Nitrogen contents in the northwest Netherlands offshore area

H. Kombrink, D. Della Lunga, H. Mijnlieff, I. Kroon

Summary

Relatively high nitrogen contents are found in Carboniferous rocks in the southern part of the D&E-blocks in the Netherlands offshore area. Unfortunately, data are lacking for the northern D&E-blocks, which are open for exploration. This report aims to explain the observed nitrogen contents in the southern part of the D&E-blocks, which might help predict nitrogen contents further north. A few factors possibly cause enhanced nitrogen contents in the study area. First, due to a low maturity in the northern part of the E-blocks, the succession might still be (partly) in the “early nitrogen” phase of generation (prior to the main gas generation phase). Secondly, limited availability of high-quality source rocks in the northern part of the E-blocks might have led to a relative enrichment in nitrogen. The influence of volcanic rocks is another factor that has to be taken into account. Local heating might have caused local enhanced generation of nitrogen, possibly from shales. Although these factors might have resulted in higher nitrogen contents, migration of gas (generated in the Step or Central Graben or Cleaverbank High) to the adjacent northern E-blocks is a process which can well be active today. Unfortunately, the nitrogen content of this gas from the Step Graben is unknown. Although these factors pose uncertainties to the expected nitrogen content in the northern D&E-blocks, the area can still be regarded as prospective.

Introduction

The D&E-blocks in the northern Netherlands offshore, of which the northern parts are open for exploration, locally show high values of nitrogen (N_2). Nitrogen may limit the economic prospectivity by lowering the caloric value. Therefore it is necessary to have a better grip on the factors causing nitrogen enrichment in these areas.

Nitrogen can have various sources (Krooss, et al., 2008; Littke, et al., 1995; Verweij, 2008) and references therein: (1) atmospheric contamination, (2) mantle degassing, (3) thermochemical sulphate reduction (TSR), (3) clay diagenesis and (4) maturation of coals. These factors are discussed in the context of the geological setting of the D&E-blocks area. Unfortunately, no gas-composition data are available in the northern part of the E-blocks in the TNO dataset (www.nlog.nl). Therefore, nitrogen contents and isotopic values from the southern part of the D&E-blocks, plus a smaller area in the surrounding blocks, are investigated to set up an hypothesis on expected nitrogen contents in the northern parts of the D&E-blocks. Emphasis is on nitrogen contents of Carboniferous and Rotliegend rocks. For completeness, nitrogen contents are also shown for Zechstein, Mesozoic and Tertiary strata.

Geological setting

Carboniferous strata play an important role in the study area since the most important source rocks were deposited in this period. The structural model for the Carboniferous adopted here is one of a horst and graben topography (Figure 1). This setting was recently suggested to exist in the northern onshore Netherlands (Kombrink, 2008) and has been proven in the UK and Belgium (Gawthorpe, et al., 1989; Muchez and Langenaeker, 1993; Poty, 1997; Figure 1). Probably, the northern D&E-blocks were part of a shelf area (horst), while a graben existed further south (Cleaverbank High; Figure 1). The Central and Step Graben areas are interpreted as structural lows during the Carboniferous (see figure 6 for Mesozoic structural elements).

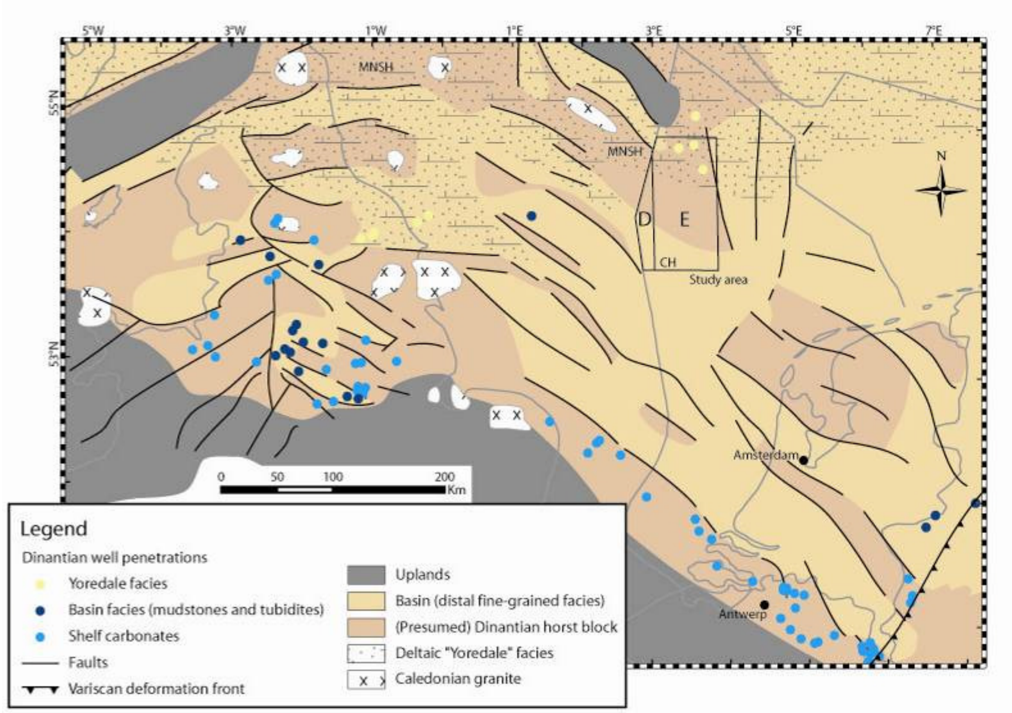


Figure 1. Structural and depositional setting of the Netherlands and surrounding areas during the Early Carboniferous. The northern part of the D&E-blocks is interpreted as a shelf area (horst), surrounded by basinal areas. The horst blocks in the northern part of the Netherlands onshore have been proven to be characterised by carbonate platforms (Kombrink, 2008). In the study area however, mainly siliciclastic sediments were deposited during the Early Carboniferous. CH: Cleaverbank High; MNSH: Mid North Sea High.

In the northern Netherlands onshore and in the UK and Belgium, platform carbonates developed on the horst blocks during the Dinantian. However, in the northern offshore mainly siliciclastic sediments are found (Figure 1); the southward advancing Yoredale delta-complex probably prevented the formation of carbonate platforms. The Namurian is characterised by a continuation of fluvio-deltaic deposition in the northern E blocks. Westphalian sediments were mainly deposited in a fluvial depositional environment, changing from poorly drained conditions during the Westphalian A and B to well drained conditions during the Westphalian C and D.

The most important source rocks in the area consist of Westphalian coals. These are found in the Cleaverbank High area and possibly in the Step and Central Grabens, but have been eroded (or were not deposited) further north (northern part of the D&E-blocks; Figure 2). The Dinantian and Namurian succession in the study area (Figure 2) is characterised by a very limited amount of thin coal seams. Due to a lack of well-control the characteristics of Dinantian and Namurian source rocks in the Cleaverbank High area further south is unknown. However, a pre-Westphalian marine source rock is proposed by (Gerling, et al., 1999) in the Cleaverbank High area based on an interpretation of Carboniferous gases as a mixture of dry gas from a sapropelic source (Namurian or Dinantian shales) and wet gas from a terrestrial source (Westphalian coals). Altogether, the southern part of the D&E-blocks is characterised by the presence of high quality coal seams from the Westphalian B/C (also present in the Step Graben), while further north the amount of source rocks is probably much more limited.

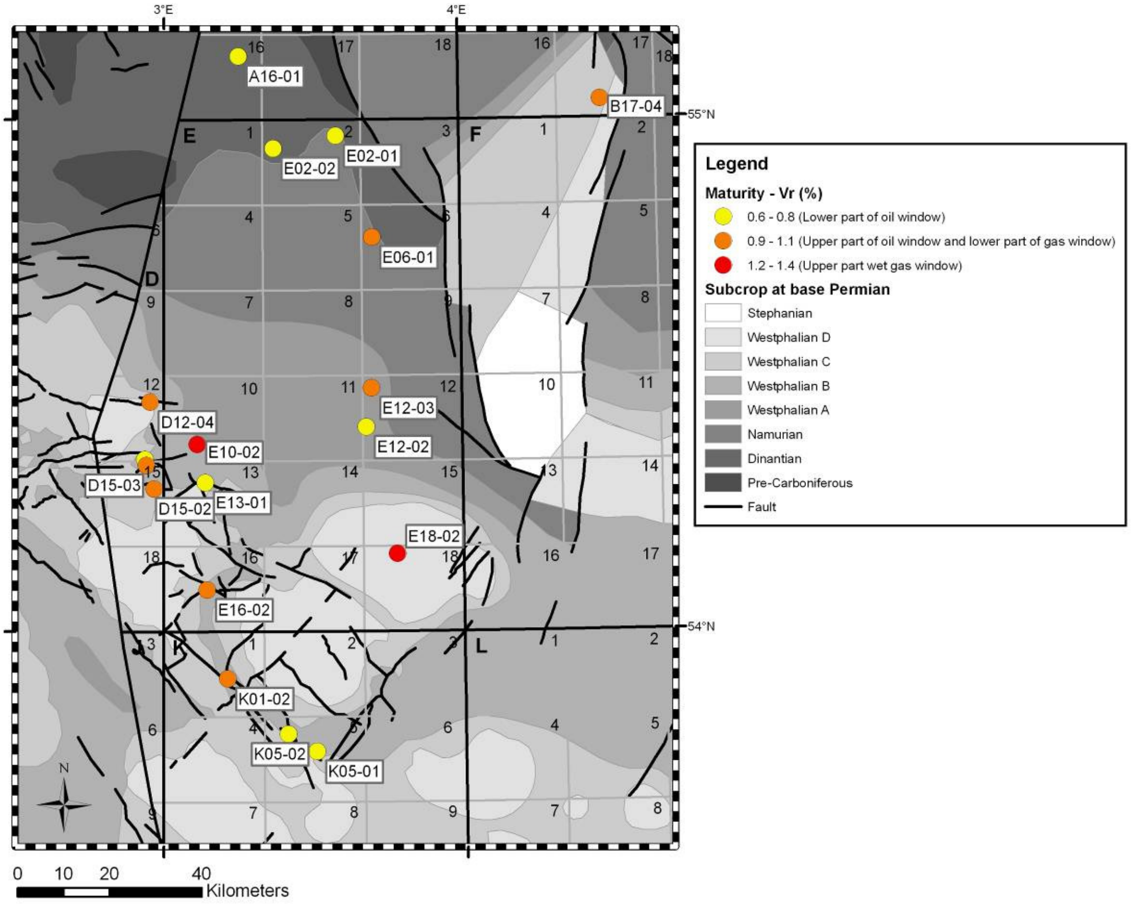


Figure 2. Maturity at top Carboniferous for the wells in and around the D&E-blocks. Background: subcrop of Carboniferous or older rocks against the base Permian.

Burial history and maturation

The maturation and burial history of the northern D&E-blocks reflect their position on a stable horst block (Elbow Spit High; Figure 6). For the central area of the Elbow Spit High, Schroot et al. (2006) interpret only one phase of hydrocarbon generation from Carboniferous strata from 60 Ma to present-day. This is caused by only moderate Mesozoic burial. During the Tertiary sagging phase an increase in burial rate took place.

The Step Graben east of the Elbow Spit High experienced higher burial depths during the Late Carboniferous and Mesozoic which resulted in several generation phases (Schroot et al., 2006). The first took place during the Late Carboniferous, prior to Permo-Carboniferous uplift and resulted in generation of about 50% of the Namurian HC generation potential. HC generation from the Namurian continued until the beginning of the Jurassic when ca. 90% was generated. Hydrocarbon generation from the Westphalian coals started in the Triassic and ended when the Late Kimmerian tectonic phase caused severe uplift. Afterwards the area subsided gradually, interrupted by minor phases of uplift and erosion. The main phase of hydrocarbon generation from the Westphalian started around 60 Ma and continues until present day.

The situation on the Cleaverbank High south of the Elbow Spit High is in between the two scenarios described above. The Namurian rocks started generating hydrocarbons in the Late Carboniferous but had their main generation phase in the Early Triassic. The Westphalian Coals only started generating hydrocarbons during the Cenozoic.

In the graben areas the Westphalian coals as well as the Dinantian/Namurian shales experienced higher temperatures during the Mesozoic for the same burial depth compared to Tertiary-Quaternary times. This is caused by the Late Jurassic-Early Cretaceous extensional tectonic phase which was associated with magmatic activity in the onshore and offshore of the Netherlands (Sissingh, 2004) and an (associated) increase of basal heat flow (Verweij, 2003). Moreover, surface temperatures were significantly higher than today. The platform areas were not affected by the higher heat flow during the Mesozoic due to shallower burial depths.

Results

Nitrogen contents measured from Carboniferous rocks in the D&E-blocks range from 11.9 % (average) in D12-03, up to 83.5 % in D15-04 (Table 1 and Figure 3). These values are somewhat higher than those from the northern K-blocks, where the nitrogen percentages are generally lower than 10%. There are no data available from Rotliegend rocks in the D&E-blocks; those obtained from the northern J and K-blocks show relatively low nitrogen contents (< 12.5 %; Figure 4). High nitrogen contents were found in Zechstein rocks in the wells E09-01 and E17-01 (86 and 58 % respectively; Figure 5). These are the only measurements obtained from Zechstein rocks in the study area. No nitrogen contents are known from Mesozoic rocks in the D&E-blocks. The surrounding blocks show a percentage lower than 10 % in general (Figure 6), with the exception of well F06-01 where 69% was found. Tertiary rocks also show low nitrogen contents (< 1%; Figure 7).

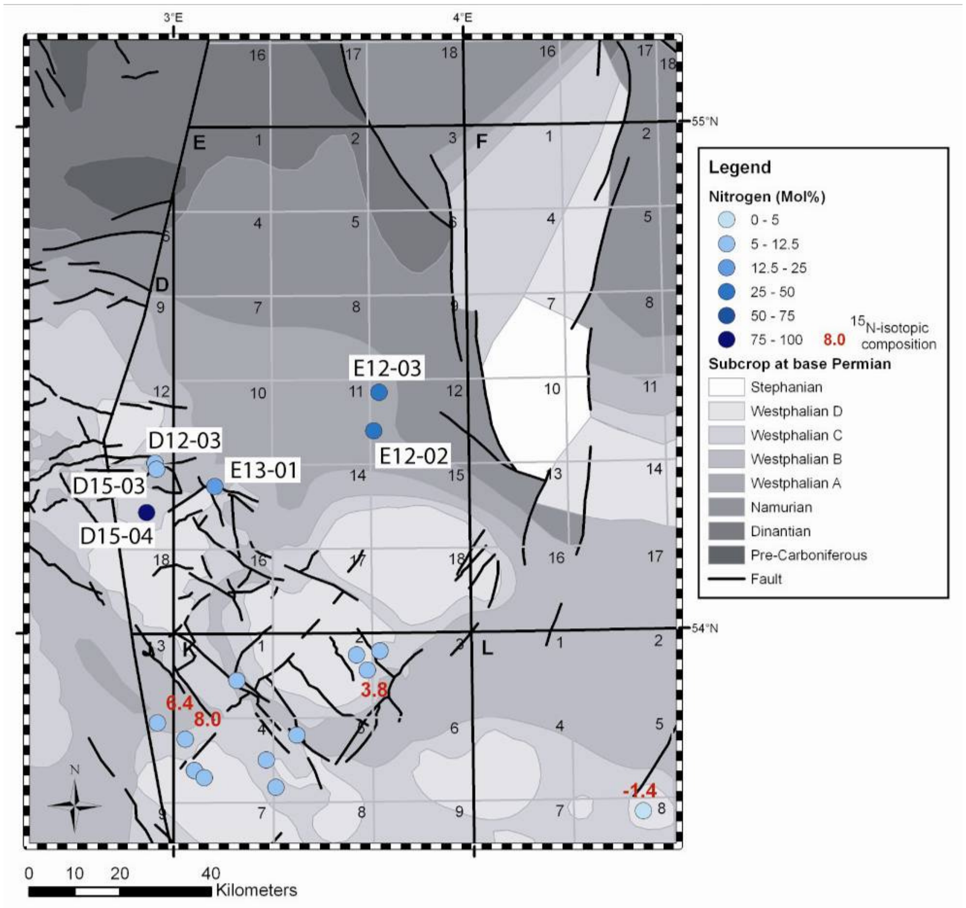
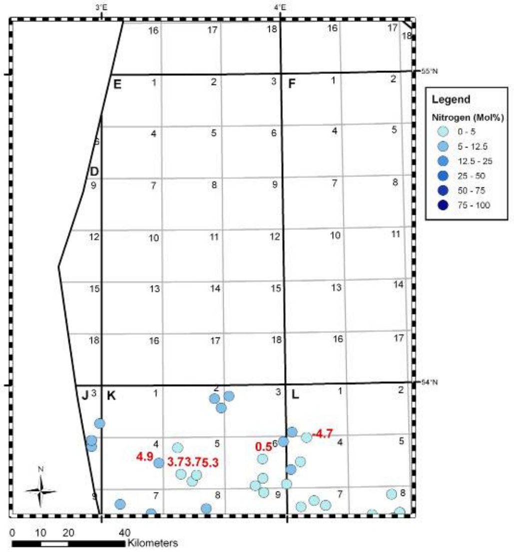


Figure 3.Nitrogen in Carboniferous rocks in and around the D&E-blocks. The red numbers indicate nitrogen isotopes.



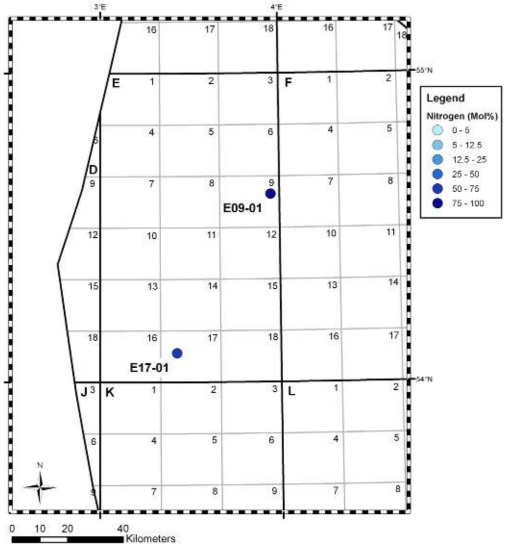
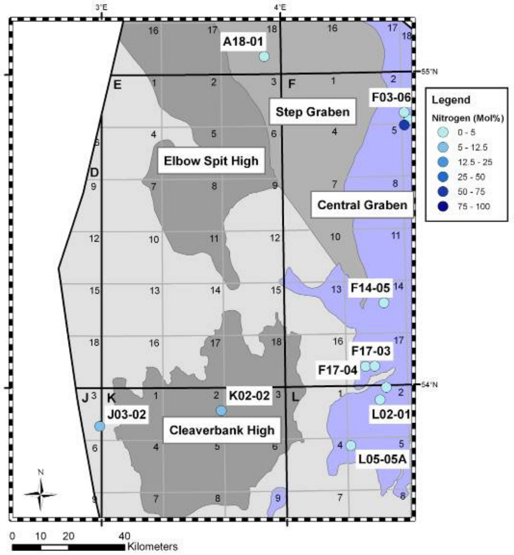


Figure 4 (left). Nitrogen in Rotliegend rocks around the D&E-blocks. The red numbers indicate nitrogen isotopes.

Figure 5 (right). Nitrogen in Zechstein rocks in the D&E-blocks.



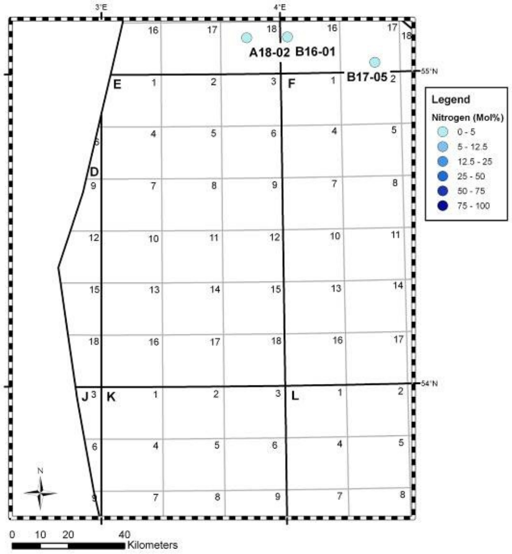


Figure 6 (left). Nitrogen in Mesozoic rocks around the D&E-blocks. The blue color represents Jurassic graben areas, the grey colors (from dark to light) structural highs, platforms and Late Jurassic grabens.

Figure 7 (right). Nitrogen in Tertiary rocks around the D&E-blocks.

Despite the limited number of ^{15}N measurements (Figure 3 & Figure ***4***), a north-south oriented zone including most of the L- and Q-blocks shows a depletion in ^{15}N, while an enrichment can be observed in the blocks further to the west. When ^{15}N values are plotted for all L and M blocks together (Figure 8), an area of negative values becomes evident, ranging from -0,8 to -4,7‰, while positive values are found to the east and west, ranging from +0,3 to +7,1‰.

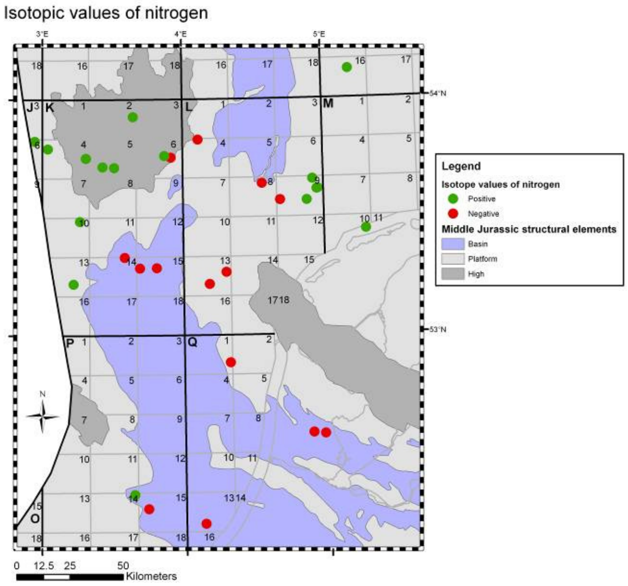


Figure 8. Nitrogen isotopes from various reservoir units in the Netherlands' on- and offshore.

Interpretation of results

As mentioned in the introduction, nitrogen can have various sources (Littke, et al., 1995; Verweij, 2008) and references therein): (1) atmospheric contamination, (2) mantle degassing, (3) thermochemical sulphate reduction (TSR), (4) clay diagenesis and (5) maturation of coals.

Atmospheric contamination can be neglected in the study area, as nitrogen could easily escape from the source rocks due to an absence of a seal at the moment of the hypothetic contamination (Littke, et al., 1995).

Mantle degassing is expected to form an unlikely source of nitrogen enrichment too. Mantle-derived gases are usually characterised by a significant amount of carbondioxide (CO_2) next to helium and argon. High concentrations of these gases have not been reported yet.

The migration path of hydrocarbons sourced from Carboniferous rocks in the Netherlands northwest offshore is, in most cases, limited to the Carboniferous and Rotliegend succession. Since the main anhydrite layers (necessary for TSR) are found in the overlying Zechstein rocks, thermochemical sulphate reduction seems unlikely to have taken place in Rotliegend and Carboniferous rocks. Only when juxtaposition of Zechstein rocks against Rotliegend reservoirs occurs, it may be possible that excess nitrogen finds its way into stratigraphically lower units. In appendix 1 a short summary is given on the mechanisms behind TSR.

Finally, the two most probable sources for nitrogen in the study area are organic matter (in the form of coals) and ammonium fixed in shales. For an extensive description of these processes the reader is referred to Verweij (2006).

Maturity

Based on the maturity-data (Figure 2) and the burial history of the northern E-blocks (see above), it is assumed that the maturity of Carboniferous rocks is relatively low in the greater part of the area. The release of nitrogen from shales, which only takes place at very high temperatures (see Verweij, 2006), might thus be very limited. Therefore, nitrogen must have been predominantly released from organic matter. Considering an overall low maturity, the Carboniferous succession may still be in the "early nitrogen" phase which precedes the main gas generating phase, as shown in Figure 9. This might be a reason for slightly elevated nitrogen contents in the area. The limited availability (and possibly a low quality) of source rocks in the northern E-blocks (see above) may also result in a relatively high nitrogen content because of limited methane generation (dilution-effect). However, this process remains to be tested and is unproven to date.

Some wells show exceptionally high maturities, possibly as a consequence of the emplacement of igneous rocks. High temperatures may have caused nitrogen liberation from shales in these cases, leading to high local nitrogen concentrations. Volcanic rocks were found in the wells E06-01, E12-03 and E18-02 and vitrinite data indeed testify that Carboniferous rocks reached high maturities in those places (maturity reaches up to 2.25 Rr% and even higher than 4 Rr% in E06-01 and E12-03 respectively).

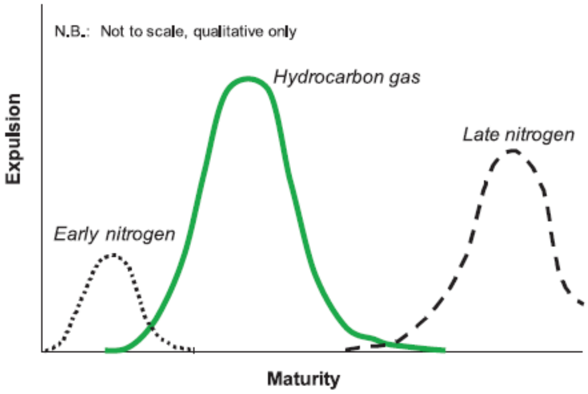


Figure 9: Nitrogen expulsion relative to the main phase of gas generation (From: De Jager and Geluk, 2007).

In summary, considering the factors influencing nitrogen enrichment in Carboniferous (and possibly Rotliegend) reservoirs, it is envisaged that local sourcing in the northern E-blocks might have resulted in slightly higher nitrogen contents because 1) the sediments are partly in the "early stage" of nitrogen generation (Figure 9), 2) limited availability of high quality source rocks might have led to a relative enrichment in nitrogen and 3) igneous activity probably caused enhanced local nitrogen generation.

Sourcing from adjacent areas

Although there might be a low amount of source rocks in the northern part of the D&E-blocks, lateral sourcing is a process which has to be taken into account. For example, it is known from the Cleaverbank High area that the coal-bearing Maurits Formation (Westphalian B) in some parts is not mature enough to have been fully responsible for charge. Lateral migration from nearby kitchen areas is a likely alternative, next to the possibility of charge from deeper Namurian source rocks. Since it is to be expected that the Coal Measures are still present in the Step Graben just east of the E-blocks (Figure 6), lateral migration from this area might be a process responsible for the filling of reservoirs especially in eastern part of the E-blocks. Similarly, lateral migration of gas from the Silverpit Basin in the adjacent UK offshore area may play a role in the D-blocks. It is important to realise that the quality of the gas that has eventually been sourced from Carboniferous coals in the Step Graben is unknown. Late nitrogen may be an important constituent in "Step Graben" gas, depending on the depth of burial and the structural style. Moreover, Namurian shales may have liberated nitrogen too. This is envisaged for the other Jurassic graben areas in the Netherlands based on nitrogen isotopes (see discussion below), although the overall nitrogen contents are in general relatively low in these areas (Verweij, 2006).

Nitrogen in Rotliegend, Mesozoic and Tertiary strata in the area

Rotliegend strata clearly have the same source as the Carboniferous rocks in the Cleaverbank High area, regarding the similar nitrogen contents of both successions (Figure 3 & Figure ***4***). The high nitrogen content in the Zechstein rocks possibly indicates that thermochemical sulfate reduction took place, whereby nitrogen is relatively enriched. The other overlying rock units (Mesozoic and Tertiary) almost exclusively display low nitrogen contents. Tertiary gas is believed to be of (partly) biogenic origin, which involves a different generation-process (Schroot and Schüttenhelm, 2003).

Isotopic composition

The $\delta^{15}N$ isotopic composition (Figure 8) is thought to reflect a difference in burial history between the Jurassic grabens and the surrounding areas (Verweij, 2006). It is thereby important to keep in mind that the release of nitrogen from coals seems to take place without fractionation, while the release of inorganic fixed ammonium in shales involves fractionation, leading to depletion in ^{15}N (Verweij, 2006).

During Jurassic rifting hydrocarbons and nitrogen were generated from Westphalian coals in the graben areas. Moreover, the fixed nitrogen in Namurian shales also experienced enhanced thermal conditions (caused by burial and high heat flow only and/or locally enhanced due to heat pulses related to magmatic activity). During Tertiary and Quaternary times hydrocarbons and nitrogen were generated from Westphalian coals that have exceeded previous burial temperature; however, the underlying Namurian shales may not have exceeded previous burial temperatures yet as basal heat flow is much lower. In that case, no nitrogen is liberated from fixed ammonium in the shales. The $\delta^{15}N$ variation seems to testify that areas in the above mentioned north-south oriented zone with negative values were affected by enhanced thermal conditions that could have generated nitrogen liberation from ammonium minerals, thereby contributing to a decrease in the values of $\delta^{15}N$.

Conclusions

There are a few factors possibly leading to enhanced nitrogen contents in the D&E-blocks. First, due to the overall low maturity in the northern part of the E-blocks, the succession might still be (partly) in the “early nitrogen” phase of generation. Secondly, limited availability of high quality source rocks in the northern part of the E-blocks might have led to a relative enrichment in nitrogen. The influence of volcanic rocks is the last aspect that has to be taken into account. Local heating might have caused local enhanced generation of nitrogen.

Although local sourcing might have resulted in higher nitrogen contents, migration of gas (generated in the Step or Central Graben or Cleaverbank High) to the adjacent northern E-blocks is a process which may be active today. The nitrogen content of this gas is unknown and depends on the thermal maturity of Carboniferous source rocks (late nitrogen generation) in the Step/Central Graben. Altogether, the northern E-block, especially the areas adjacent to the Cleaverbank High and the Step Graben, must still be regarded as prospective for exploration.

Appendix 1

Thermochemical sulfate reduction

Thermochemical sulfate reduction (TSR) is the abiological, thermally-driven reaction between hydrocarbons and sulphates (mainly anhydrite). The chemical reactions for TSR, as proposed by (Worden and Smalley, 1996) are:

$CH_{4(g)} + CaSO_{4(s)} \rightarrow CaCO_{3(s)} + H_2S_{(g)} + 2H_2O_{(g)}$

$C_2H_{6(g)} + 2CaSO_{4(s)} \rightarrow 2CaCO_{3(s)} + H_2S_{(g)} + S_{(l)} + 2H_2O_{(g)}$

TSR has a high activation energy of 142 kJ/mol which causes the reactions to be highly dependent upon temperature. According to Worden and Smalley (1996) the standard Gibbs energies values for these reactions are:

$\Delta_r G° = 41.49-0.20T$
$\Delta_r G°= 39.91-0.373T$

where T is the temperature in Kelvin. These values show that the reactions start to proceed from left to right at the temperature of 207.45 K and 107 K. Nevertheless, if we consider H_2O in the reservoir to be in a liquid phase the Gibbs energy values decrease and we can observe that TSR is an irreversible thermodynamic process from 20 °C to 240 °C. Sulfate reduction is independent of pressure and the rate of the process is independent of the formation water's pH, although it has been suggested that the rate of TSR is catalyzed at extremely low pH.

This process has been proposed to cause high H_2S concentrations in a number of deeply buried petroleum reservoirs (Heydari, 1997; Worden and Smalley, 1996), but it could also be the cause of enrichment in others gas components of the reservoir, such as nitrogen. In fact, the only gas phase produced in the reactions 1 and 2 (except of water) is H_2S, which, in presence of hematite, can react according to the following reaction:

$4Fe_2O_3 + 9H_2S \rightarrow 8FeS + (SO_4)^{2-} + 8H_2O + 2H^+$

Therefore, the process causes a consumption of the main gas phases of the reservoir whereas liquid species (H_2O, S), solid species ($CaCO_3$, FeS) and species in solution ($(SO_4)^{2-}$, H^+) are produced. This leads to a relative enrichment of others gas components, among which the N_2 is one of the most common.

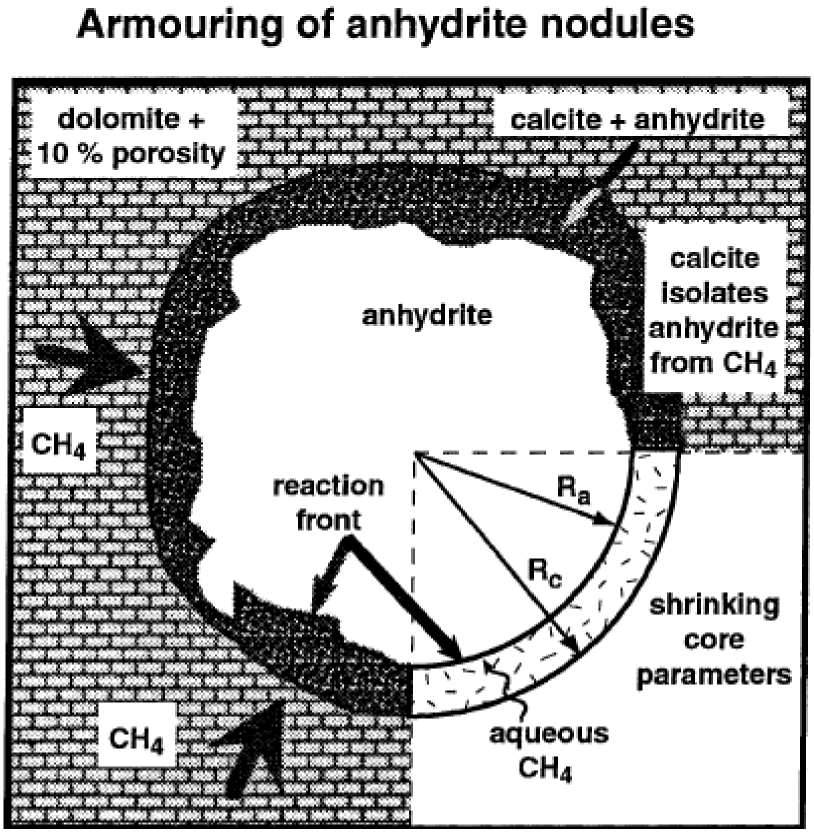


Figure 10. Evolution of textures during TSR (modified from Worden and Smalley, 1997). TSR calcite precipitates as a front, from the edge towards the nodule center, surrounding the anhydrite and isolating it from methane. The aqueous methane has to diffuse through the calcite armoring to get the reaction location at the surface of anhydrite.

Well	X	Y	Age hostrock	CH4 (mol%)	N2 (mol%)
D12-03	495886	6021143	Carboniferous	80.1	11.3
				78.9	12.5
	Average			79.5	11.9
D15-03	496215	6019812	Carboniferous	78.9	12.5
				78.9	12.5
				79.0	12.4
				78.9	12.4
				78.6	12.7
	Average			78.9	12.5
D15-04	494055	6010339	Carboniferous	10.2	86.2
				14.1	80.8
	Average			12.1	83.5
E09-01	561371	6051807	Zechstein	9.3	85.7
E12-02	544026	6028262	Carboniferous	63.5	32.7
E12-03	545198	6036716	Carboniferous	64.0	32.2
				64.0	32.3
				63.9	32.4
				63.8	32.5
				63.8	32.5
				63.6	32.7
				63.5	32.8
	Average			63.8	32.5
E12-03	545198	6036716	Unknown	27.6	39.8
E13-01	509007	6016047	Carboniferous	75.2	18.1
				75.2	18.1
				75.3	18.0
	Average			75.2	18.1
E17-01	527727	5994204	Zechstein	15.9	58.0
				17.8	63.7
	Average			16.9	60.9

Table 1. Nitrogen and methane contents of wells in the D&E-blocks.

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