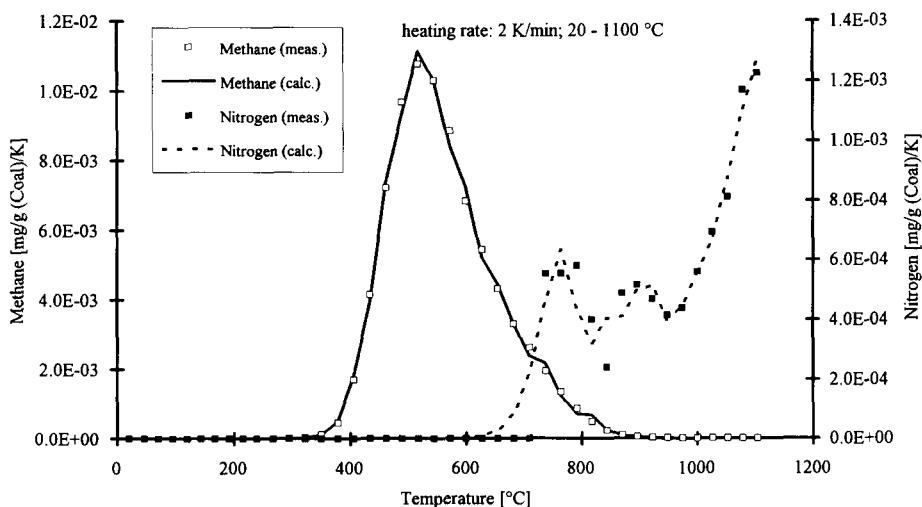


Fig. 9. Methane and nitrogen evolution on non-isothermal pyrolysis of humic coal from northern Germany.

under the simplifying assumptions that: (i) the generation reactions of both gases could be explained by a set of parallel first-order reactions with Arrhenius-type temperature dependence, and (ii) the pre-exponential factors for all reactions are identical. The resulting fitted generation curves are also shown in this diagram. The corresponding kinetic parameters are given in Krooss et al. (1993). The precision of the kinetic parameters, in particular the pre-exponential factor, can be improved by performing pyrolysis experiments at different heating rates.

5.3.1. Nitrogen generation from coals of different rank and type

Fig. 10 shows the methane and nitrogen generation curves ($\mu\text{l/g TOC/K}$ vs. temperature) obtained for the four coal samples listed in Table 9 at a heating rate of 0.1°C/min . The total methane and nitrogen yields are given in Table 6. Both the methane and nitrogen generation curves show distinct differences in terms of shape and the position of the generation maximum. The highest yields of both methane and nitrogen are observed for the immature humic coal (HUM). The methane generation maximum at the experimental heating rate is at 479°C . Measurable evolution of N_2 starts only above 580°C with a distinct generation peak at 685°C . Nitrogen generation continues up to the final temperature of 1000°C and on approaching this temperature a clear increase in generation rate is observed. The first N_2 generation maximum overlaps with the final phase of methane generation. Above 760°C methane generation ceases and N_2 remains the only product generated. This result can be considered as a hint that periods of preferential or exclusive generation of nitrogen from coals may also occur in natural systems. This would be the case if both reactions could be attributed equal or similar frequency factors. Under these circumstances lower heating rates would result in an increased separation of the methane and nitrogen generation phases.

In contrast to the humic coal the other coal samples show a much less distinct first nitrogen generation peak. The but slightly more mature sapropelic coal (SAP) starts generating nitrogen above 630°C , i.e. 50°C higher than the humic coal. This is attributed to a compositional rather than to a maturity-related effect.

The torbanite, an immature algal coal, is characterized by a very broad methane generation maximum

suggesting a heterogeneous composition. The relatively low generation potential for methane indicates that this coal is oil-prone rather than gas-prone. The nitrogen generation potential of this algal coal is the lowest of all samples (Table 6) with only a slight maximum in the temperature range from 600 to 800°C .

Evolution of nitrogen from the anthracite (ANT) starts at 650°C and the small peak indicates that the coal has lost much of its initial N_2 generation potential.

All nitrogen generation curves show the same distinct increase in generation rate in the final temperature range (900 – 1000°C). In recent experiments the temperature range has been extended to higher values (max. 1100°C) in order to quantify this refractory nitrogen and assess its generation kinetics.

5.3.2. Kinetic parameters for methane and nitrogen generation

For the kinetic evaluation of the experimental data it is assumed that the generation of methane and nitrogen gas from coal can be described by a set of parallel reactions following a first-order rate law (Jüntgen and Klein, 1975). The reaction rate, r_i , of the i th parallel reaction is expressed as:

$$r_i = \frac{dm_i}{dt} = k_i(m_{0i} - m_i)$$

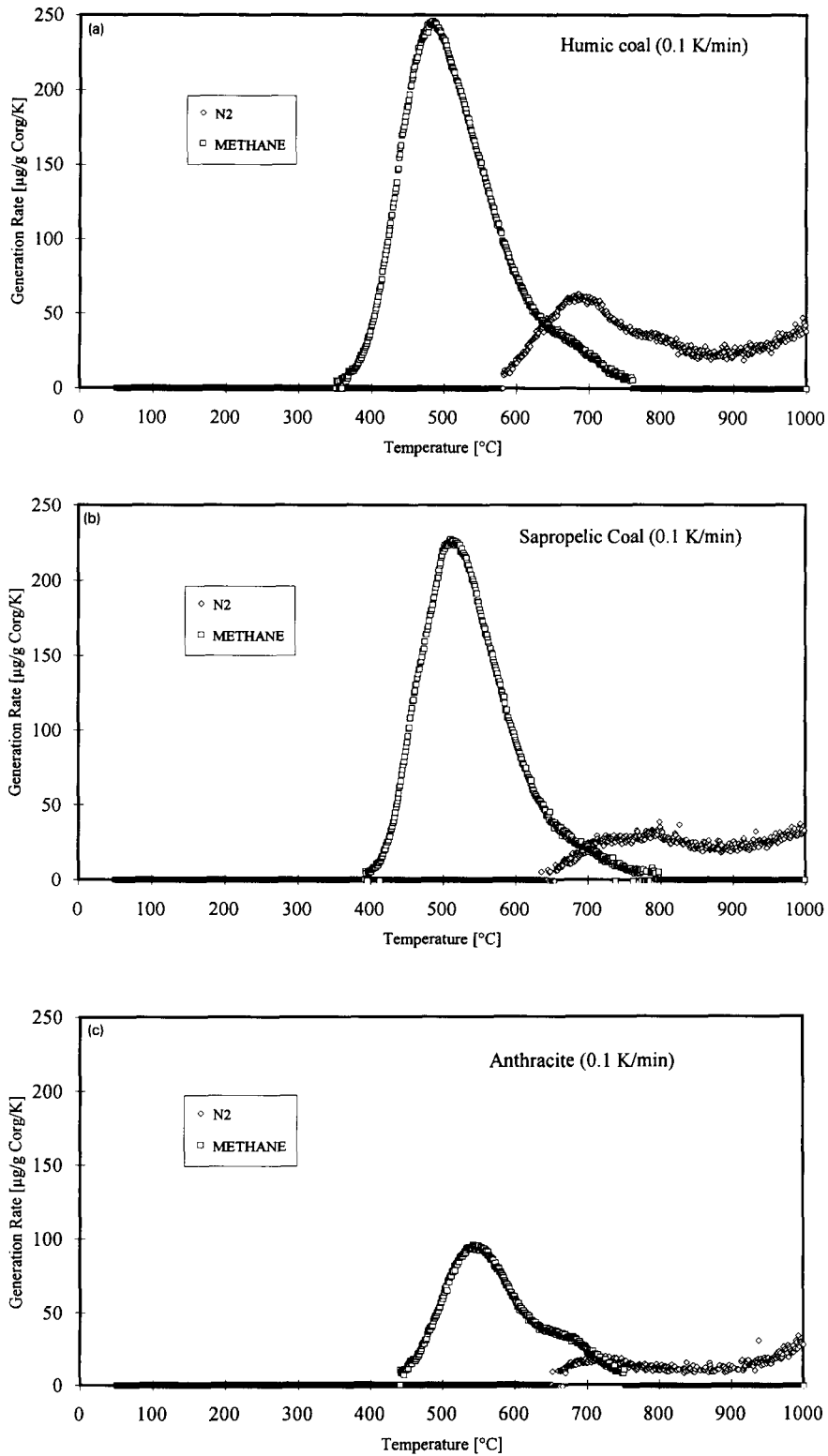
where m_{0i} is the total amount of gas that can be generated from the coal (ultimate gas yield) via reaction i and m_i is the amount of gas that has been generated by this reaction until time t . The factor k_i is the rate constant of the reaction which is a function of temperature according to the Arrhenius relationship:

$$k_i = A_i \cdot \exp\left(-\frac{E_i}{RT}\right)$$

where A_i is pre-exponential factor of the i th reaction ('frequency factor') [s^{-1}], E_i is activation energy of the i th reaction [J/mol], T is absolute temperature [K], R is the gas constant [$\text{J mol}^{-1} \text{K}^{-1}$].

Evaluations were carried out assuming up to 40 parallel reactions ($i = 1$ to 40) each of which was attributed a specific activation energy. In order to reduce the number of parameters the same pre-exponential factor A was taken for all reactions ($A_i = A$ for all i).

The humic coal (HUM) was pyrolysed at three different heating rates (0.1 , 0.5 and 2 K/min) in order to



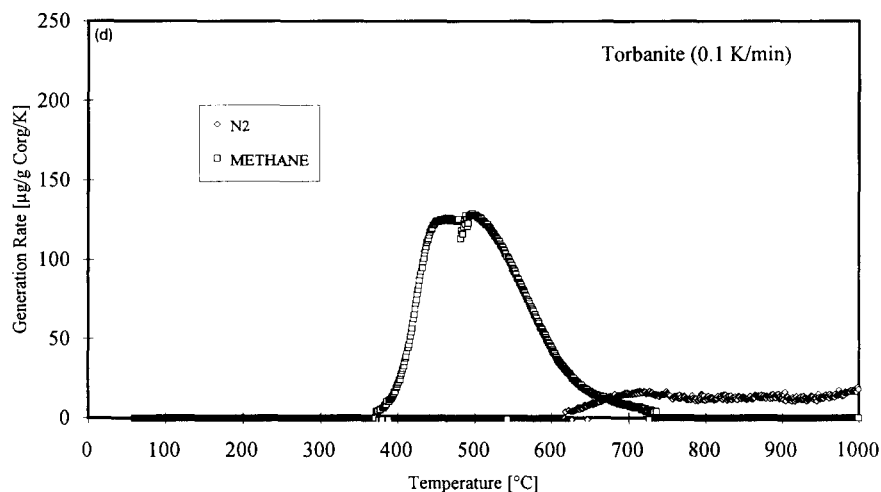


Fig. 10. Methane and nitrogen generation curves from different coals up to 1000°C.

achieve a more reliable determination of the kinetic parameters, in particular the pre-exponential factor. Using a non-linear least-squares fit procedure (Schaefer et al., 1990) the generation potentials (m_{0i}) for the i reactions and the common pre-exponential factor (A) were adjusted to obtain the best fit of the calculated generation curves to the experimental curves for all three heating rates.

The evaluation of the generation curves for nitrogen involved some problems because, within the temperature range of these experiments, they could not be recorded completely, i.e. until the end of the second nitrogen peak. This second generation maximum was therefore only insufficiently defined with respect to its peak shape and the overall generation potential.

The results of the kinetic evaluation for methane and nitrogen generation from the humic coal (HUM) in terms of an activation energy distribution (generation potentials in $\mu\text{g/g Corg}$ vs. activation energies) are shown in Fig. 11. The pre-exponential factors obtained from this evaluation were $3.18 \cdot 10^9$ [1/s] and $2.85 \cdot 10^7$ [1/s] for methane and nitrogen, respectively. In all evaluations performed by this procedure the pre-exponential factor for nitrogen generation was found to be significantly lower than for methane generation. It should also be noted that the frequency factor for methane is lower by 5–6 orders of magnitude than values reported by Reynolds and Burnham (1993) for total hydrocarbon generation from coals from the San Juan

Basin, USA. Further measurements to verify these kinetic parameters are in progress.

5.3.3. Quantification of nitrogen evolution during pyrolysis

In order to achieve an improved understanding of the fate of the nitrogen in coals it is essential to relate the quantities of nitrogen released during pyrolysis to the initial contents and the maturity levels of the coals as precisely as possible. Klein and Jüntgen (1972) reported experimental nitrogen emission data from four coals of different rank from the Ruhr area and compared the amounts of molecular nitrogen (N_2), released up to a temperature of 1000°C, to the initial nitrogen contents of the corresponding coals. As shown in Table 10 the percentage of nitrogen released as N_2 (recorded by a TCD) is highest for the most immature coal and decreases with increasing maturity from 53 to 20%. Table 10 also lists the corresponding results from our pyrolysis experiments. Here, too, the highest N_2 yield was observed for the humic coal (HUM). Fig. 12 shows that both the humic coal (HUM) and the anthracite (ANT) used in our study match the trend of the data of Klein and Jüntgen (1972), whereas the N_2 yields from the low rank sapropelic coal (SAP) and the algal coal torbanite (TOR) are significantly lower than for the low rank humic coals. Non-isothermal pyrolysis, up to 1100°C, of another humic coal ($R_r = 0.70\%$) from the Ruhr area (Krooss et al., 1993)

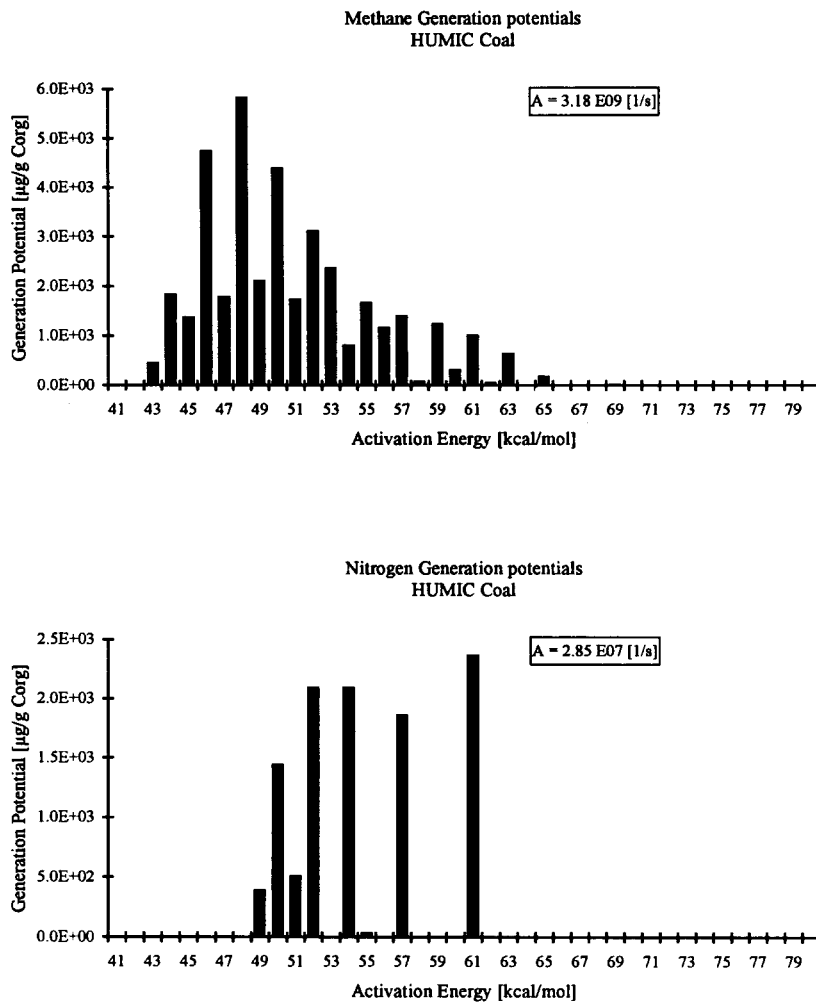


Fig. 11. Distribution of generation potentials for methane and nitrogen from humic coal.

Table 10

Nitrogen release from coals of different rank and type.

	% vol. matter	R _r	C _{org} (waf)	N ₂ content [%]	N ₂ loss [%]	% of N ₂ lost
Fürst Leopold ¹	35	0.85		1.42	0.76	53%
Gustav ¹	28	1.15		1.45	0.53	37%
Dickebank ¹	19.5	1.49		1.41	0.33	23%
Heinrich ¹	12	2.04		1.39	0.28	20%
HUM (E32719) ²		0.76	64%	1.90	0.95	50%
ANT (E35630) ²		2.3	88%	2.10	0.43	21%
SAP (E32731) ²		0.79	68%	1.90	0.58	31%
TOR (E30133) ²		0.48	71%	1.40	0.35	25%
HUM		0.70	76%	1.03	1.0	97%

¹Data from Jüntgen and Klein (1972). ²Data from Müller (1993). ³Data from Krooss et al. (1993).

with a heating rate of 2°C/min resulted in a practically quantitative release of the nitrogen from the coal sample. An elemental analysis was not performed on the residue after this experiment.

Based on pre- and post-experiment elemental analysis data of the four samples used in this study (Table 9) it was attempted to perform an absolute quantification of the mass losses of the elemental coal components (C, O, H, N, S) during laboratory pyrolysis. The ash content of the coal samples before and after the experiment was used as a basis for normalization.

The procedure assumes that the ash represents a mineral component which is not mobilized or otherwise affected by the pyrolysis experiment and retains its original mass. This assumption disregards potential effects like pyrite decomposition, oxidization of mineral components or clay dehydration, but these effects are considered of minor importance in comparison, for instance, with the analytical errors.

The results of the mass balance calculations are summarized in Table 11. Carbon loss is around 35% for the lower mature humic and sapropelic coals (HUM, SAP). It is significantly higher (52%) for the hydrogen-rich torbanite (TOR) and much less (11%) for the anthracite (ANT). This coal also shows the lowest oxygen loss (10%). (Fig. 13)

The nitrogen loss during pyrolysis exceeds 90% of the initial nitrogen content in all samples except for the humic coal (HUM). This coal on the one hand exhibits

Table 11

Calculated losses of coal components during open-system non-iso-thermal pyrolysis up to 1000°C

	HUM (E32719)	SAP (E32731)	ANT (E35630)	TOR (E30133)
R _m	0.76	0.79	2.3	0.48
Component	% loss	% loss	% loss	% loss
C _{tot}	34%	37%	11%	52%
O	86%	87%	10%	83%
H	43%	64%	50%	74%
N	47%	91%	96%	91%

the highest yield of molecular nitrogen (N₂) during pyrolysis (50%) and, on the other hand, loses only about 50% of its original nitrogen content.

The reason for the discrepancy between detectable N₂ yield and practically complete nitrogen loss for the other coals is not yet clear and requires further investigation. The present results indicate a strong influence of the organic matter type on the N₂ release characteristics. Most probably significant amounts of the nitrogen contained in the sapropelic and algal coals are liberated with the tar and condensate formed during the pyrolysis experiment and removed from the hot zone of the oven before further decomposition to N₂ can take place. Thus, Oh et al. (1988) state that most organic nitrogen in raw oil shale is evolved as nitrogen in oil. Other potential products could be ammonia (NH₃) or HCN which is known to be a by-product of the coking process (cf. Klein and Jüntgen, 1972).

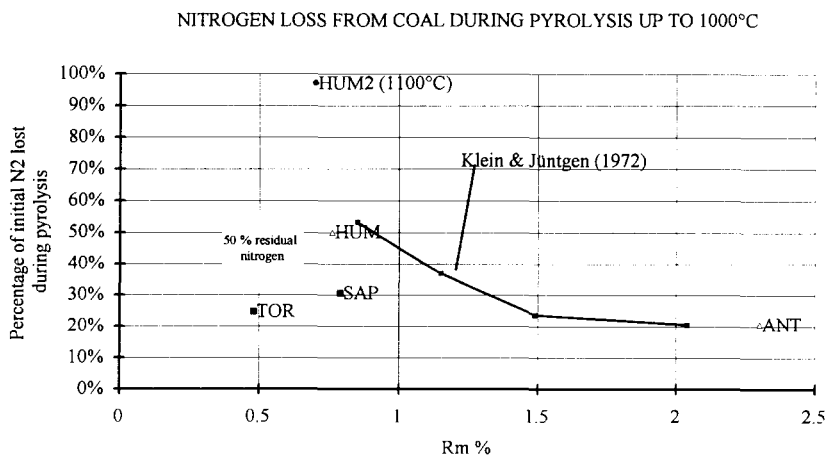


Fig. 12. Nitrogen loss from coals of different rank and type during pyrolysis up to 1000°C.

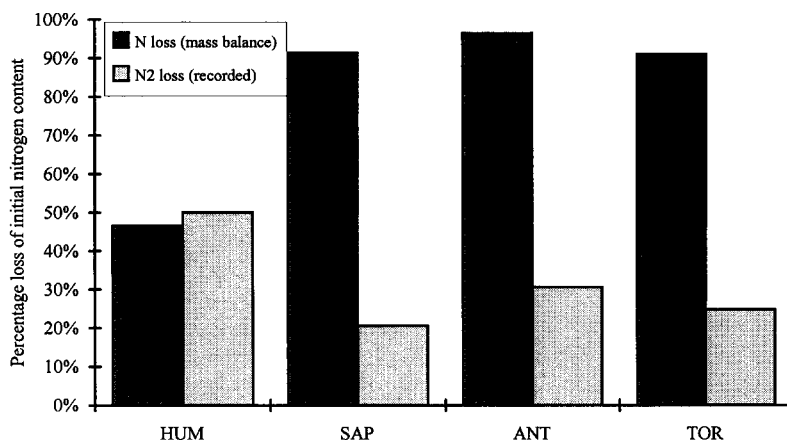


Fig. 13. Comparison of mass balance results for total nitrogen loss and N₂ evolution during pyrolysis.

6. Application of laboratory kinetic results to geologic heating rates

The establishment of more precise kinetic parameters on the formation of molecular nitrogen from coals requires further research efforts. Nevertheless, the set of kinetic data assessed during the first stage of our study provides a means to test the hypothesis of fractional generation of methane and nitrogen in natural systems and to evaluate the temperature conditions required for nitrogen generation from coals on a geologic time scale. A meaningful application of these

parameters is only possible in the framework of integrated basin modelling. Meanwhile a case study on the formation and accumulation of nitrogen-rich gases has been performed on a series of selected well locations in northern Germany using the 2D Petromod software of IES Ltd. (Littke et al., 1995).

Some general conclusions can be drawn on the basis of the present kinetic data and hypothetical thermal histories. The result of such an evaluation is shown in Fig. 14. Here the methane and nitrogen generation curves were calculated for a linear heating rate of 5.3°C/Ma starting at a temperature of 15°C. The gen-

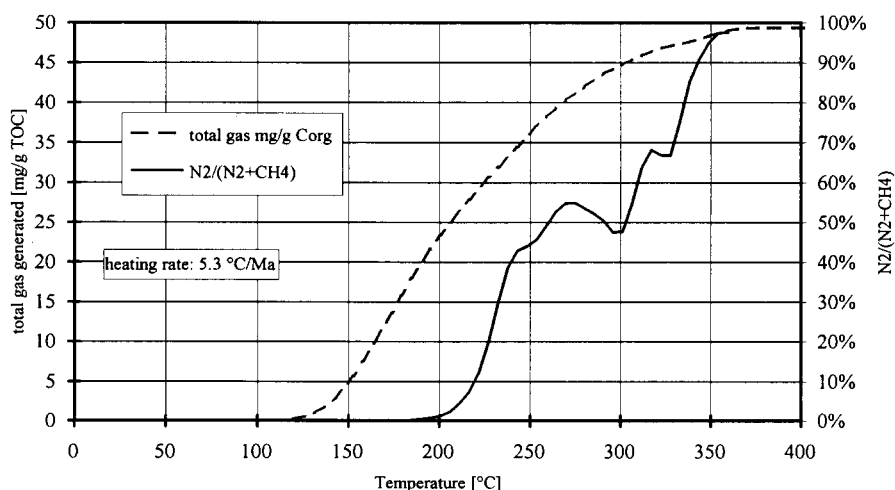


Fig. 14. Calculated N₂ content of gas and cumulative gas generation for humic coal at geologic heating rate (5.3°C/Ma)

eration potentials were chosen according to the values in Table 6 for the humic coal. Plotted in Fig. 14 is the cumulative amount of gas generated as a function of temperature (and time) and the nitrogen content of the generated gas expressed as the ratio $N_2/(N_2 + CH_4)$. Evidently, the nitrogen content in the gas generated exceeds 50% at a temperature around 300°C. At this stage of conversion of the coal 90% of the initial gas generation potential has been converted. Gas generated and trapped beyond this maturity level will become increasingly enriched in nitrogen. The ultimate composition of the reservoir gas thus will depend on the time period during which the gas was collected. According to this calculation a gas containing >90% of nitrogen is only generated above a temperature of 340°C and represents less than 5% of the total gas generation potential. If the methane generation potential is higher than the experimental value used in this calculation, this percentage will be even lower. As discussed above, the total gas generation potential in the North German basin exceeds by far the available reservoir capacities. According to an estimate of Jurgan et al. (1983) the gas in place in Rotliegend reservoirs of eastern Lower Saxony corresponds to only 0.1% of the gas generated within the corresponding drainage area. It is therefore reasonable to consider the present-day reservoirs, on a geologic time scale, as containers which have been flushed by large amounts of gas and which represent probes of the gas that has been supplied 'most recently'. This point of view is shown schematically in Fig. 15.

7. Conclusion

It has been demonstrated that organic matter, and in particular coal, is one, and probably the most important, source of molecular nitrogen in the subsurface. Laboratory measurements on coals of different types and rank have yielded kinetic data on the formation of methane and nitrogen from coals which support the hypothesis that fractional generation of methane and nitrogen leads to phases of preferential and even exclusive nitrogen generation in deeply buried sedimentary basins. The onset of nitrogen generation from coals in geologic systems occurs between 200 and 250°C and N_2 becomes the major gas component at temperatures above 300°C. Comparison of gas generation potentials

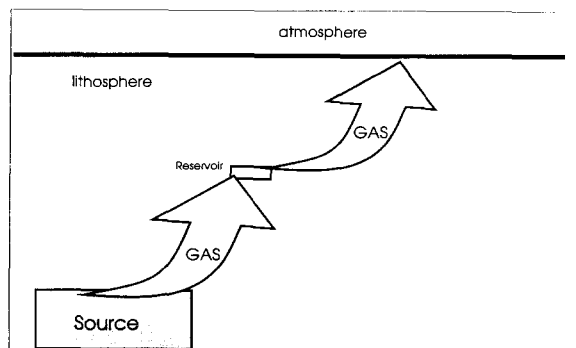


Fig. 15. Dynamics of natural gas accumulations (schematic view).

and reservoir capacities show that nitrogen contents of coals in the North German basin can easily account for the absolute N_2 quantities in reservoir gases.

The understanding and quantification of the dynamics of natural gas accumulations remain a complex and largely unresolved problem. We believe, however, that our present study will help to clarify a small aspect of this question. Ongoing work is directed towards the verification and further improvement of the kinetic parameters and the investigation of the molecular mechanisms controlling the retention and release of nitrogen in organic matter. It is clear that the alternative mechanisms proposed for the supply of nitrogen from different sources cannot be simply dismissed but must be reconsidered thoroughly.

A dynamic gas reservoir model on the geologic time scale involves numerous additional aspects (e.g. sealing capacity, sorption and desorption of gas on/from coals, drainage area), some of which are currently investigated by our group. Basin modelling represents an indispensable tool to test the hypotheses, calibrate the models and compare predictions with actual case histories.

8. Discussion of reviewer's comments

The two reviewers of this paper pointed out several important aspects which they wished to be discussed in more detail. Their comments indicate that a considerable amount of uncertainty and controversy still exists on this topic. We decided to address the reviewers' comments in an additional section, believing that this discussion will contribute to a more precise for-

mulation of the remaining questions and ultimately help in the clarification of the nitrogen problem.

8.1. Kinetic parameters of methane and nitrogen generation from coals

Dr. Burnham notes in his review that both activation energies and frequency factors for methane and nitrogen generation (Fig. 11) appear rather low compared to usual main activation energies for total hydrocarbons being around 55 kcal/mol with frequency factors of the order 10^{14} s^{-1} .

The assessment of our kinetic parameters was based on the experimental generation curves recorded at three different heating rates (0.1, 0.5 and 2 K/min). The evaluation was carried out using the non-linear least-squares fit procedure described by Schaefer et al. (1990). Standard evaluation indeed gave unexpectedly low frequency factors and activation energies for the humic coal sample investigated here. Recent experiments yielded, in some instances, substantially higher frequency factors for methane (10^{16} s^{-1}) with correspondingly higher activation energies. The strong variability of the experimental kinetic data indeed poses a problem which is being reconsidered with the ongoing extension of our database.

As pointed out above, some uncertainty arises in the evaluation of the nitrogen generation curves which could not be recorded completely within the temperature range accessible with our experimental equipment (1100°C). Higher temperatures may result in a more complete release of nitrogen but will also render the extrapolation to geologic temperatures more questionable.

8.2. NH_3 evolution vs. N_2 evolution

According to Oh et al. (1988, 1993) ammonia, released predominantly from the inorganic portions of oil shales (ammonium-bearing clays) and from ammonium feldspars (buddingtonite) during retorting, decomposes into N_2 and H_2 at elevated temperatures ($> 500^\circ\text{C}$). The ratio of NH_3 and N_2 depends on the experimental conditions (i.e. steel reactors catalyze ammonia decomposition and H_2 and steam inhibit ammonia decomposition). Dr. Burnham comments that these results may be taken as an indication that geologically most of the nitrogen evolves as ammonia

and the detection of N_2 in pyrolysis experiments is merely an effect of the high reaction temperatures.

In contrast to shale retorting the amounts of ammonia detected during coal pyrolysis are generally low to negligible compared to N_2 quantities (cf., Whelan et al., 1988; Boudou, 1993). This may be due to the larger amounts of 'fixed nitrogen' (e.g. buddingtonite in Green River shale) in shale source rocks. Our own elemental analyses of Palaeozoic coals and sediments (Littke et al., 1995) show that the percentage of inorganic ('fixed') nitrogen is in most cases negligible. We agree that this question deserves increased attention in future work and that a simultaneous detection of NH_3 , H_2 and N_2 release during pyrolysis of different types of organic matter (marine, terrestrial, shale, carbonate) could shed light on this problem.

8.3. Ammonium minerals as a nitrogen source

Dr. Burnham solicits a stronger emphasis on ammonium minerals as a potential nitrogen source.

Most authors seem to agree that ammonium minerals are usually associated with organic matter as a nitrogen source. The timing and mechanisms of incorporation (i.e. during early diagenesis or during the smectite-illite transformation phase), however, appear to be disputed. Furthermore, the variability of inorganic nitrogen content in different shales seems to be very high, ranging from 50% to essentially 0% (Oh et al., 1988). In the North German basin Carboniferous coals are the main source of natural gas and, based on their nitrogen content, also represent the major reservoir of nitrogen in the crust. We are not aware of any reports about noticeable quantities of ammonium minerals in this region. The potential contribution of pre-Westphalian marine source rocks to the methane and nitrogen found in this basin has been hypothesized but remains to be investigated.

8.4. Stratigraphic occurrence of high N_2 gas and isotope evidence

Dr. Claypool's main criticism of our paper is that it omits evidence for other sources of nitrogen in the North German gas fields.

We do not exclude the possibility of additional sources contributing to the nitrogen in the gas fields. We simply state that from a kinetic/experimental

approach and a volumetric approach the Westphalian and Namurian coals of the Carboniferous appear to be the most obvious and probable source. The two points on this issue raised by Dr. Claypool are: (a) the evidence from stacked reservoirs indicating that nitrogen contents are predominantly higher in Rotliegend and Buntsandstein reservoirs; (b) the isotopic evidence from gases in these fields indicating similarities in the carbon isotope data for hydrocarbon components, despite a variation in the nitrogen contents.

In fact, the prime control on the significant variation in nitrogen contents in gas fields in northern Germany (from the Dutch border to the Polish border) is geographic and not reservoir-dependent. The highest nitrogen contents (70–99%) regionally occur in the former GDR Brandenburg basin where gases are reservoirized in both Zechstein and Rotliegend formations. These areas coincide with areas where the underlying Westphalian and Namurian strata (and source rocks) are buried very deep and attain maturities of up to 5% vitrinite reflectance. The situation with the stacked reservoirs mentioned by Dr. Claypool occurs predominantly in the South Oldenburg area, where nitrogen contents are overall very low. The exceptions with high nitrogen contents tend to be related to major structural lineaments and associated fractured reservoirs where access to deeper, highly mature sources is possible.

The evidence from the gas geochemistry is also far from clear-cut. Regional variations in C1–C4 carbon and hydrogen isotope data and the gas wetness indicate a complex pattern of fractional gas trapping, probable mixing of multiple source levels and are further compounded by the problem of access of Carboniferous generated gases into the shallower reservoirs. Furthermore, the presence of significant amounts of H₂S in Zechstein reservoirs of this area (a product of TSR) renders the use of hydrocarbon isotope data almost useless for maturity correlation purposes. We believe the evidence from all these data are too complex to use for a simple interpretation or conclusion about single or multiple sources for both the hydrocarbons and the nitrogen.

Isotope data for the nitrogen are also problematic. The values range to isotopically very heavy nitrogen (> +15‰) in some of the Zechstein reservoirized gases. The bulk of the nitrogen in the other reservoirs tends to be somewhat lighter (0 to +5‰). These data have been used to suggest an 'evaporite' source for the

nitrogen in the Zechstein reservoirs. However, there are many exceptions to this pattern and we believe that this is insufficient evidence for such a conclusion to be made. One other very significant point is from the Groningen gas field. This field contains 15% nitrogen which, given the total volume of 3 trillion cubic metres of gas, comprises about 450 billion cubic metres of nitrogen alone. The isotopic value of this nitrogen is +17‰. It is very difficult to envisage an evaporite source in the Zechstein or the Rotliegendes to yield such phenomenal volumes of nitrogen into the Groningen structure. Yet, given the experimental results from our study, a drainage area of less than 2000 km² and 10 m net coal thickness is sufficient to generate these quantities of nitrogen from the Westphalian.

In conclusion, we do not want to appear dogmatic about the exclusively organic source for nitrogen in the fields. However, we feel at the moment there is no other source that can explain the volumes and regional distribution satisfactorily. Furthermore, the evidence from the gas isotope geochemistry is far too inconclusive to either support or disprove such a source.

Specific gas volumes and densities at standard conditions

Standard cubic metre [Std. m³]: $T_{sc} = 15.0^{\circ}\text{C}$,
 $P_{sc} = 1 \text{ atm (101325 Pa)}$

	CH ₄	CO ₂	N ₂
Std. m ³ /kg	1.4778	0.5374	0.8444
kg/Std. m ³	0.6767	1.8609	1.1842

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