DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2012/17

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Niels Schovsbo & Troels Laier

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DANISH MINISTRY OF CLIMATE, ENERGY AND BUILDING

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1. Introduction

This report summarises the composition and isotope signature of hydrocarbon gas measured in core samples from the five scientific wells: Albjära-1, Lönstorp-1, Gislövshammar-2, Hällekis-1 and Djupvik-1 (Figure 1).

The samples and analysis were prepared in 1991-1992 as part of the Energy Research Project EFP-1313/88-2 (T. Laier, B. Buchardt, A.T. Nielsen unpublished) and the Pre-Westphalian Source-Rocks in Northwest Europe (PREWSOR) project (Warming et al. 1994).

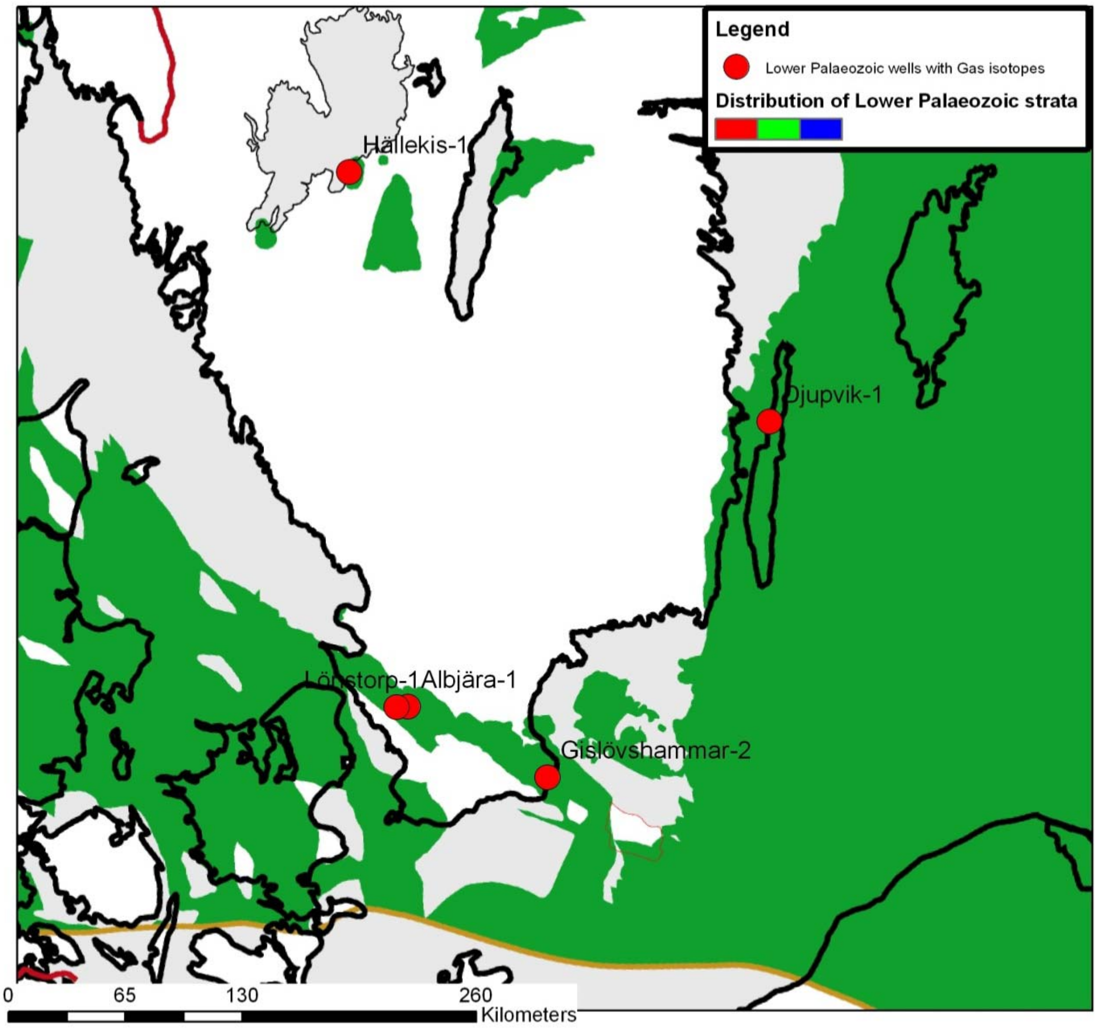

Figure 1. Locality map of Southern Scandinavia including the five scientific wells included in this study. Green fill indicates the presence of Palaeozoic strata (from Nielsen & Schovsbo 2011).

2. Samples and analytical methods

The composition and isotope signature of hydrocarbon gases were measured on 27 samples (Table 1). The samples represent all formations present in the cores. The majority of the samples were picked from the Alum Shale (14 samples) followed by the Tøyen Shale (6 samples) and Rastrites shale (6 samples). One sample was picked from the Almelund Shale.

The five wells represent both thermally mature and immature organic-rich rocks (Table 1). Thermally immature source rocks are found in the Djupvik-1 and Hällekis-1 wells showing a ‘vitrinite-like’ reflectance of <0.6% Ro. Thermally mature organic-rich rocks are present in the Gislövshammar-2, Albjära-1 and Lönstorp-1 wells that all have vitrinite-like reflectance >1.9% Ro.

Table 1. Samples analysed for gas composition and isotope signature. The measured gas types include sorbed and head space gas. Average vitrinite-like reflectances for the wells (% Ro) are from Schovsbo (2011). The TOC concentration of the samples are either measured or have been estimated based on the lithology (indicated with a ‘<’).

Well average %Ro	TOC%	Age	Well	Depth	Sample	Formation
2.0	0.3	L Ordovician	Gislövshammar-2	19.8		Tøyen Shale
	7.2	L Ordovician	Gislövshammar-2	31.8		Alum Shale
	13.7	Furongian	Gislövshammar-2	44.5		Alum Shale
	9.1	Furongian	Gislövshammar-2	65.2		Alum Shale
	5.8	M. Cambrian	Gislövshammar-2	88.3		Alum Shale
0.6	10.2	L Ordovician	Djupvik-1	2.0		Alum Shale
0.5	0.2	L Ordovician	Hällekis-1	9.9		Tøyen Shale
	0.5	L Ordovician	Hällekis-1	17.3		Tøyen Shale
	14.5	Furongian	Hällekis-1	23.4		Alum Shale
	13.4	Furongian	Hällekis-1	30.4		Alum Shale
	11.4	M. Cambrian	Hällekis-1	35.8		Alum Shale
	10.2	M. Cambrian	Hällekis-1	39.8		Alum Shale
2.1	<2%	M. Ordovician	Albjära-1	99.6		Almelund Shale
	<1%	L Ordovician	Albjära-1	114.8		Tøyen Shale
	<1%	L Ordovician	Albjära-1	126.3		Tøyen Shale
	<1%	L Ordovician	Albjära-1	134.5		Tøyen Shale
	7.5	L Ordovician	Albjära-1	139.6		Alum Shale
	8.4	Furongian	Albjära-1	145.2		Alum Shale
	8.1	Furongian	Albjära-1	149.0		Alum Shale
	14.0	Furongian	Albjära-1	153.0		Alum Shale
	12.6	Furongian	Albjära-1	157.0		Alum Shale
1.9	<0.5%	Silurian	Lönstorp-1	30.2	Letgas I	Rastrites shale
	<0.5%	Silurian	Lönstorp-1	44.0	Letgas II	Rastrites shale
	0.4	Silurian	Lönstorp-1	54.0	Letgas III	Rastrites shale
	3.1	Silurian	Lönstorp-1	64.0	Letgas IV	Rastrites shale
	1.0	Silurian	Lönstorp-1	71.8	Letgas V	Rastrites shale
	<1%	Silurian	Lönstorp-1	80.1	Letgas VI	Rastrites shale

2.1. Lönstorp-1 and Albjära-1 samples

The samples were picked during drilling of the wells. Each sample consisted of an approximately 8 cm long core piece. The samples were sealed in metal cans and kept cool.

Head space and sorbed gas analysis was done by the Geological Survey of Denmark. Sorbed gas in the rock matrix was liberated by treating the sample with acid following the procedure outlined by Faber & Stahl (1983). Head space gas was measured by puncturing the can through a septum before opening.

2.2. Gislövshammar-2, Hällekis-1 and Djupvik-1 samples

The samples were picked at the drill site. The samples each consisted of 5-8 cm long core pieces. The samples were wrapped in aluminium foil and kept at -18 ^{o}C at the drill site. After a few days the samples were transferred to a container filled with liquid nitrogen at -196 ^{o}C following the recommended practice as described by Faber & Stahl (1983). The samples were transferred to Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) where the analyses were made according to the procedure outlined in Faber & Stahl (1983).

Free gas measurements were measured by allowing the deep frozen sample to equilibrate to room temperature in a sealed container. This fraction is equivalent to head space gas in lower pressure systems.

No specification was made on the method used for analysis of the shale bound gas content. The most likely method used is the standard acid procedure (Faber & Stahl, 1983) that was developed by the staff at the laboratory. This methods librates sorbed gas from the shale. The use of this methods is also strongly indicated by the presence of small amounts of unsaturated gasses such as ethene (C_2H_4) and propene (C_3H_6) in some of the samples (see full analysis of the gas composition in Appendix A). The source of these gases is likely from side-reactions during the acid treatment of the samples as part of the gas-desorption procedure of Faber & Stahl (1983) since the unsaturated gases are not stable over geological time. Alternatively the unsaturated gas stems from the drilling process (‘bit metamorphism’). This is however less likely since the drillings were made as diamond coring.

Other likely methods used by the laboratory are measurements of occluded gas. This gas type is librated by crushing of the sample using a ball mill. The difference on the resulting composition and isotope signature between the two gas measurements (sorbed versus occluded) is, however, not significant.

3. Results

3.1. Gas composition

Sorbed methane concentrations range from 118 to 23867 ppb (microgram per kg of rock) (Figure 2A). Head space gas content range from 3 to 13420 ppm (µL/L) (Figure 2B). The concentrations thus far exceed the threshold for background gas (20-50 ppb for C_1 and 2-5 ppb for the sum C_{2+}) as defined by Whiticar (1996).

The sorbed gas has a significantly higher content of high molecular weight hydrocarbon gas (C_2 to C_5) compared to head space gas (Figure 2).

The methane yield of the sorbed gas fraction appears to be independent of the TOC content of the sample. Highest sorbed gas yields are thus measured in the Rastrites shale (TOC <1%) and lowest yields are measured in an Alum Shale sample which contains 6% TOC. Instead yields appears to be related to the thermal rank as depicted by the ‘vitrinite-like’ reflectance value. The mature samples from the Gislövshammar-2, Albjära-1 and Lönstorp-1 wells thus have approximately 10 time higher yields compared to yields in the immature samples from the Hällekis-1 and Djupvik-1 wells.

Full presentation of the analysis are given in Appendix A and B.

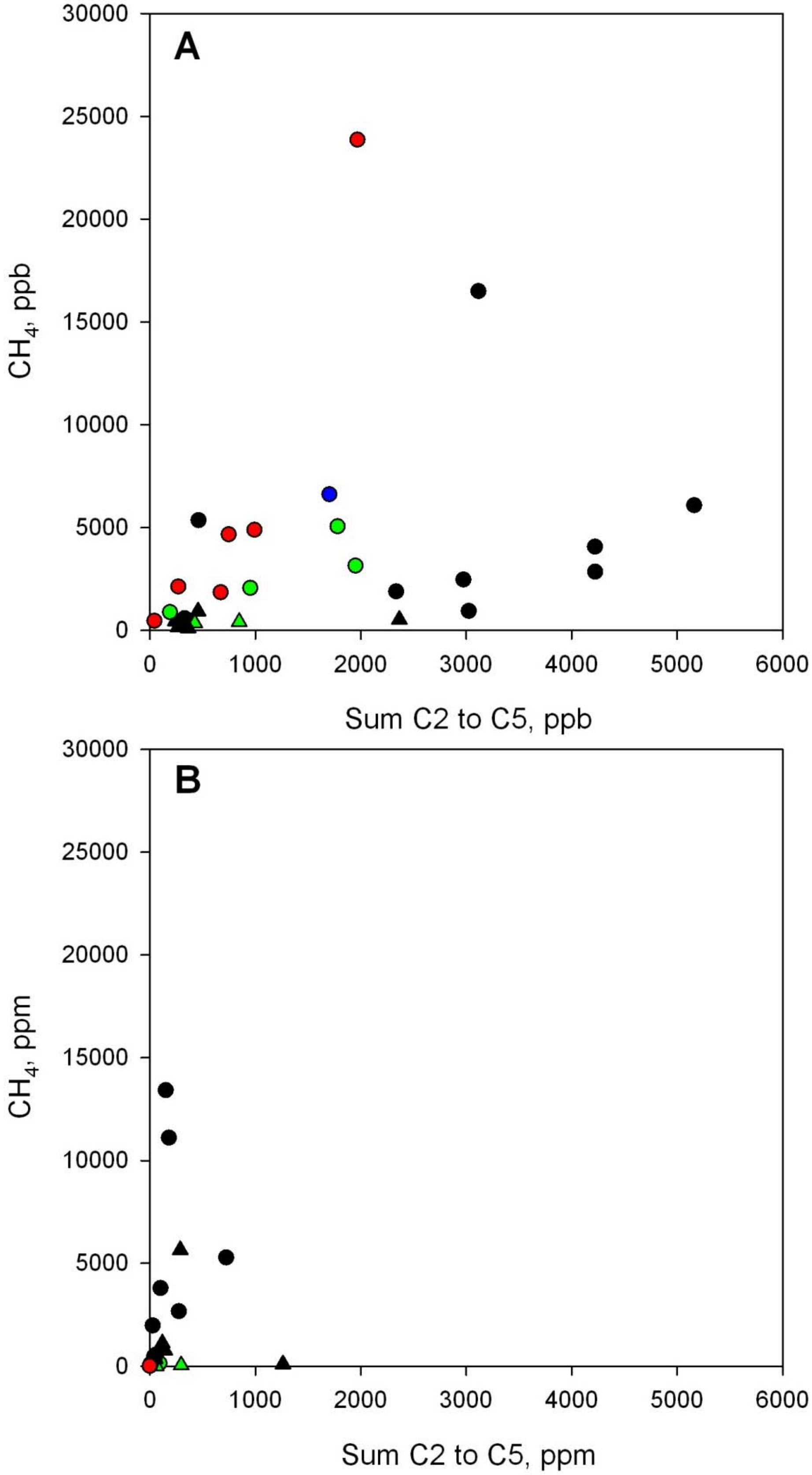

Figure 2. CH_4 yield versus the sum of the C_2 to C_5 yields for (A) sorbed gas and (B) head space gas. Legend: circles: thermal mature, triangles: thermal immature. Fill colour: black: Alum Shale, green: Tøyen Shale, blue: Almelund Shale, red: Rastrites shale.

3.2. Bernard diagram

The various data have been plotted in the classical Bernard diagram (Figure 3) to help determine the origin of the hydrocarbon gases.

Sorbed gas samples plots within the field of ‘thermogenic gas’ though mixing with microbial gas and is indicated by a more depleted methane isotope signature for some samples (Figure 3A).

Head space gas samples has a more depleted methane isotope signature and about 10 to 100 time higher $C_1/(C_2+C_3)$ ratios than the sorbed gas (Figure 3B). The kinetic isotope fractionation between desorbed and head space gas can range up to about 5‰ (Xia & Tang 2012). The more negative isotope signature of the head space gas relative to sorbed gas cannot solely be explained by kinetic fractionation. The head space gas thus has a more clearly expressed microbial signature than the sorbed gas. The microbial methane probably formed by low temperature degradation of the organic-rich rocks.

The head space gas composition appears to lie on a straight line in the Bernard diagram (Figure 3B). The ‘straight line mode’ indicates that the gas composition might be controlled by oxidation processes (Whiticar 1996).

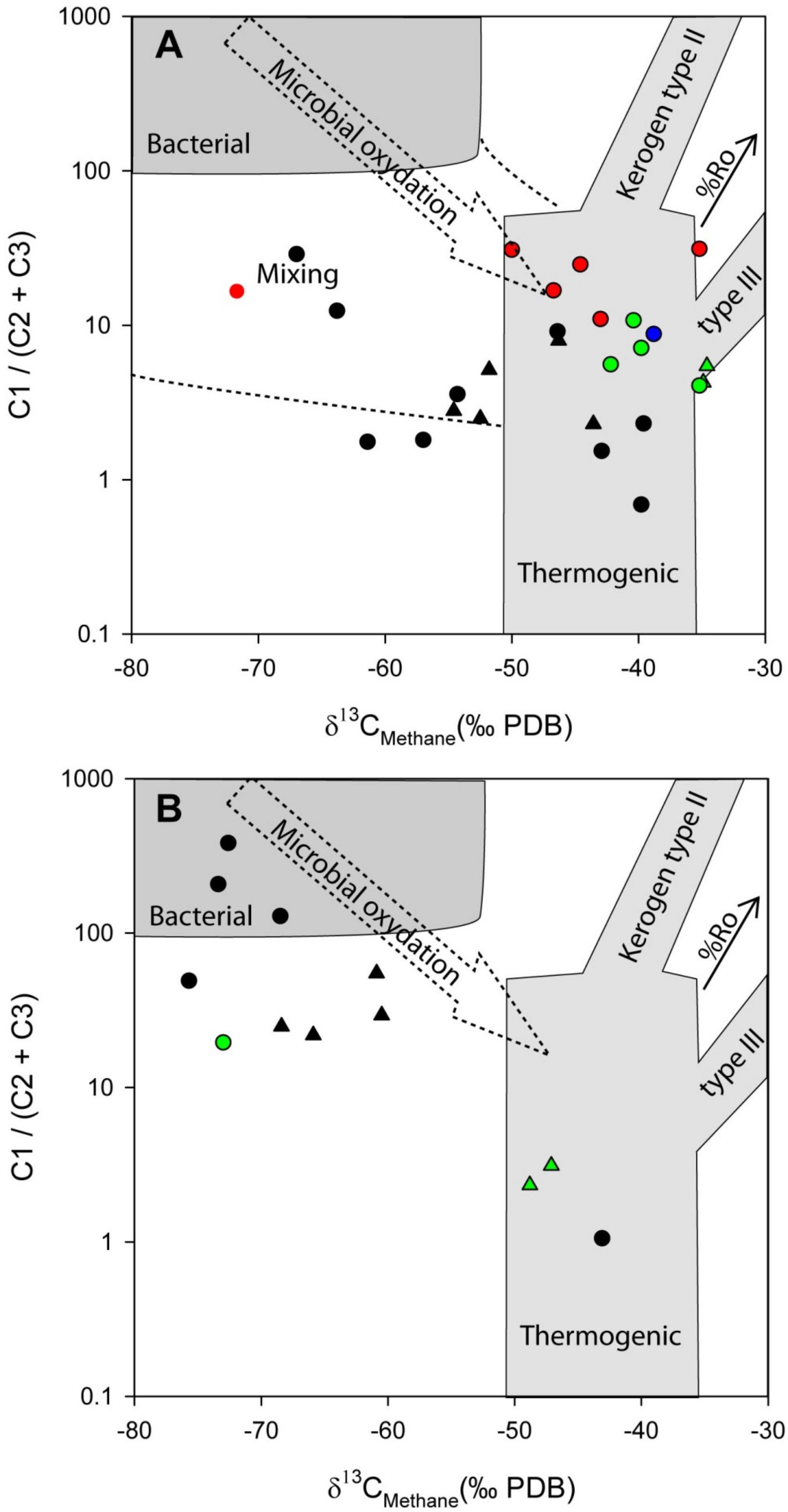

Figure 3. A 'Bernard diagram' showing the ratio $C_1/(C_2+C_3)$ (vol.%) versus $\delta^{13}C_{CH4}$ for (A) sorbed gas and (B) head space gas (B). Legend as in Figure 2. The diagram is after Whiticar (1996).

3.3. $\delta^{13}C_{C2H6}$ versus $\delta^{13}C_{CH4}$

The ethane versus methane isotope signature of sorbed and head space gas shows no relationship to each other (Figure 4). A relationship, however, is only expected for instantaneously generated and co-existing ethane and methane since the isotopic fractionation between the different gasses is a function of the thermal rank of the kerogen/precursor to the hydrocarbons (Berner & Faber 1996, Whiticar 1996).

The lack of relationship between the isotope signature of ethane and methane indicates that the original gas composition has been modified. As indicated by the Bernard diagram (Figure 3) the isotopic variation can be explained by mixing of bacterial derived methane with thermogenic generated gas.

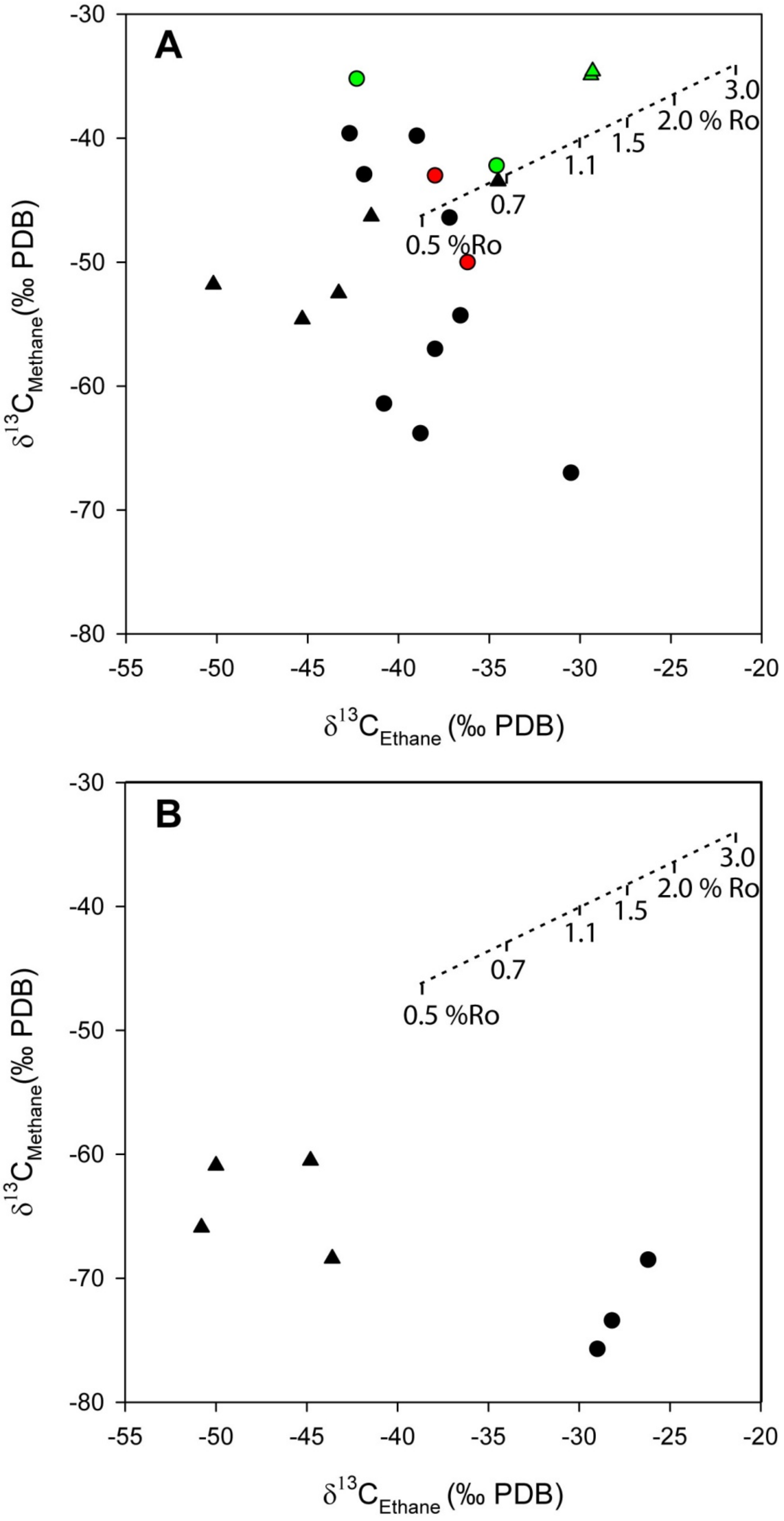

Figure 4. Relationship between $\delta^{13}C_{C2H6}$ and $\delta^{13}C_{CH4}$ for (A) sorbed gas, and (B) head space gas (B). Legend as in Figure 2. The relationship between the isotope signature for co-genetic ethane and propane (broken line) and vitrinite equivalent values (0.5 - 3.0 %Ro) are from Whiticar (1996) and is shown for reference.

3.4. $\delta^{13}C_{C2H6}$ versus $\delta^{13}C_{C3H8}$

The relationship between isotope signature of hydrocarbon gas and the maturity of the kerogen is more reliable using higher molecular weight hydrocarbon gases such as ethane, propane than by using methane. The reason is that methane may have several different sources and is involved in many bacterial processes (Whiticar 1996). Microbial generated C_{2+} gas has been identified in the literature (Whiticar 1996) but only in extremely low quantities. If present such occurrence are not likely to influence the isotopic signature of the samples reported here.

It is expected based on empiric data and based on isotope kinetic considerations that ethane and propane isotope signatures should become less negative with increasing maturation rank (Berner & Faber 1996, Whiticar 1996). This is also the general trend in the Alum Shale data (Figure 5).

Alum Shale samples from the thermally immature Hällekis-1 well plot with relatively depleted isotope signatures of propane and ethane compared to Alum Shale samples from the thermally mature Gislövshammar-2 well. The Gislövshammar-2 samples exhibit, however, a considerably large range in propane isotope composition ranging from -22 to -39‰ PDB. The Alum Shale from the thermally immature Djupvik-1 well plot within the variation field defined by the Gislövshammar-2 samples (Figure 5).

Isotope data from Polish oil and gas fields reservoired in Mid Cambrian sandstone and sourced by Alum Shale equivalent mudstones have been included in Figure 5. The Polish samples plot at intermediate isotope signatures of ethane and propane. The Alum Shale in the area of the Polish oil and gas fields range between 0.8 and 1.4% Ro judged from the Alum Shale maturity map published by Buchardt et al. (1997).

The isotopic signature of ethane versus propane defines a positive linear correlation (Figure 5). The regression line is, however, significantly different than the relationship between ethane and propane defined by Whiticar (1996). Although the gas analysis exhibit the same overall trend with more depleted ethane and propane isotope signatures with increasing maturation rank then the variation cannot be translated directly into maturity by using the Whiticar (1996) equation.

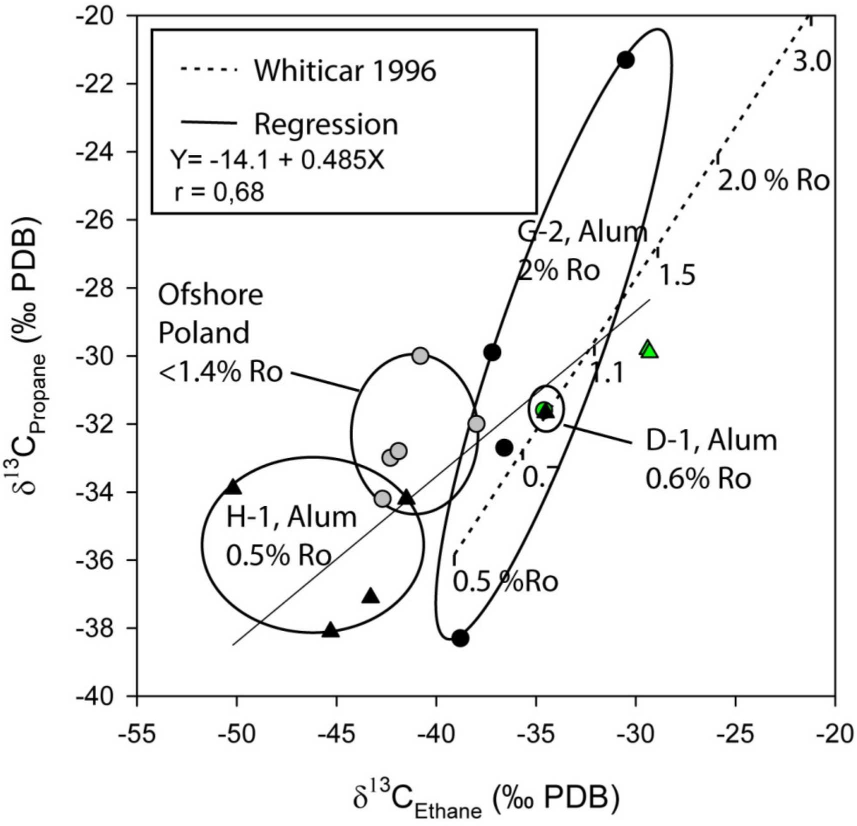

Figure 5. Relationship between $\delta^{13}C_{C2H6}$ and $\delta^{13}C_{C3H8}$. Legend as in Figure 2 with the addition that grey fill in circles represent gas samples from fields offshore North Poland that are sourced by Alum Shale (Kotarba 2010). The %Ro of the source for this gas is estimated from Buchardt et al. (1997). The relationship between isotope signature for co-genetic ethane and propane (broken line) and vitrinite equivalent values (0.5 - 3.0 %Ro) are from Whiticar (1996). The relationship is valid for kerogen type II with an average bulk kerogen isotopic composition of -30‰ PDB. The Alum Shale fulfils both criteria in being a typical type II kerogen and by having bulk kerogen that range between -29.5‰ - -30.5‰ PDB (Buchardt et al. 1986). Abbreviations: G-2: Gislövshammar-2; H-1: Hällekis-1; D-1: Djupvik-1. The linear regression is statistical significant on the 95% level.

3.5. Hydrogen isotopes

Hydrogen isotopes measured in combination with carbon isotopes of methane offers additional information on the sources of the natural gases and also on the processes that may have modified the composition (Whiticar 1996).

Figure 6 shows the hydrogen versus carbon isotope composition of methane (termed 'CD diagram'). The sorbed gases plot within the 'thermogenic' field stretching towards the 'bacterial carbonate reduction' field (Figure 6A).

The head space gas composition of the Alum Shale from the Gislövshammar-2 well all plot within the 'bacterial carbonate reduction' field suggesting that this type of microbial activity contributed to the gas composition (Figure 6B). Immature samples from the Tøyen Shale from the Hällekis-1 well plot in the mixing field between 'bacterial methyl type fermentation' and 'bacterial carbonate reduction'. This may suggest that different microbial activities dominate in thermally immature wells compared with those dominating in thermally mature wells.

Isotopic composition of CO_2 was measured on one sample from the Gislövshammar-2 well and on two samples from the Hällekis-1 well. The isotopic signature of the CO_2 range from -9.8 to +3.7 ‰ PDB and according to discrimination diagrams presented by Whiticar (1996) the measurements also indicates that both bacterial carbonate reduction and methyl fermentation processes were active in the shales.

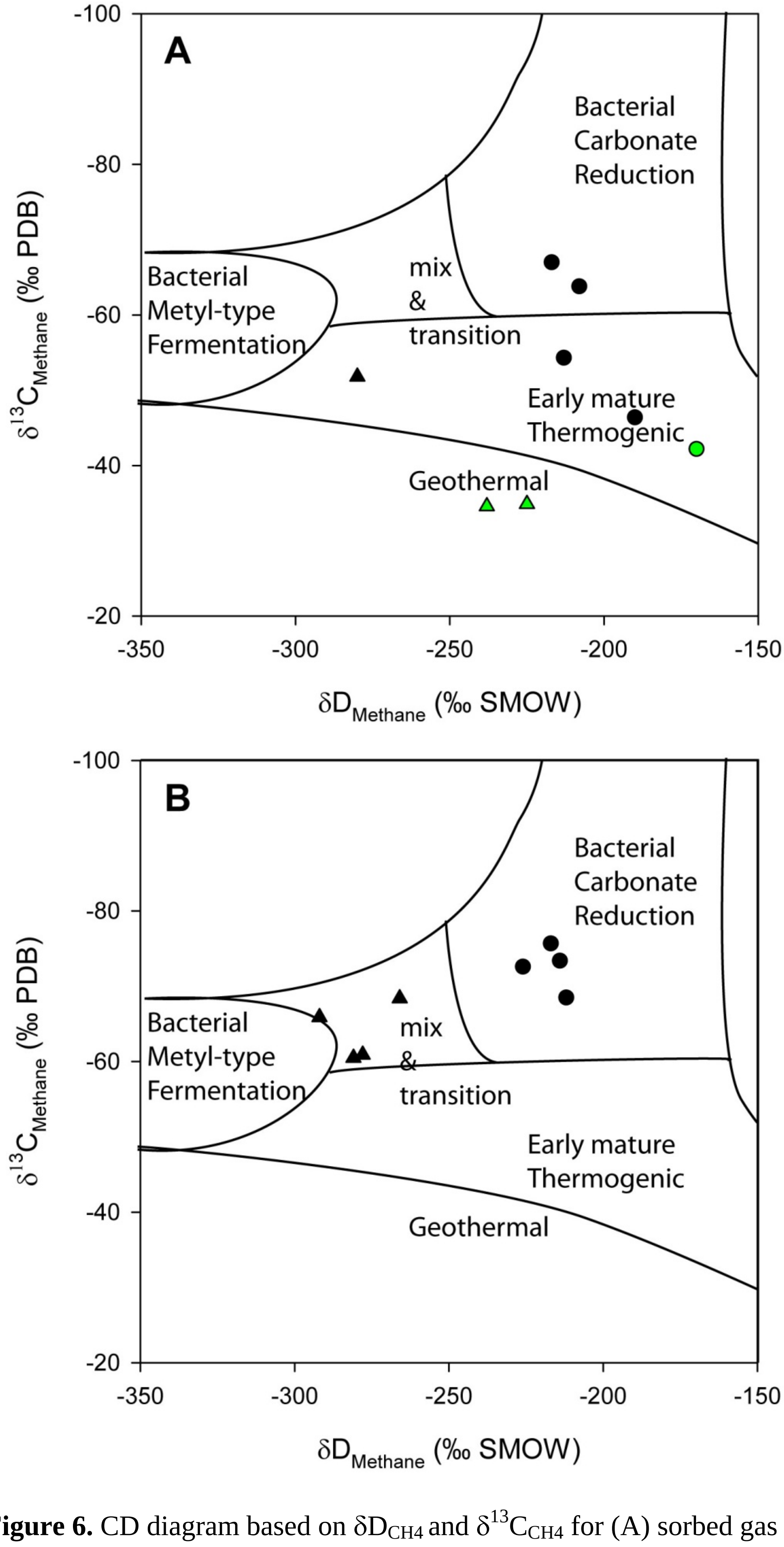

Figure 6. CD diagram based on δD_{CH4} and $\delta^{13}C_{CH4}$ for (A) sorbed gas and for (B) head space gas. Legend as in Figure 2. The isotope signatures of the various sources are from Whiticar (1996).

4. Conclusions

Shale samples picked from shallow scientific wells contain free and sorbed hydrocarbon gases with concentrations significantly above the background gas level.

The hydrocarbon gas constitutes a mixture of thermogenic generated gas and gas derived from microbial activity. The microbial methane may arise from both carbonate reduction and from methyl fermentation processes.

The ethane and propane isotopic signatures are positively correlated to each other. Gases in immature samples show the most depleted isotope signatures whereas gas in thermally mature samples has less depleted isotope signatures. Gas from Polish oil and gas fields sourced from the Alum Shale exhibit intermediated isotope compositions. This suggests that the isotopic signature may be used to evaluate the maturity rank of the source.

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6. Data included on CD

Attached to this report is a CD that contains the following documentation:

1. Folder: Literature. Pdf of public available literature cited in the report.
2. File: Appendix A and B.xlsx. Digital version of Appendix A and B
3. File: Gas_isotopes_GEUS_2012.xlsx. Complete data set of composition and isotope variation.
4. File: Composition and gas isotope signature of shale samples. Pdf of this report.

Appendix A: Sorbed gas composition and isotope signature

Composition and gas isotope signature of shale samples

Well	Depth	Sample	Formation	Laboratory	CH_4 %	C_2H_4 %	C_2H_6 %	C_3H_6 %	C_3H_8 %	I-C4 %	N-C4 %	DMP %	I-C5 %	N-C5 %	Sum %
Gislövshammar-2	19.8		Tøyen Shale	BGR	82.83	0.31	11.87	0.07	2.97	0.42	0.83	0.06	0.36	0.28	100
Gislövshammar-2	31.8		Alum Shale	BGR	74.16	0.24	14.85	0.2	5.85	1.16	1.98	0.03	0.8	0.73	100
Gislövshammar-2	44.5		Alum Shale	BGR	91.96	0.02	6.14	0	1.28	0.12	0.3	0.01	0.09	0.08	100
Gislövshammar-2	65.2		Alum Shale	BGR	96.22	0	3.07	0	0.26	0.13	0.12	0.01	0.11	0.08	100
Gislövshammar-2	88.3		Alum Shale	BGR	83.94	0	7.06	0	2.14	1.15	2.07	0.01	1.88	1.66	100
Djupvik-1	2.0		Alum Shale	BGR	41.94	3.13	8.57	4.19	9.46	5.93	9.54	3.31	4.96	8.98	100
Hällekis-1	9.9		Tøyen Shale	BGR	61	1.81	8.18	2.28	6.12	3.5	5.96	2.06	3.31	5.78	100
Hällekis-1	17.3		Tøyen Shale	BGR	71.35	1.14	8.42	1.58	4.67	2.11	3.98	1.14	2.01	3.59	100
Hällekis-1	23.4		Alum Shale	BGR	83.38	0.52	8.27	0.34	2.19	0.84	1.58	0.45	0.85	1.56	100
Hällekis-1	30.4		Alum Shale	BGR	81.1	0.24	14.95	0.14	0.77	0.41	0.98	0.18	0.37	0.38	100
Hällekis-1	35.8		Alum Shale	BGR	63.11	0.61	15.1	0.84	7.43	1.77	5.24	0.39	2.13	3.39	100
Hällekis-1	39.8		Alum Shale	BGR	50.99	0.9	13.65	1.02	6.78	3.56	7.07	1.01	5.98	9.04	100
Albjära-1	99.6		Almelund Shale	GEUS	89.18	0.02	8.54	0.00	1.63	0.18	0.29	0.05	0.07	0.04	100
Albjära-1	114.8		Tøyen Shale	GEUS	86.52	0.03	9.35	0.00	2.78	0.78	0.00	0.06	0.28	0.20	100
Albjära-1	126.3		Tøyen Shale	GEUS	90.87	0.02	7.24	0.00	1.22	0.14	0.18	0.09	0.14	0.09	100
Albjära-1	134.5		Tøyen Shale	GEUS	78.42	0.06	14.95	0.00	4.30	0.52	1.14	0.02	0.32	0.27	100
Albjära-1	139.6		Alum Shale	GEUS	67.89	0.15	23.04	0.00	6.31	0.56	1.54	0.00	0.28	0.23	100
Albjära-1	145.2		Alum Shale	GEUS	62.94	0.00	29.26	0.00	6.45	0.31	0.85	0.00	0.08	0.11	100
Albjära-1	149.0		Alum Shale	GEUS	59.21	0.01	30.57	0.00	8.00	0.41	1.42	0.00	0.15	0.21	100
Albjära-1	153.0		Alum Shale	GEUS	40.04	0.00	44.55	0.00	13.36	0.36	1.47	0.01	0.08	0.12	100
Albjära-1	157.0		Alum Shale	GEUS	63.74	0.00	27.39	0.00	7.82	0.17	0.70	0.03	0.05	0.09	100
Lönstorp-1	30.2	Letgas I	Rastrites shale	GEUS	94.75	0.14	2.64	0.00	0.44	0.10	0.08	0.13	1.18	0.56	100
Lönstorp-1	44.0	Letgas II	Rastrites shale	GEUS	91.19	0.01	7.16	0.00	1.15	0.12	0.24	0.01	0.06	0.07	100
Lönstorp-1	54.0	Letgas III	Rastrites shale	GEUS	95.78	0.00	3.33	0.00	0.54	0.06	0.12	0.07	0.00	0.10	100
Lönstorp-1	64.0	Letgas IV	Rastrites shale	GEUS	89.69	0.01	4.19	0.00	1.15	0.55	0.42	0.69	2.27	1.03	100
Lönstorp-1	71.8	Letgas V	Rastrites shale	GEUS	94.12	0.00	5.12	0.00	0.55	0.05	0.09	0.01	0.03	0.03	100
Lönstorp-1	80.1	Letgas VI	Rastrites shale	GEUS	96.48	0.00	2.72	0.00	0.37	0.04	0.06	0.01	0.19	0.13	100

Composition and gas isotope signature of shale samples

Well	Depth	Formation	CH_4 ppb	C_2H_4 ppb	C_2H_6 ppb	C_3H_6 ppb	C_3H_8 ppb	I-C4 ppb	N-C4 ppb	DMP ppb	I-C5 ppb	N-C5 ppb	C_2-C_5 ppb	C1/(Sum C2-C5)	C1/(Sum C1-C5)
Gislövshammar-2	19.8	Tøyen Shale	2062	14	554	5	203	38	75	7	40	31	953	2	0.68
Gislövshammar-2	31.8	Alum Shale	6086	34	2285	43	1320	345	589	15	295	270	5162	1	0.54
Gislövshammar-2	44.5	Alum Shale	16497	6	2065		631	78	195	8	73	65	3115	5	0.84
Gislövshammar-2	65.2	Alum Shale	5356		320		40	28	22	3	28	20	461	12	0.92
Gislövshammar-2	88.3	Alum Shale	588		93		41	29	53	3	59	52	330	2	0.64
Djupvik-1	2.0	Alum Shale	531	69	203	139	329	272	438	189	283	512	2365	0	0.18
Hällekis-1	9.9	Tøyen Shale	422	22	106	41	116	88	149	64	103	180	847	0	0.33
Hällekis-1	17.3	Tøyen Shale	356	10	79	21	64	38	72	26	45	81	426	1	0.46
Hällekis-1	23.4	Alum Shale	455	5	85	5	33	17	31	11	21	38	241	2	0.65
Hällekis-1	30.4	Alum Shale	934	5	323	4	24	17	41	9	19	20	457	2	0.67
Hällekis-1	35.8	Alum Shale	163	3	73	6	53	17	49	5	25	39	267	1	0.38
Hällekis-1	39.8	Alum Shale	118	4	59	6	43	30	59	11	62	94	364	0	0.24
Albjära-1	99.6	Almelund Shale	6613	2	1188		332	48	79	17	25	14	1702	4	0.95
Albjära-1	114.8	Tøyen Shale	5060	3	1025		447	166	0	15	74	53	1780	3	0.92
Albjära-1	126.3	Tøyen Shale	887		133		33	5	7	4	6	4	191	5	0.96
Albjära-1	134.5	Tøyen Shale	3147	5	1125		475	75	166	3	58	50	1951	2	0.87
Albjära-1	139.6	Alum Shale	4067	16	2588		1040	122	334	1	75	63	4221	1	0.79
Albjära-1	145.2	Alum Shale	1893	0	1650		534	34	92	0	11	15	2336	1	0.78
Albjära-1	149.0	Alum Shale	2853	1	2763		1060	71	249	1	34	47	4223	1	0.73
Albjära-1	153.0	Alum Shale	947		1975		869	31	126	1	9	13	3024	0	0.52
Albjära-1	157.0	Alum Shale	2467		1988		832	24	98	5	9	16	2972	1	0.75
Lönstorp-1	30.2	Rastrites shale	4673	12	244		59	17	14	29	262	123	748	6	0.98
Lönstorp-1	44.0	Rastrites shale	4893	1	720		170	23	46	2	15	16	992	5	0.97
Lönstorp-1	54.0	Rastrites shale	461		30		7	1	2	2		2	44	10	0.98
Lönstorp-1	64.0	Rastrites shale	1853		163		65	41	31	64	211	96	671	3	0.97
Lönstorp-1	71.8	Rastrites shale	2133		218		34	4	7	1	3	3	271	8	0.98
Lönstorp-1	80.1	Rastrites shale	23867	1	1263		253	32	53	15	207	146	1968	12	0.99

Composition and gas isotope signature of shale samples

Well	Depth	Formation	$\delta^{13}CH_4$ ‰ PDB	$\delta^{13}C_2H_6$ ‰ PDB	$\delta^{13}C_3H_8$ ‰ PDB	δDCH_4 ‰ SMOW
Gislövshammar-2	19.8	Tøyen Shale	-42.2	-34.6	-31.6	-170
Gislövshammar-2	31.8	Alum Shale	-54.3	-36.6	-32.7	-213
Gislövshammar-2	44.5	Alum Shale	-63.8	-38.8	-38.3	-208
Gislövshammar-2	65.2	Alum Shale	-67	-30.5	-21.3	-217
Gislövshammar-2	88.3	Alum Shale	-46.4	-37.2	-29.9	-190
Djupvik-1	2.0	Alum Shale	-43.4	-34.5	-31.7	
Hällekis-1	9.9	Tøyen Shale	-34.9	-29.4	-29.8	-225
Hällekis-1	17.3	Tøyen Shale	-34.6	-29.3	-29.9	-238
Hällekis-1	23.4	Alum Shale	-46.3	-41.5	-34.2	
Hällekis-1	30.4	Alum Shale	-51.8	-50.2	-33.9	-280
Hällekis-1	35.8	Alum Shale	-54.6	-45.3	-38.1	
Hällekis-1	39.8	Alum Shale	-52.5	-43.3	-37.1	
Albjära-1	99.6	Almelund Shale	-38.8			
Albjära-1	114.8	Tøyen Shale	-39.8			
Albjära-1	126.3	Tøyen Shale	-40.4			
Albjära-1	134.5	Tøyen Shale	-35.2			
Albjära-1	139.6	Alum Shale	-39.6			
Albjära-1	145.2	Alum Shale	-61.4			
Albjära-1	149.0	Alum Shale	-42.9			
Albjära-1	153.0	Alum Shale	-39.8			
Albjära-1	157.0	Alum Shale	-57			
Lönstorp-1	30.2	Rastrites shale	-50			
Lönstorp-1	44.0	Rastrites shale	-43			
Lönstorp-1	54.0	Rastrites shale	-44.6			
Lönstorp-1	64.0	Rastrites shale	-46.7			
Lönstorp-1	71.8	Rastrites shale	-71.7			
Lönstorp-1	80.1	Rastrites shale	-35.2			

Appendix B: Free gas composition and isotope signature

Composition and gas isotope signature of shale samples

Laboratory	Well	Depth	Formation	CH_4 %	C_2H_4 %	C_2H_6 %	C_3H_6 %	C_3H_8 %	I-C4 %	N-C4 %	DMP %	I-C5 %	N-C5 %	Sum %
BGR	Gislövshammar-2	19.8	Tøyen Shale	83.36	0.99	2.44	0.88	1.82	1.4	2.87	0.99	1.73	3.52	100
BGR	Gislövshammar-2	31.8	Alum Shale	95.67	0.1	1.31	0.19	0.64	0.4	0.69	0.14	0.37	0.48	100
BGR	Gislövshammar-2	44.5	Alum Shale	99.45	0.01	0.47		0.01		0.01		0.01	0.02	100
BGR	Gislövshammar-2	65.2	Alum Shale	99.19		0.76		0.01		0.01		0.01	0.01	100
BGR	Gislövshammar-2	88.3	Alum Shale	99.56		0.15		0.11	0.1	0.05		0.04	0.04	100
BGR	Djupvik-1	2.0	Alum Shale	21.27	2.72	8.02	5.4	12.1	8.9	15.5	5.5	8.26	12.4	100
BGR	Hällekis-1	9.9	Tøyen Shale	34.38	2.37	6.13	4	8.6	6.7	12.8	4.43	7.85	12.8	100
BGR	Hällekis-1	17.3	Tøyen Shale	33.11	3.31	4.55		6.06	5.8	12.3	4.35	10.6	19.4	99
BGR	Hällekis-1	23.4	Alum Shale	97.72	0.04	1.69	0.03	0.09	0.1	0.11	0.04	0.01	0.15	100
BGR	Hällekis-1	30.4	Alum Shale	94.4	0.19	2.6	0.12	0.62	0.4	0.79	0.23	0.44	0.72	101
BGR	Hällekis-1	35.8	Alum Shale	95.17	0.04	4.24		0.12	0.1	0.12	0.03	0.08	0.15	100
BGR	Hällekis-1	39.8	Alum Shale	94.52		3.62		0.19	0.2	0.47	0.07	0.37	0.55	100
GEUS	Albjära-1	99.6	Almelund Shale	88.15		11.85								
GEUS	Albjära-1	114.8	Tøyen Shale	95.24		4.76								
GEUS	Albjära-1	126.3	Tøyen Shale	96.57		3.43								
GEUS	Albjära-1	134.5	Tøyen Shale	89.45		7.69		2.86						
GEUS	Albjära-1	139.6	Alum Shale	90.65		5.72		0.41	0.01	3.20				
GEUS	Albjära-1	145.2	Alum Shale	97.38		2.42		0.18		0.02				
GEUS	Albjära-1	149.0	Alum Shale	90.29		8.98		0.68		0.05				
GEUS	Albjära-1	153.0	Alum Shale	91.92		7.43		0.65						
GEUS	Albjära-1	157.0	Alum Shale	92.20		7.35		0.45						
GEUS	Lönstorp-1	30.2	Rastrites shale	95.45		4.55								
GEUS	Lönstorp-1	44.0	Rastrites shale	96.23		3.77								
GEUS	Lönstorp-1	54.0	Rastrites shale	100.00										
GEUS	Lönstorp-1	64.0	Rastrites shale	94.74		5.26								
GEUS	Lönstorp-1	71.8	Rastrites shale	93.33		6.67								
GEUS	Lönstorp-1	80.1	Rastrites shale	100.00										

Composition and gas isotope signature of shale samples

Well	Depth	Formation	CH_4 ppm	C_2H_4 ppm	C_2H_6 ppm	C_3H_6 ppm	C_3H_8 ppm	I-C4. ppm	N-C4. ppm	DMP. ppm	I-C5. ppm	N-C5. ppm	C_2-C_5 ppm	C1/(C2_C5)
Gislövshammar-2	19.8	Tøyen Shale	137	3	8	4	8	8	17	7	13	26	91	2
Gislövshammar-2	31.8	Alum Shale	5278	10	136	28	97	80	138	35	92	119	725	7
Gislövshammar-2	44.5	Alum Shale	13420	2	119	0	4	5	5	0	6	12	151	89
Gislövshammar-2	65.2	Alum Shale	11108	0	160	0	3	4	4	0	5	5	181	61
Gislövshammar-2	88.3	Alum Shale	1972	0	6	0	6	4	4	0	4	4	28	70
Djupvik-1	2.0	Alum Shale	100	22	71	67	157	152	263	116	175	261	1262	0
Hällekis-1	9.9	Tøyen Shale	45	5	15	14	31	32	61	23	46	75	297	0
Hällekis-1	17.3	Tøyen Shale	8	1	2	0	4	5	11	5	12	22	61	0
Hällekis-1	23.4	Alum Shale	5652	4	183	5	14	13	23	10	2	39	289	20
Hällekis-1	30.4	Alum Shale	770	3	40	3	14	12	23	8	16	26	142	5
Hällekis-1	35.8	Alum Shale	1111	1	93	0	4	2	5	2	4	8	118	9
Hällekis-1	39.8	Alum Shale	353	0	25	0	2	3	6	1	6	9	52	7
Albjära-1	99.6	Almelund Shale	9		1.21								1,21	7
Albjära-1	114.8	Tøyen Shale	3		0.15								0,15	20
Albjära-1	126.3	Tøyen Shale	31		1.1								1,1	28
Albjära-1	134.5	Tøyen Shale	5		0.43		0.16						0,59	8
Albjära-1	139.6	Alum Shale	2661		168		12.1	0.41	94				274,5	10
Albjära-1	145.2	Alum Shale	3787		94		7.04	0.13	0.6				101,8	37
Albjära-1	149.0	Alum Shale	555		55.2		4.21		0.3				59,71	9
Albjära-1	153.0	Alum Shale	476		38.5		3.35						41,85	11
Albjära-1	157.0	Alum Shale	125		9.97		0.61						10,58	12
Lönstorp-1	30.2	Rastrites shale	12.6		0.6								0,6	21
Lönstorp-1	44.0	Rastrites shale	5.1		0.2								0,2	26
Lönstorp-1	54.0	Rastrites shale	3.3										0	
Lönstorp-1	64.0	Rastrites shale	3.6		0.2								0,2	18
Lönstorp-1	71.8	Rastrites shale	5.6		0.4								0,4	14
Lönstorp-1	80.1	Rastrites shale	3.8										0	

Composition and gas isotope signature of shale samples

Well	Depth	Formation	$\delta^{13}CH_4$ ‰ PDB	$\delta^{13}C_2H_6$ ‰ PDB	$\delta^{13}CO_2$ ‰ PDB	δDCH_4 ‰ SMOW	Bernard
Gislövshammar-2	19.8	Tøyen Shale	-73				20
Gislövshammar-2	31.8	Alum Shale	-75.7	-29	-9.5	-217	49
Gislövshammar-2	44.5	Alum Shale	-73.4	-28.2		-214	207
Gislövshammar-2	65.2	Alum Shale	-68.5	-26.2		-212	129
Gislövshammar-2	88.3	Alum Shale	-72.6			-226	383
Djupvik-1	2.0	Alum Shale	-43.1				1
Hällekis-1	9.9	Tøyen Shale	-48.8				2
Hällekis-1	17.3	Tøyen Shale	-47.1				3
Hällekis-1	23.4	Alum Shale	-60.9	-50	-9.8	-278	55
Hällekis-1	30.4	Alum Shale	-60.5	-44.8	3.7	-281	29
Hällekis-1	35.8	Alum Shale	-65.9	-50.8		-292	22
Hällekis-1	39.8	Alum Shale	-68.4	-43.6		-266	25
Albjära-1	99.6	Almelund Shale					
Albjära-1	114.8	Tøyen Shale					
Albjära-1	126.3	Tøyen Shale					
Albjära-1	134.5	Tøyen Shale					
Albjära-1	139.6	Alum Shale					
Albjära-1	145.2	Alum Shale					
Albjära-1	149.0	Alum Shale					
Albjära-1	153.0	Alum Shale					
Albjära-1	157.0	Alum Shale					
Lönstorp-1	30.2	Rastrites shale					
Lönstorp-1	44.0	Rastrites shale					
Lönstorp-1	54.0	Rastrites shale					
Lönstorp-1	64.0	Rastrites shale					
Lönstorp-1	71.8	Rastrites shale					
Lönstorp-1	80.1	Rastrites shale					