Biogenic gas(?) in fluid inclusions from sandstones in contact with oil-mature coals

Sverre Ekrene Ohm and Dag A. Karlsen

ABSTRACT

This study was initiated to investigate if coals on the Norwegian offshore continental shelf (NOCS) expel petroleum and in which form. The results revealed that equally isotopically light methane (C_1) was released from fluid inclusions in sandstones and from adjacent coal (-60.9 to -72.7‰). The analyzed samples were collected from cored northern North Sea and mid-Norwegian shelf wells in the depth interval 3924–5095 m (12,874–16,716 ft). The vitrinite reflectance (R_o) values of the coals range between 0.53 and 1.12%, with most values between 0.8 and 1.0%. Only minor C_{2+} fractions were released showing much heavier gas isotope signatures similar to values seen in our in-house NOCS gas isotope database for comparable depths. The similar light C_1 isotope values released both from the coals and from the fluid inclusions in the adjacent sandstones suggest that the origin of the gas is the coal, and that no isotope fractionation occurs during release of the gas in nature. Traditional isotope interpretation schemes suggest the C_1 to have a biogenic origin, whereas recently published data also show the possibility for an early mature thermogenic origin.

The isotope values represent averages of the total gas released from all the individual disintegrated fluid inclusions in each sample. These did not form simultaneously, but during multiple events potentially covering several million years. The release of isotopically light C_1 proves gas presence in the sandstone at the time of fluid-inclusion formation. We therefore speculate that significant volumes of isotopically light C_1 have been expelled from the analyzed coals over time.

The expelled isotopically light C_1 may mix with mature thermogenically produced gas and skew the overall methane isotope values of gas accumulations toward lighter values, thus explaining the isotopically lighter-than-expected gas accumulations on the NOCS (e.g., Troll, Frigg, and Draugen fields).

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INTRODUCTION

Isotope Values of Coal Gases: Traditional View

According to classic coal gas isotope literature (cf. Stahl et al., 1977, 1981; Schoell, 1983; Whiticar, 1994, 1996), gas expelled from oil-mature coals is isotopically heavy (cf. Whiticar, 1996: type III kerogen gives $\delta^{13}C_1$ of -46 to -35‰ at R_o of 0.5 and 2.5%, respectively, and type II kerogen gives $\delta^{13}C_1$ of -37 to -20‰ at R_o of 0.5 and 3.0%, respectively). However, we suspect the database for these articles to be strongly influenced by Westphalian coals and their equivalents, which have experienced a complex burial history (cf. Price, 1983, 1985). Huge volumes of gas in the southern gas basin of the North Sea are believed to have been sourced from these coals (Cornford, 1984). Schenk et al. (1997) reported that the volume of gas in traps of Rotliegend (Permian) age only makes up about 0.1% of the cumulative amount of gas liberated from Westphalian coals during burial. This suggests that the gas charge in these traps today, in terms of composition and $\delta^{13}C$ values, is reflected only by the most mature gas liberated recently from the coals and not by the accumulated isotopic average.

Isotopically light C_1 is commonly associated with coalbed C_1 production (Scott et al., 1994; Smith and Pallasser, 1996; Boreham et al., 1998; Smith, 1999; Boreham et al., 2001; Faiz, 2004). This gas is commonly generated by secondary biogenic processes, which are triggered by bacterial activity resulting from methanogens being introduced to permeable coal beds by meteoric water (Scott et al., 1994). The bacteria are thus introduced to the coal beds after burial, coalification, and subsequent uplift and erosion of basin margins conversely to primary biogenic gases (Scott and Kaiser, 1993).

C_1 in Coals

Sedimentation of plant material initiates biochemical processes forming peat, and later, upon subsidence and burial when biochemical processes no longer give rise to peat formation, geochemical coal-forming processes take over, with anthracite as an end-product (Tissot and Welte, 1984). During the peatification and early coalification processes, considerable amounts of biogenic gas can be generated (Hunt, 1979; Faiz, 2004), of which C_1 requires the action of a suite of microbes including methanogens (Smith and Pallasser, 1996; Faiz, 2004). Most of the known methanogens are active up to temperatures of approximately 75°C (167°F), after which the reservoir becomes sterilized (Wilhelms et al., 2001). Biogenic C_1 are, however, also described to be formed by thermophilic methanogens at temperatures above 100°C (212°F) (Welhan and Craig, 1979; Knurr et al., 1991), but the relative importance of this mechanism is uncertain. C_1 produced by bacterial activity is described as being isotopically light (Bernard et al., 1978; Schoell, 1983; Faber and Stahl, 1984; Whiticar, 1994). It can, however, have a wide range in $\delta^{13}C$ values (-40 to -110‰), depending on the isotope value of the precursor organic material (Faiz, 2004).

During burial, peat transforms successively to high-rank bituminous coal and compacts by, on average, 11 times (Ryer and Langer, 1980). In this process, water and gases are expelled. Coals, however, have a tremendous capacity to adsorb generated hydrocarbons and, therefore, act as both a source and as a reservoir (Hunt, 1995). The adsorption capacity of coal increases with increasing pressure and rank, and each gas component has unique sorption characteristics. For example, C_2 and CO_2 are strongly sorbed to coal, whereas C_1 and N_2 are less strongly sorbed (Arri et al., 1992; Scott et al., 1994). This complicates straightforward predictions of the released gas isotope composition during the early and intermediate part of the coalification window.

Coals have a very broad activation energy distribution (cf. Tissot et al., 1987). Hence, some thermocatalytic cracking is likely to occur very early, at shallow depths and/or low temperatures, even before the oil window. Little is known about the carbon isotope composition of this early thermogenic C_1. Models for release of isotopically light C_1 from early mature humic organic matter have, however, been described (Stroganov, 1973; Monnier et al., 1983; Galimov, 1988). Galimov (1988) also suggests that humic organic matter has a high C_1-generating potential at low maturity.

Coalbed methane is being produced worldwide. Scott et al. (1994) argue that most of the biogenic gases found in coal beds are secondary biogenic gases.

Aim of the Study

The study was initiated to investigate if coals on the mid-Norwegian shelf and in the northern North Sea had expelled petroleum. The background for this was the ongoing discussion, over several years, of the source for the proven petroleum in the mid-Norwegian shelf area (see below). Wells, which cored Lower to Middle Jurassic (Åre and Tilje-Brent Formation) intervals and whose sandstone and coal layers are in contact, were sampled (Figure 1; Table 1). Gas was liberated from fluid inclusions and coals and then analyzed for molecular and carbon isotope compositions. The isotopic similarity between the fluid-inclusion gas and gas liberated from the coals strongly suggested that the inclusion gas originated from the coals. Thus, the original question of the study was answered: the coals had expelled gas.

The isotopically light methane (C_1) values (-60.9 to -72.7‰), measured both in the fluid-inclusion gas and in the gas liberated from the coals, were unexpected. Several questions arose from our observations, not all of which could be satisfactorily answered, but which will be addressed in this article:

- Is isotopic light C_1 in gas accumulations, reported elsewhere, related to coal?
- Could the isotopically light fluid-inclusion C_1 be an artificial effect of fractionation during migration out of the coals?
- Is the C_1 in the fluid inclusions biogenic, or could there be other sources?
- Is there a relationship between the recorded gas isotope values and the different coals analyzed?
- Can our observations contribute to our understanding of the origin of gas on the Norwegian offshore continental shelf (NOCS)?
- What are the quantities of isotopically light gas released in the temperature range 80–100°C (176–212°F) where quartz fluid-inclusion formation is initiated?
- What could be the implications of these findings to our understanding of the total gas budget in the petroleum system of the NOCS and elsewhere?

Petroleum from Coals on the Mid-Norwegian Continental Shelf: A Review

The hydrocarbon expulsion products from the ubiquitous Lower to Middle Jurassic coals on the NOCS have been debated over the last 20 yr. The gas and oil accumulations discovered in the Norwegian Sea off mid-Norway were initially argued to stem from the Lower to Middle Jurassic Åre Formation coals (Thompson et al., 1985; Heum et al., 1986; Cohen and Dunn, 1987; Ungerer et al., 1987; Mo et al., 1989; Espitalié et al., 1991; Forbes et al., 1991), mainly based on the results of basin modeling, which suggested that not enough mature Late Jurassic Spekk Formation source rock existed in the region to account for all of the petroleum discovered.

Karlsen et al. (1995) did not find any geochemical evidence for the oils and condensates of the region to stem from coals and concluded that type II kerogen of the Spekk Formation source rock is the source for the C_{15+} fraction. Similarly, light hydrocarbon studies by Dale (1997) and Odden et al. (1998) also concluded that the oil originated from marine type II shales. Patience (2002), concurring with this view, questioned why no sign was found of isotopically heavy coal-derived gas in the region. In a series of detailed studies on traps in the region, it was concluded that no evidence was found for

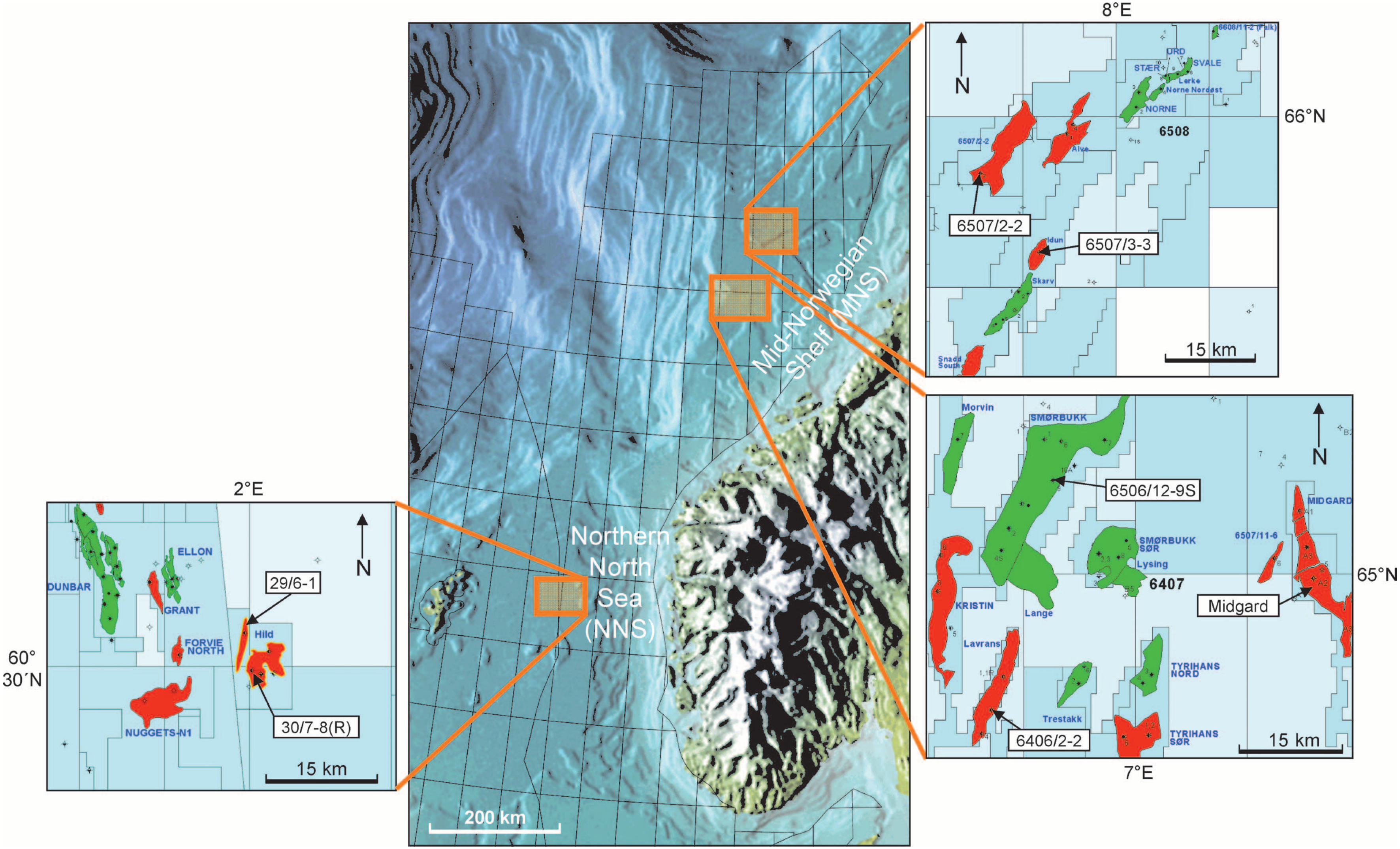


Figure 1. Location map of the NOCS. Oil fields are colored green, whereas gas fields are colored red. The sampled wells are highlighted.

Table 1. Data Set Grouped into Corresponding Sandstone-Coal Sample Pairs*

			Sample Depth		Formation	Formation		
Sample ID**	Well	Field	(m)	(ft)	Chronostratigraphy	Lithostratigraphy	Lithology	R_o (%)
2	29/6-1		4265.5	13,994	M. Jurassic	Brent	sst[†]	
3			4265.6	13,995	M. Jurassic	Brent	Coal	1.12
4	30/7-8	Hild	4107	13,474	M. Jurassic	Brent	sst	
5			4107.2	13,475	M. Jurassic	Brent	Coal	1.03
10			4123.5	13,528	M. Jurassic	Brent	sst	
9			4123.5	13,528	M. Jurassic	Brent	Coal	1.02
11			4128.9	13,546	M. Jurassic	Brent	sst	
8	30/7-8R	Hild	4116.5	13,505	M. Jurassic	Brent	sst	
7			4116.6	13,506	M. Jurassic	Brent	Coal	1.03
13	6406/2-2		5092.0	16,706	E. Jurassic	Tilje	sst	
12			5095.0	16,716	E. Jurassic	Tilje	shale	1.36
30	6506/12-9S	Smørbukk	4707.5	15,444	E. Jurassic	Tilje	sst	
29			4707.7	15,445	E. Jurassic	Tilje	Coal	0.96
17	6507/2-2		3924.5	12,876	E. Jurassic	Tilje(?)-Åre	Coal	0.86
18			3927.6	12,886	E. Jurassic	Tilje(?)-Åre	sst	
19			3927.6	12,886	E. Jurassic	Tilje(?)-Åre	sst	
20			3928.9	12,890	E. Jurassic	Tilje(?)-Åre	sst	
21			3929.4	12,892	E. Jurassic	Tilje(?)-Åre	Coal	0.82
22	6507/3-3	Idun	3381.3	11,093	M. Jurassic	Garn	sst	
23			3381.6	11,094	M. Jurassic	Garn	Coal	0.53
24			3383.5	11,100.6	M. Jurassic	Garn	sst	
25			3383.9	11,101.7	M. Jurassic	Garn	Coal	
26			3399.0	11,151.4	M. Jurassic	Garn	sst	

*Data show well numbers, name of corresponding field, if any, stratigraphic names at sample depth, lithology, and optically measured maturity of the coals.

**Sample ID 2–11 = northern North Sea samples; sample ID 12–26 = mid-Norwegian shelf samples.

[†] sst = sandstones.

coal-derived C_{15+} petroleum in any trap in the region, apart from in the Idun trap north of Skarv (Figure 1) (Angard, 1996; Steinhoff, 1996; Sletten, 2003; Winterstad, 2003; Xu, 2003). Karlsen et al. (2004) argued that the Idun trap contains coal-derived (Åre Formation) gas and condensate, and that a paleopetroleum charge to Midgard is also coal derived. In the latter case, later derived Spekk condensate has mixed with and partly displaced the original coal-migrated gas. It is a likely scenario in such a multilayered source rock basin, as discussed above, that gas from the Åre Formation did, in the past, fill most of the traps and was later lost by leakage through the seal (cf. Sales, 1993, 1997) because of the long time span between the expulsion of gas from the Åre Formation and the shallower Spekk Formation and displacement by later arriving petroleum. Thus, evidence for isotopically heavy coal-derived gas may today only be found in traps on the margin of the basin, which lacked sourcing from the Spekk Formation.

We note that the giant Norwegian Troll gas field contains gas (mainly C_1) with $\delta^{13}C$ values mostly between -45 and $-47‰$. Similar gas is also observed in the grossly undersaturated Draugen field (-46 to $-51‰$) off mid-Norway, whereas C_1 values in the range of -38 to $-45‰$ are normal on the NOCS. Thus, the C_1 in these fields show lighter-than-normal $\delta^{13}C$ values. The result of this study will attempt to explain why this is the case.

Samples

Samples of Jurassic coals and adjacent sandstones from depths between 3.4 and 5 km (2.1 and 3.1 mi) (Table 1) from the mid-Norwegian shelf and northern North Sea (Figure 1) were collected. Ideally, samples should have been collected from wells drilled downflank of petroleum accumulations. However, wells with sandstone-coal contacts in this setting were not found. Samples were, however, collected close to the oil-water contacts in petroleum-filled traps to maximize the chance that the inclusions were formed prior to the trap being completely filled with oil or gas (cf. Karlsen et al., 1993). All sandstone samples were tested for the presence of fluorescent oil and condensate inclusions according to the methods of Karlsen et al. (1993) and Nedkvitne et al. (1993), whereas all coal samples were examined in detail for the presence of invaded reservoir oil.

Fluorescent petroleum inclusions (implying trapped oil) were only found in minor quantities in one of the samples (well 6406/2-2, 5092 m [16,706 ft]). In the other samples, gas in inclusions should consequently have its origin from aqueous gas inclusions instead of oil-gas inclusions. Abundant aqueous gas inclusions were found to contain sufficient gas to allow the determination of molecular and carbon isotope measurements. See Appendix for description of sample preparation and analytical methods.

Subsidence and Temperature History of Sampled Areas

Figure 2 shows the sampled intervals from both the Hild (northern North Sea) and Smørbukk field (mid-Norwegian shelf) to have subsided continuously through geologic time. Well 30/7-8 in the Hild field shows a minor phase of uplift during the late Early Cretaceous, after which the area subsided rapidly (Figure 2A). The sampled Brent Formation has a present temperature of nearly 150°C (302°F). It is modeled to have reached 100°C (212°F) at roughly 50 Ma and probably reached 80°C (176°F), at which temperature fluid inclusions started to form at about 70 Ma. The maximum temperature of known active biodegradation of reservoired oil is 88°C (190°F) (Connan, 1984). The burial history of the Smørbukk field illustrated by well 6506/12-1 subsided rapidly during an early Late Cretaceous episode and again recently (Figure 2B). The sampled Lower Jurassic sediments have a present temperature of nearly 160°C (320°F), whereas the Middle Jurassic rocks have reached roughly 140°C (284°F). The Lower Jurassic is modeled to have reached the minimum required temperature (80°C; 176°F) for the formation of fluid inclusions about 85 Ma, whereas this temperature for Middle Jurassic rocks was reached later, roughly 65 Ma. Although subsidence curves in other parts of the mid-Norwegian shelf do not exactly match the one shown in Figure 2B, they follow a similar trend and experienced no uplift.

The temperature history of the two investigated areas (northern North Sea and mid-Norwegian shelf) (Figure 2) shows that biodegradation and, consequently, bacterial activity have not been an issue for the last approximately 80–65 m.y.

RESULTS

Reservoir fluid data are given in Table 2. Note the generally high gas/oil ratio (GOR) of the reservoir fluids, showing the sample areas to be gas rich. The carbon isotope values of the reservoir gases are much heavier than those found in the analyzed quartz inclusions and coals (Table 3), suggesting that the latter gases have a different origin and are not contaminated by the reservoir gas.

Maceral Composition of the Coals

The maceral composition of the coals is dominated by vitrinite and inertinite, with only minor to trace amounts of other macerals (Table 4). The sample from well 6406/2-2 (5095 m; 16,716 ft), which had the visual appearance of a coal, was characterized as shale by the coal petrologist.

Extracts: Contamination of Some Coals

Samples 3 and 7 from Hild (Figure 3) contain light-oil compounds, which apparently have infiltrated the coals. This is suggested by the n-alkanes dominating over the aromatics on the gas chromatography–flame ionization detector (GC-FID) in Figure 3. Clearly, pyrolysis on such coals will result in the cracking of allochthonous petroleum and breakdown of the coaly structure, leading to erroneous gas compositions. In addition, gas isotope values achieved in this way will be nonrepresentative of the coal gas. The sandstone fluid-inclusion sample from Hild (sample 8) also shows allochthonous hydrocarbons. Drilling mud or core preservatives do not compromise fluid-inclusion analysis because these were added after the formation of the inclusions.

For comparison, sample 29 from Smørbukk represents one of the cleanest coals in our sample set followed by sample 21 (well 6507/2-2). The corresponding sandstone sample of the latter (sample 20) shows a good noncontaminated n-alkane profile.

Biomarkers of extracts from pure coals, i.e., coals not infiltrated by reservoir oil, normally have very high pristane/phytane (Pr/Ph) values (generally from 5 to 11), are dominated by C_{29} relative to C_{27} and C_{28} steranes, and have high hopane/sterane ratios (Hunt, 1995).

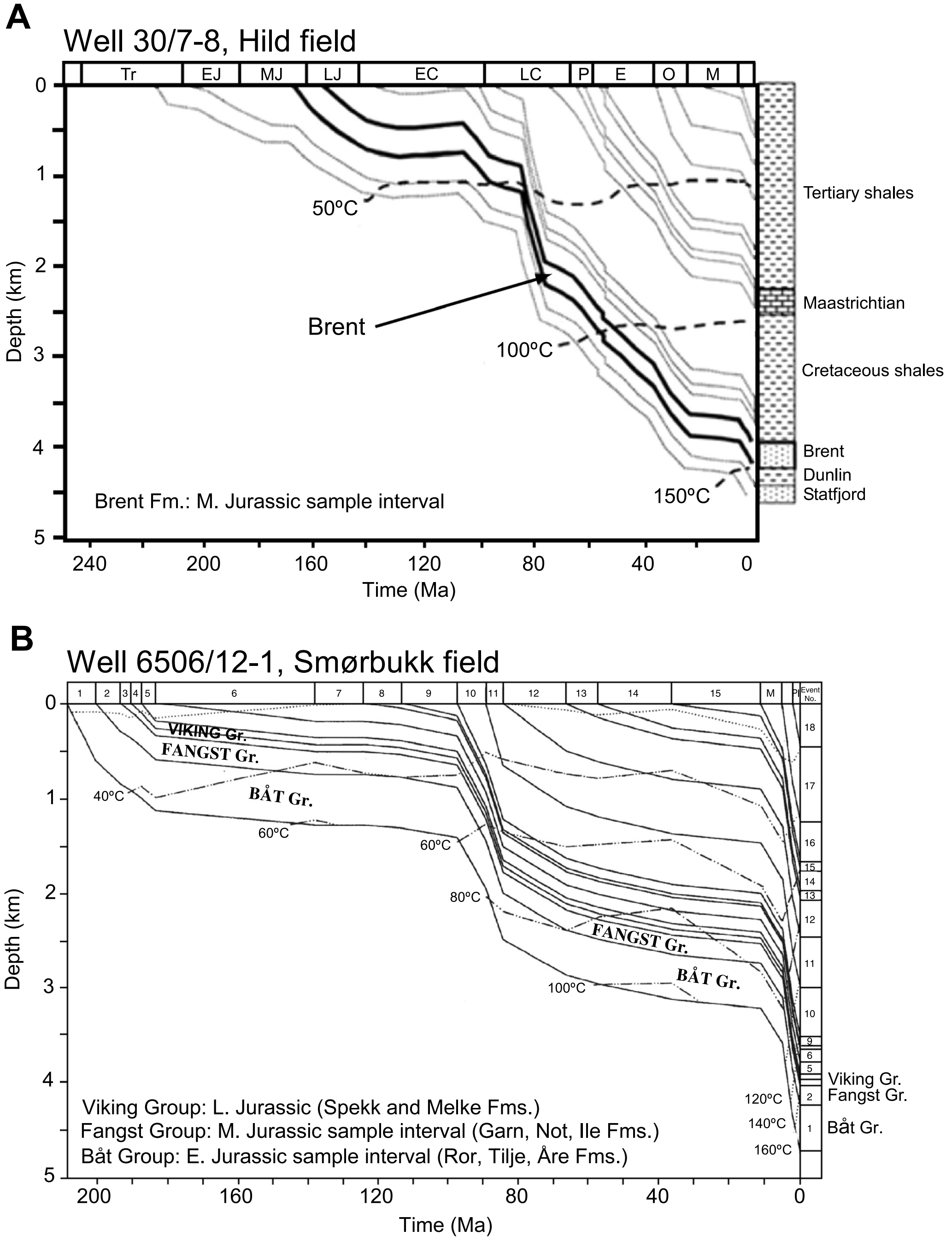


Figure 2. Subsidence and modeled temperature history diagrams. (A) Hild field, well 30/7-8. Apart from a small Early Cretaceous uplift phase, the Hild field has subsided continuously through geologic time. A particularly high subsidence rate is shown during the Late Cretaceous. The sampled Brent Formation coals and sandstones presently have a temperature of about 150°C (302°F) (after Girard et al., 2002; the Society for Sedimentary Geology is thanked for allowing us to use the figure). (B) Smørbukk field, well 6506/12-1. Two episodes of rapid subsidence are observed: the first has a Late Cretaceous age, whereas the second is recent. The present temperature of the sampled coals and sandstones is here in the range 120–160°C (248–320°F) (after Karlsen and Skeie, 2006; the *Journal of Petroleum Geology* is thanked for permitting us to use the figure.).

This is not observed in the analyzed coals of this study (Table 5), substantiating the interpreted invasion of allochthonous hydrocarbons (condensate) into several of the studied coals.

Gases

All the sandstone samples, except sample 19 (well 6507/2-2), are devoid of observable fluorescent petroleum inclusions. This means that the gas found in the samples has originated from nonfluorescent aqueous gas inclusions and not reservoir oil. Figure 4 shows examples of sand grains with several nonfluorescing (transparent) gas-water inclusions.

The results of the analyses performed on the inclusion gases are presented in Tables 3 and 6. The inclusion gases are dry, with C_1 concentrations in the range 60.9–96.1% of the total concentration (Table 6). One exception, the 6406/2-2 sandstone sample, is in contact with shale and not a coal.

Table 2. Drillstem Test (DST) Data from the Sampled Wells and Reservoir Gas Isotope Data*

Well	Field	TD** (m MD)	TD** (ft MD)	DST Number	DST Depth (m)	DST Depth (ft)	DST Chronostratigraphy	DST Lithostratigraphy	Flow rate oil (m^3/day)	Flow rate oil (scf/day)
29/6-1		4832	15,854	?	4208	13,807	M. Jurassic	Brent	220	7769
30/7-8	Hild	4287	14,066	RFT[‡‡]	4065.5	13,339	M. Jurassic	Brent	n.d.	n.d.
30/7-8R	Hild	4812	15,788	1	4064–4070	13,334–13,354	M. Jurassic	Tarbert	445	15,715
6406/2-2	Lavrans	5367	17,609	1	4868–4927	15,972–16,166	n.d.	Tofte	91	3214
6406/2-2				2	4714–4745	15,467–15,568	M. Jurassic	Ile	575	20,306
6506/12-9S	Smørbukk	4910	16,110	1	4846–4876	15,900–15,998	E. Jurassic	Åre	840	29,664
6506/12-9S				2	4805–4834	15,765–15,860	E. Jurassic	Tilje	900	31,783
6506/12-9S				3	4742–4751	15,559–15,588	E. Jurassic	Tilje	567	20,023
6506/12-9S				4B	4695–4709	15,404–15,450	E. Jurassic	Tilje	n.d.	n.d.
6506/12-9S				5	4477–4510	14,689–14,797	M. Jurassic	Ile	17	600
6507/2-2		3958	12,986	1A	3285–3294	10,778–10,808	E. Cretaceous	Lange	107	3779
6507/2-2				2	2820–2831	9252–9289	U. Cretaceous	Lysing	80	2825
6507/3-3	Idun	3830	12,566	?	3700.5	12,141	E. Jurassic	Åre	n.d.	n.d.

*Note that the samples are collected from high gas/oil ratio areas, and that the reservoir gases are isotopically heavy compared to the fluid inclusion and coal gases (−58 to −72‰).

**TD = total depth; MD = measured depth.

[†] GOR = gas/oil ratio.

[††] BHT = bottom-hole temperature.

[‡] n.d. = no data.

[‡‡] RFT = repeat formation tester.

The gas liberated from the coals is depleted in C_1 and C_2, with C_1 amounting to less than 5% of the total C_1–C_4 (Table 6), except for sample 5, having a value of 50.3%, for which we have no explanation. C_1 and C_2 compounds can easily escape from the coals during storage because of their small kinetic diameters (C_1 = C_2 = 3.8 Å; C_{3+} = 4.3 Å; Karlsen, 1987; Karlsen et al., 1988). The wetness of this gas is thus an artificial effect related to preferential and selective loss of C_1 and C_2 during core retrieval and storage. This is similar to the loss of hydrocarbon gas species from shale (Karlsen, 1987; Karlsen et al., 1988), which results in the residual gas becoming systematically wetter as the degassing becomes more effective. The concentration of gases released from the coals and sandstone fluid inclusions is low (Table 6; Figure 5A, C) but well above the 100-ppb (0.1-ppm) C_1 threshold for reliable interpretations (Figure 5B, D) suggested by Whiticar (1994).

These coal samples were also rich in C_4 and higher molecular weight hydrocarbons, which do not degas as readily as C_1 and C_2 (Table 6; Figure 5C). However, C_1 and C_2 were found in sufficient quantities to allow the measurement of their carbon isotope compositions.

Maturation

The R_o of the coals and one shale sample are plotted against depth in Figure 6, confirming the expected maturity increase with depth. The $\delta^{13}C_2$ and δn-$^{13}C_4$ show no trends versus depth (Figure 7), suggesting that the gas was trapped when the samples were at shallower depths. The average temperature gradient in the mid-Norwegian shelf sample area (cf. Table 2) is 34.4°C/km (29°F/1000 ft), giving a subsurface temperature range of 117–175°C (243–347°F) at sample locations. These are temperatures higher than required for the formation of quartz inclusions (see discussion below) and suggest trapping over a wide temperature range (80–175°C [176–347°F], with the rate of formation increasing exponentially with increasing temperature). Homogenization temperatures were not measured because of the well-defined and narrow focus of the original study outline.

DISCUSSION

Walderhaug (1994) reports the formation of quartz fluid inclusions, with a diameter of 4 μm in the temperature range 80–120°C (176–248°F), to take between 40 and

Flow rate gas		GOR[†]			Reservoir	Reservoir	Temperature		BHT[††]		
(m^3/day)	(scf/day)	(m^3/m^3)	(ft^3/ft^3)	API°	$\delta^{13}C_1$	$\delta^{13}C_2$	(°C)	(°F)	(°C)	(°F)	Well Comments
300,000	10,594,400	1363	7652	43.6	n.d.[‡]	n.d.	n.d.	n.d.	n.d.	n.d.	Gas and condensate discovery
n.d.	n.d.	n.d.	n.d.	40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	RFT data; gas and condensate discovery
612,000	21,612,576	1375	7719	43.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Gas and condensate discovery
223,000	7,875,171	2450	13,754	44.5	−42.6	−29.7	160	320	183	361	Gas and condensate discovery
1,037,000	36,621,309	1808	10,150	49	−42.4	−29.8	167	333	n.d.	n.d.	
444,000	15,679,712	749	4205	42	−44.4	−31.2	n.d.	n.d.	166	331	Oil and gas discovery
249,000	8,793,352	390	2190	35	−44.4	−31.0	163	325	n.d.	n.d.	
138,000	4,873,424	292	1639	40	−44.8	−32.6	164	327	n.d.	n.d.	
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
33,000	1,165,384	1379	7742	44	−44.4	−30.9	n.d.	n.d.	n.d.	n.d.	
80	2825	n.d.	n.d.	49.9	−38.5	−30.1	n.d.	n.d.	n.d.	n.d.	Oil and gas discovery
865	30,547	n.d.	n.d.	47.6	−38.2	−30.5	n.d.	n.d.	n.d.	n.d.	
n.d.	n.d.	n.d.	n.d.	n.d.	−34.4	−27.1	n.d.	n.d.	138	280	No oil stain; gas discovery

6 m.y., respectively. After formation of the fluid inclusion, the content is hermetically sealed, and no molecular, isotopic, or compositional changes will occur. The fluid-inclusion data prove that gas was available for trapping and give the bulk composition and isotope value of the gas during the time of its formation.

The isotopically similar light $\delta^{13}C_1$ being released from the coals during crushing and from the fluid inclusions supports a common source, and that the source of the inclusion gases is the coals. Release of such isotopically light C_1 is surprising because the temperature of the coals must have equalled the adjacent sandstones where formation of fluid inclusions occurred (>80°C; >176°F) (Walderhaug, 1994). Most of the coals in this study presently have optically measured maturities between 0.8 and 1.0% R_o and are therefore in the oil window at the present day. The $\delta^{13}C_1$ values of the released C_1 (-65.6 to -58‰) are therefore lighter than expected from an oil-mature source rock (-55 to -45‰) (Schoell, 1983).

Some of the fluid inclusions could potentially be inherited (primary inclusions) (cf. Peters et al., 2005, p. 194). Karlsen et al. (1993) describe inherited gas in fluid inclusions from the Ula field, North Sea, and their impact on the bulk gas isotope value. The $\delta^{13}C_1$ values in inclusions from magmatic systems are reported to be heavy, -8 to -12‰ (Galimov, 1973). A contribution from this will skew the measured $\delta^{13}C_1$ to heavier values as reported from the Ula field (Karlsen et al., 1993). In this scenario, the gas encapsulated in secondary fluid inclusions (formed during cementation) would be isotopically even lighter than shown by the actually measured bulk gas.

Extracts from sandstones close to coals in the Hild field have been shown to consist entirely of aromatics (Skålnes, 1993). Vitrinitic coals, as analyzed in this study (Table 4), typically contain about 70% aromatic carbon atoms (Tissot and Welte, 1984). During burial, coalification, and compaction, much early biogenically produced gas and water are described to be expelled from coal (cf. Tissot and Welte, 1984; Hunt, 1995). Because aromatics have higher solubility in water than aliphatics (Tissot and Welte, 1984), some aromatics are expected to be expelled from coal dissolved in water during compaction. Figure 8 shows an extract from the Hild coal and from crushed fluid inclusions in the adjacent sandstone. The fluid-inclusion extract shows trace amounts of similar aromatic hydrocarbons as in the coals, thus suggesting the coal to be the source. This observation supports our assumption that the coal is also the

Table 3. Carbon Isotope Gas Data of the Released Quartz Fluid Inclusion and Coal Gases*

Sample ID**	Well	Depth (m)	Depth (ft)	Field	Lithology	C_1 $\delta^{13}C$	C_2 $\delta^{13}C$	C_3 $\delta^{13}C$	i-C_4 $\delta^{13}C$	n-C_4 $\delta^{13}C$	C_5 $\delta^{13}C$
2	29/6-1	4265.5	13,994.3		sst[†]	−62.5	−32.2	−39.1	n.m.[††]	n.m.	
3	29/6-1	4265.6	13,994.6		Coal	−72.7	−31.8	−34.1	−23.4	−25.2	−30.1
5	30/7-8	4107.2	13,474.9	Hild	Coal	−60.9	−28	−34.2	n.m.	n.m.	n.m.
7	30/7-8R	4116.6	13,505.6	Hild	Coal	−67.1	−26.9	−34.1	n.m.	n.m.	n.m.
8	30/7-8R	4116.5	13,505.6	Hild	sst	−68.3	−27.1	−33.5	n.m.	n.m.	n.m.
9	30/7-8	4123.5	13,528.4	Hild	Coal	−70.1	−23.1	−28.4	−28.7	−26	−32.6
11	30/7-8	4128.9	13,545.9	Hild	sst	−64.4	n.m.	n.m.	n.m.	n.m.	n.m.
12	6406/2-2	5095.0	16,715.7		shale	−27.7	−27.5	−24.7	−27.8	−32.9	
13	6406/2-2	5092.0	16,705.8		sst	−65.6	−24.3	−24.6	−26.5	−33	−32.8
17	6507/2-2	3924.5	12,875.5		Coal	−72.5	n.m.	−19.1	−26.5	−33.5	n.m.
19	6507/2-2	3927.6	12,885.7		sst	−59.2	n.m.	n.m.	n.m.	−33.4	n.m.
22	6507/3-3	3381.3	11,093.4	Idun	sst	−59.6	n.m.	−14.2	n.m.	−32.9	n.m.
23	6507/3-3	3381.6	11,094.4	Idun	Coal	−69.7	−24.3	−24.5	−27.2	−32.7	−26.4
29	6506/12-9S	4707.7	15,445.0	Smørbukk	Coal	−61.4	−26.6	n.m.	−34.8	−34.3	n.m.
30	6506/12-9S	4707.5	15,444.4	Smørbukk	sst	−58.3	n.m.	n.m.	−34.1	−36	−29.1
Coal average						−67.8					
Sandstone average						−62.6					

*Note the very light isotope values of methane, much lighter than the reservoir gases (Table 2). The heavier propane isotope values of some samples compared to higher homologs suggest biodegradation of the gas.

**Sample ID 2–11 = northern North Sea samples; sample ID 12–26 = mid-Norwegian shelf samples.

[†] sst = Sandstone.

[††] n.m. = not measured.

source of the isotopically light analyzed C_1, and that this gas originates from secondary fluid inclusions.

Several questions were raised during the introduction section based on our discovery of the light C_1 isotope values in the quartz inclusions and are sequentially addressed below.

Is Isotopic Light C_1 in Gas Accumulations Reported Elsewhere Related to Coal?

Isotopically light methane related to bacterial activity is common in connection with production from coal beds (coalbed methane) (Scott et al., 1994; Price, 1995; Boreham et al., 1998, 2001; Smith, 1999; Faiz, 2004).

Hosgörmez et al. (2002) showed Westphalian coalbed methane from the Amasra region of the western Black Sea to have $\delta^{13}C$ values in the range −51 to −48‰. The $\delta^{13}C$ values of the coals themselves were between −27 and −23‰. T_{max} maturity (temperature at maximum hydrocarbon generation from Rock-Eval pyrolysis; see Peters et al., 2005, p. 1026) of the coals ranges from 440 to 450°C (824 to 842°F), suggesting maturities from the early to middle part of the oil window ($R_o \sim 0.6$ to 0.9%). Their data are, to a large extent, in agreement with our findings. These authors concluded the gas to be of mixed biogenic and thermogenic origin as also suggested by Scott et al. (1994) for coalbed gas from the San Juan Basin.

Coal-derived methane from the Fernie coals of southeast British Columbia were reported by Whiticar (1996) to have $\delta^{13}C_1$ in the range −61 to −45‰. The depleted C_1 values suggest a bacterial origin. The observed consistency in $\delta^{13}C_1$ between locations is, however, not to be expected for bacterial methane (Whiticar, 1996). C_2 is present in concentrations of less than 1%, with a $\delta^{13}C_2$ range from −17.2 to −12.5‰, suggesting high maturity ($R_m \sim 3\%$), but this is not reflected in the bulk $\delta^{13}C$ composition of the coal. Whiticar (1996) reports that studies were ongoing to ascertain if these isotope values were typical or merely represent a particular coal type or occurrence. Unfortunately, no recent publications have been found addressing this further.

Galimov (1988) reports $\delta^{13}C_1$ values in the range of −60.3 to −47‰ in all the Cenomanian supergiant

Table 4. Petrographic Analysis of the Data Set Showing the Coals Are Dominated by Vitrinitic Macerals*

	Depth					Inertinite			Liptinite		Mineral content			
Well	(m)	(ft)	Chronostratigraphy	Lithostratigraphy (Fm.)	Vitrinite	Low R_o Semifus.**	High R_o Semifus.	Fusinite	Sporinite	Resinite	Clay	Pyrite	Quartz	Carbonate
29/6-1	4265.6	13,995	M. Jurassic	Brent	339 (67.8%)	4 (0.8%)	13 (2.6%)	17 (3.4%)	–	–	112 (22.4%)	10 (2.0%)	4 (0.8%)	1 (0.2%)
30/7-8	4107.2	13,475	M. Jurassic	Brent	275 (55.0%)	70 (14.0%)	105 (21.0%)	8 (1.6%)	–	8 (1.6%)	26 (5.2%)	6 (1.2%)	–	2 (0.4%)
30/7-8	4123.5	13,528	M. Jurassic	Brent	438 (87.6%)	33 (6.6%)	19 (3.8%)	1 (0.2%)	–	–	7 (1.4%)	2 (0.4%)	–	–
30/7-8R	4115.45	13,502	M. Jurassic	Brent	242 (48.4%)	134 (26.8%)	109 (21.8%)	6 (1.2%)	–	–	3 (0.6%)	5 (1.0%)	–	1 (0.2%)
30/7-8R	4116.55	13,506	M. Jurassic	Brent	300 (60.0%)	33 (6.6%)	118 (23.6%)	16 (3.2%)	1 (0.2%)	–	31 (6.2%)	–	1 (0.2%)	–
6406/2-2	5095	16,716	E. Jurassic	Tilje	22 (4.4%)	4 (0.8%)	29 (5.8%)	2 (0.4%)	–	–	439 (87.8%)	3 (0.6%)	1 (0.2%)	–
6506/12-9S	4707.7	15,445	E. Jurassic	Tilje	249 (49.8%)	16 (3.2%)	44 (8.8%)	3 (0.6%)	–	–	14 (2.8%)	6 (1.2%)	17 (3.4%)	151 (30.2%)
6507/2-2	3929.4	12,892	E. Jurassic	Tilje-Åre	401 (80.2%)	23 (4.6%)	25 (5.0%)	23 (4.6%)	16 (3.2%)	–	12 (2.4%)	–	–	–
6507/2-2	3924.5	12,876	E. Jurassic	Tilje-Åre	263 (53.0%)	50 (10.1%)	108 (21.8%)	14 (2.8%)	14 (2.8%)	–	39 (7.9%)	–	8 (1.6%)	–
6507/3-3	3381.6	11,094	M. Jurassic	Garn	272 (54.4%)	55 (11.0%)	62 (12.4%)	52 (10.4%)	36 (7.2%)	4 (0.8%)	4 (0.8%)	10 (2.0%)	–	5 (1.0%)
6507/3-3	3383.86	11,102	M. Jurassic	Garn	63 (12.6%)	55 (11.0%)	86 (17.2%)	20 (4.0%)	50 (10.0%)	5 (1.0%)	183 (36.6%)	2 (0.4%)	30 (6.0%)	6 (1.2%)

*Numbers refer to points counted and proportion (in parentheses).
**R_o = reflectance; Semifus. = semifusinite.

gas fields of northern West Siberia. These gas fields, which make up more than 30% of the world's proven gas reserves, are dry and are currently at depths of approximately 1000–1200 m (3300–3900 ft). The source rock consists of coaly humic material. Galimov presented a mathematical model suggesting that humic organic matter has a high methane-generating capacity at low maturities ($R_o \sim 0.5$–0.7%), giving isotopically light C_1. Galimov states that his model supports previous work by Stroganov (1973) and Monnier et al. (1983), who also suggested that isotopically light thermogenic C_1 could be formed at low temperatures and shallow depth.

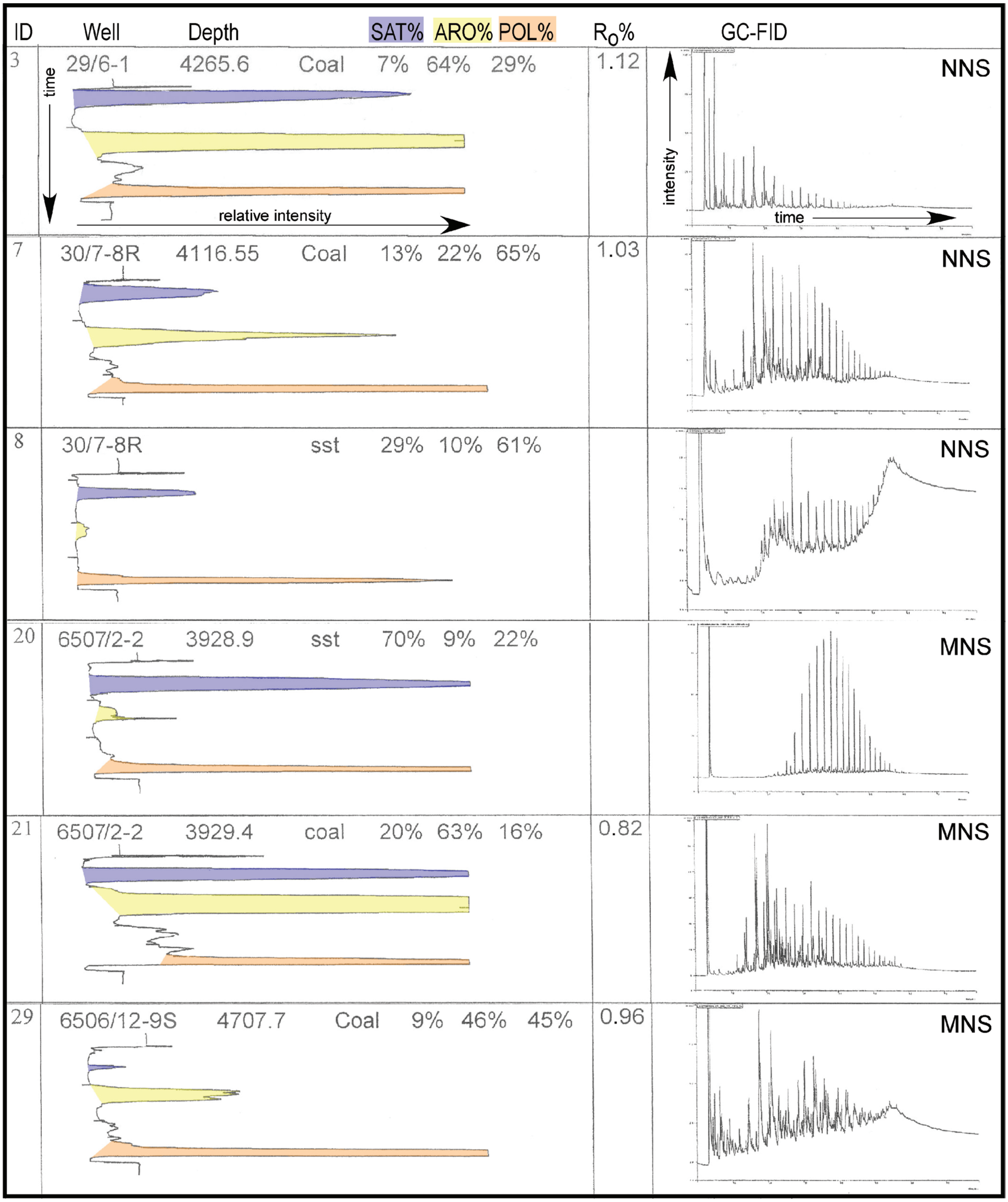
In addition, other sources for isotopically light C_1 other than coal have been reported. Biodegradation of petroleum accumulations can lead, via methanogenesis, to input of isotopically light methane (Pallasser, 2000; Boreham et al., 2001; Head et al., 2003), although the resulting $\delta^{13}C_1$ values (-55 to -45‰) are commonly heavier than our findings. This process is suggested to have contributed to the gas associated with the Canadian tar sand deposits. Hunt (1995, p. 626) states that 58% of the oil generated ends up finely dispersed as oil, gas, and pyrobitumen between source and reservoir rocks in petroliferous basins. This huge volume of disseminated oil also represents a reservoir for microbial consortia producing isotopically light methane as an end-product.

In summary, the cited literature clearly shows isotopically light C_1 accumulations to be a common phenomenon, particularly in view of the vast gas accumulations in northern West Siberia. Although the $\delta^{13}C_1$ range (-58 to -72‰) measured in the coal and inclusion gases of this study is generally lighter than the ones reported above, both mechanism(s) and mode of formation could be the same.

Could the Isotopically Light Fluid-Inclusion C_1 Be an Artificial Effect of Fractionation during Migration Out of the Coals?

Strapoc et al. (2006) show isotopic light C_1 to be desorbed from a freshly drilled coal core, and they demonstrate isotopic fractionation during the desorption process, testifying to the greater retention of $^{13}CH_4$ and $^{13}CO_2$ relative to $^{12}CH_4$ and $^{12}CO_2$ during initial expulsion. In their study, steady state was achieved after a few days, indicating that although isotopic fractionation occurred, equilibrium was quickly established.

Boreham et al. (1998) note that the extent of isotopic fractionation associated with selective migration and adsorption effects from the Natti Bulli coals, Sydney



Northern North Sea (NNS), Mid-Norwegian Shelf (MNS)
GC-FID: gas chromatography - flame ionization detector
TLC-FID: thin-layer chromatography - flame ionization detector
SAT: saturate fraction
ARO: aromatic fraction
POL: polar fraction

Figure 3. Iatroscan TLC-FID and GC-FID data for a selection of sandstones and coals from the sampled data. Several coal samples (e.g., sample 7 from Hild) contain light-oil compounds, which apparently have infiltrated the coals. The GC-FID of sample 8 shows bimodality and may be contaminated by mineral oil from the oil-based mud. Uncontaminated coals are represented by samples 3, 21, and 29.

Table 5. Terrestrial Source Indicators*

Sample ID**	Well	Depth (m)	Depth (ft)	Lithology	%C_{27}	%C_{28}	%C_{29}	Hop/Ster	Pr/Ph
1	29/6-1	4264.8	13,992	sst			–	–	2.5
2	29/6-1	4265.5	13,994	sst			–	–	3.2
3	29/6-1	4265.6	13,995	Coal			–	–	–
4	30/7-8	4107.0	13,474	sst			–	–	2.9
5	30/7-8	4107.2	13,475	Coal	30	35	35	–	0.74
6	30/7-8R	4115.5	13,502	Coal			–	–	–
7	30/7-8R	4116.6	13,506	Coal	40	29	31	–	2.5
8	30/7-8R	4116.5	13,505.6	sst			–	–	–
9	30/7-8	4123.5	13,528	Coal	65	20	14	–	–
10	30/7-8	4123.5	13,428	sst			–	–	3.6
11	30/7-8	4128.9	13,546	sst			–	–	1.6
12	6406/2-2	5095.0	16,716	shale			–	–	–
13	6406/2-2	5092.0	16,706	sst			–	–	–
17	6507/2-2	3924.5	12,876	Coal	53	12	35	2.15	0.5
18	6507/2-2	3927.6	12,886	sst	29	30	41	0.55	1.6
19	6507/2-2	3927.6	12,886	sst	28	35	37	0.18	1.2
20	6507/2-2	3928.9	12,890	sst			–	–	3.1
21	6507/2-2	3929.4	12,892	Coal	41	22	38	–	0.5
22	6507/3-3	3381.3	11,093	sst	37	20	43	–	–
23	6507/3-3	3381.6	11,094	Coal	49	26	25	4.07	–
24	6507/3-3	3383.5	11,101	sst	53	24	23	2.17	–
25	6507/3-3	3383.9	11,102	Coal	71	11	18	–	–
26	6507/3-3	3399.0	11,151	sst	63	18	19	–	–
29	6506/12-9S	4707.7	15,445	Coal			–	–	–
30	6506/12-9S	4707.5	15,444	sst	31	31	38	–	–

*None of the coal extracts show the very high Pr/Ph values, the %C_{29} dominating relative to %C_{27} and %C_{28} steranes and the high hopane/sterane ratios (Hop/Ster) expected if they originated from a terrestrial source rock. This suggests the presence of allochthonous oil in the coals.

**Sample ID 2–11 = northern North Sea samples; sample ID 12–26 = mid-Norwegian shelf samples.

Basin, has not been established. However, within shaly sequences, there appears to be little isotopic fractionation associated with the migration of methane dissolved in water (Kettel, 1995). Galimov (1973) and Karlsen et al. (1993) conclude that isotope fractionation of C_1 during migration is insignificant.

If fractionation occurred during expulsion from our investigated coals, we would expect to find isotopically heavier gas left in the coals. This was not the case. Our data showed the same isotopically light C_1 in the gas released from the coals as in those released from the quartz inclusions. This indicates that C_1 released from the coals during natural burial migrates within the coaly matrix and into the juxtaposed sandstone and becomes entrapped without carbon isotope fractionation.

Table 3 shows that the C_1 released from the coals is, on average, isotopically slightly lighter (−67.8‰) than the C_1 in the fluid inclusions (−62.6‰). This could be caused by C_1 expelled from coal mixing, with minor amounts of isotopically heavier C_1 already present in the sandstone, or alternatively, that a second biogenic phase of generation and expulsion has occurred in the coals.

In summary, we do not believe that the isotopically light C_1 released from fluid inclusions is an artificial effect of fractionation during migration out of the coals.

Is the C_1 in the Fluid Inclusions Biogenic, or Could There Be Other Sources?

Biogenic C_1 is the first hydrocarbon to be generated as the original biomass transforms to coal with increasing subsidence. The C_1 found in the analyzed coals and fluid inclusions has a dry and isotopically light biogenic

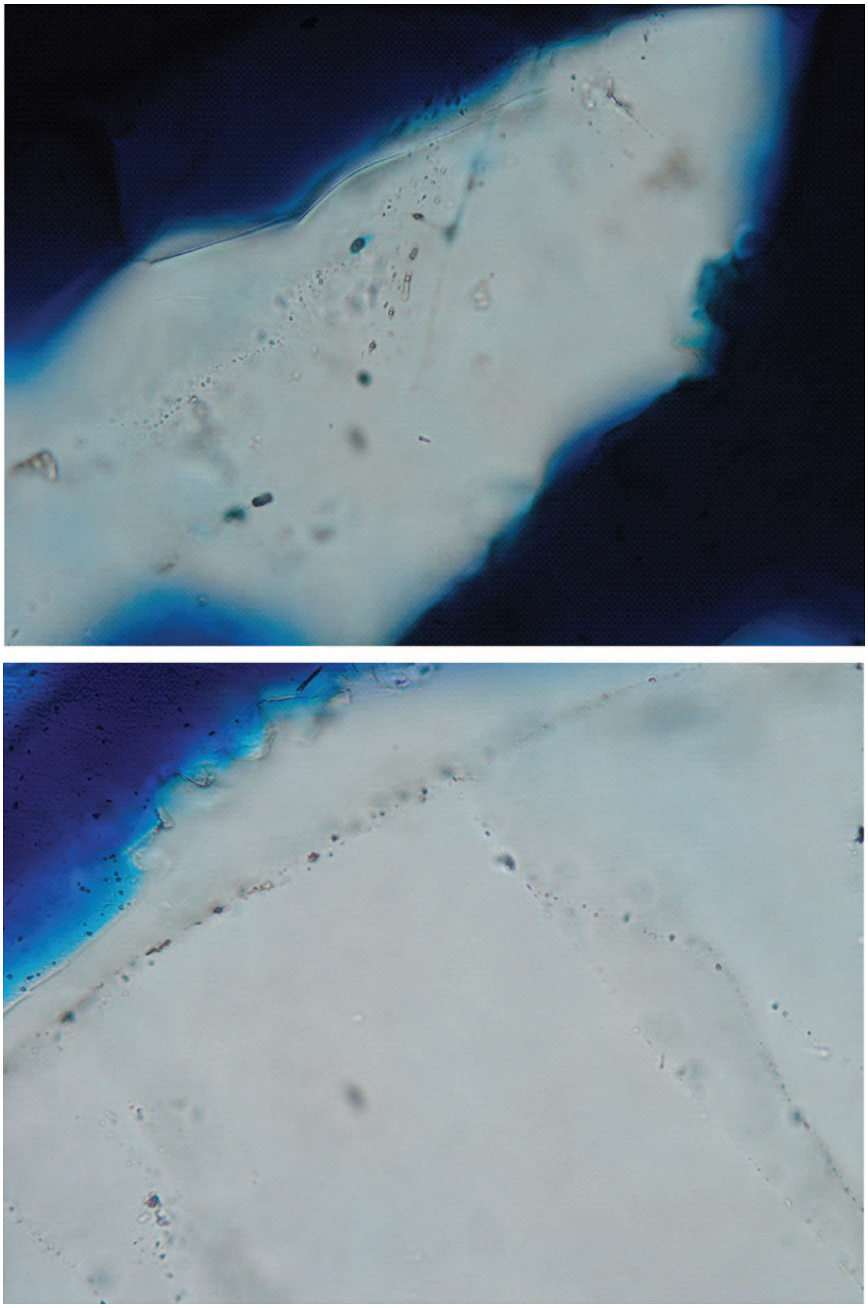


Figure 4. Photomicrographs of cleansed sandstone grain sample 6507/2-2 under ultraviolet light. Most inclusions are nonfluorescing, suggesting that they only contain water or gas. The few fluorescing inclusions contain oil. The field of view is 250 μm.

signature (cf. Schoell, 1983; Whiticar, 1996). It is intriguing, however, that this biogenic gas has been retained in the coal and then expelled later at temperatures high enough for the formation of quartz inclusions (>80°C; >176°F).

The structural heterogeneity of type III kerogens is reflected in their much wider activation energy distribution as compared to type I and type II kerogens (Tissot et al., 1987). An inference for this observation is that coals have the possibility to liberate C_1 from a vast set of precursor sites with different types of activation energy (cf. Schenk et al., 1997), implying that isotopically light C_1 could be produced over a wide range of activation energies.

An interesting observation is that the $^{13}C_1$ value of the shale sample (6406/2-2) is very heavy, suggesting that the C_1 was generated by a thermogenic mechanism. The C_1 liberated from the adjacent quartz inclusions is, however, isotopically light, similar to the rest of the analyzed samples, suggesting a different formation mechanism as compared to the shale gas (Figure 9A). This sample (6406/2-2) is the deepest in the sample set (5095 m; 16,716 ft), which may explain the thermogenic signature of the shale-derived C_1. The presence

Table 6. Percentage Gas Composition

Sample ID*	Well	Depth (m)	Depth (ft)	Field	Lithology	C_1 (%)	C_2 (%)	C_3 (%)	i-C_4 (%)	n-C_4 (%)	Concentration (ppm**)
2	29/6-1	4265.5	13,994.3		sst	73.4	5.9	3.0	12.2	5.5	24.2
3	29/6-1	4265.6	13,994.6		Coal	3.6	5.9	41.7	26.8	22.0	300.0
5	30/7-8	4107.2	13,474.9	Hild	Coal	50.3	7.5	7.3	23.3	11.6	92.9
6	30/7-8R	4115.5	13,502.0	Hild	Coal	3.1	–	13.5	34.4	49.0	28.6
7	30/7-8R	4116.6	13,505.6	Hild	Coal	4.5	–	4.6	71.9	19.0	5.7
8	30/7-8R	4116.5	13,505.6	Hild	sst	84.4	4.5	2.7	5.4	3.0	13.2
9	30/7-8	4123.5	13,528.4	Hild	Coal	–	3.2	62.8	14.8	19.2	1228.6
10	30/7-8	4123.5	13,528.4	Hild	sst	62.8	4.6	7.5	12.5	12.6	16.9
11	30/7-8	4128.9	13,545.9	Hild	sst	60.8	16.7	20.9	0.5	1.1	114.3
12	6406/2-2	5095.0	16,715.7		shale	16.0	60.0	18.5	2.5	3.0	150.0
13	6406/2-2	5092.0	16,705.8		sst	9.3	28.5	37.6	11.4	13.2	140.4
17	6507/2-2	3924.5	12,875.5		Coal	–	1.5	74.7	7.7	16.1	600.0
19	6507/2-2	3927.6	12,885.7		sst	86.7	6.5	3.9	0.9	2.0	121.4
20	6507/2-2	3928.9	12,889.9		sst	74.3	6.6	6.3	6.9	5.9	50.6
21	6507/2-2	3929.4	12,891.6		Coal	1.7	0.3	44.1	20.0	33.9	137.1
22	6507/3-3	3381.3	11,093.4	Idun	sst	90.8	6.4	1.9	0.4	0.5	750.0
23	6507/3-3	3381.6	11,094.4	Idun	Coal	2.6	3.2	45.0	20.3	28.9	131.4
24	6507/3-3	3383.5	11,100.6	Idun	sst	92.2	5.5	1.6	0.3	0.4	528.6
25	6507/3-3	3383.9	11,101.7	Idun	Coal	13.4	2.4	15.0	24.7	44.5	20.0
26	6507/3-3	3399.0	11,151.4	Idun	sst	90.1	6.3	2.3	0.5	0.8	807.1
29	6506/12-9S	4707.7	15,445.0	Smørbukk	Coal	2.4	14.2	63.2	5.2	15.0	342.9
30	6506/12-9S	4707.5	15,444.4	Smørbukk	sst	96.1	2.0	1.0	0.3	0.6	85.7

*Sample ID 2–11 = northern North Sea samples; sample ID 12–26 = mid-Norwegian shelf samples.
**ppm refers to concentrations in the crushing chamber.

of isotopic light C_1 in the adjacent quartz inclusions suggests this gas to have been trapped at a much shallower depth when isotopic light gas was being expelled from the shale (biogenic and/or from low-activation-energy precursor sites in the kerogen). It is enigmatic, however, why the coals of 6506/12-9S, also sampled at extensive depth (4707 m; 15,445 ft), liberated C_1 with an isotopic light signature (Figure 9A).

It could be argued that the isotopically light C_1 is a result of the sorption sites not being able to capture later generated isotopically heavy C_1. This is, however, apparently not the case for the shale sample, and the crushed oil-mature coals show no sign of isotopically heavy C_1, implying that it is not generated or that all is expelled. None of these seem to be likely scenarios.

Neither $\delta^{13}C_1$ nor $\delta^{13}C_4$ shows a correlation with maturity (Figure 9). This strongly suggests that they do not originate through normal thermogenic processes from oil-mature coals. However, both biogenic and early thermogenic processes could generate the analyzed C_1.

Is There a Relation between the Recorded Gas Isotope Values and the Different Coals Analyzed?

The higher molecular weight gas homologs record the original ^{13}C of the kerogen-bound precursor hydrocarbon molecule to a much higher degree than the shorter homologs (James, 1983; Chung et al., 1988). Discarding the very light C_1 isotope value of the fluid-inclusion sample from well 6506/12-9S, there is little scatter in the C_4 isotope values from our mid-Norwegian shelf samples (Figure 7B). These are also much lighter than the values from our gas database and the northern North Sea samples, which may suggest that organic materials with different isotope values, possibly reflecting different types of organic matter, were deposited in the two geographically separated areas.

Maturity of the coals versus C_4 isotope values are shown in Figure 9B. The North Sea coals are isotopically much heavier than the mid-Norwegian shelf samples, as also outlined in Figure 7B. It is, however,

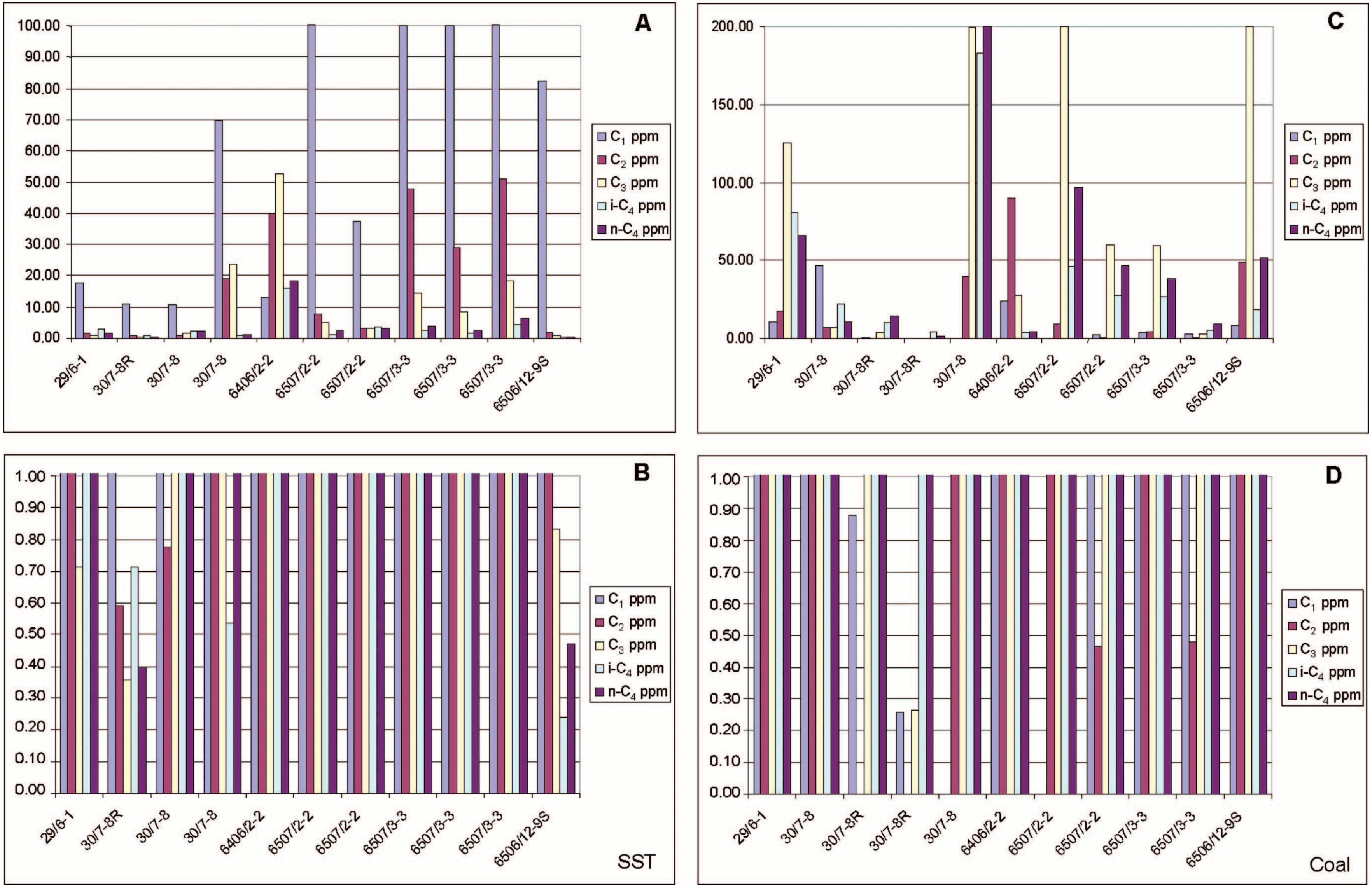


Figure 5. Concentration of gas in quartz inclusions (A) and in the sampled coals (C). A blowup of the 0–1 ppm area (B, D) show the concentrations of C_1 where present to be well above the 100-ppb (0.1-ppm) concentration suggested by Whiticar (1994) to be a threshold below which the data must be treated with caution.

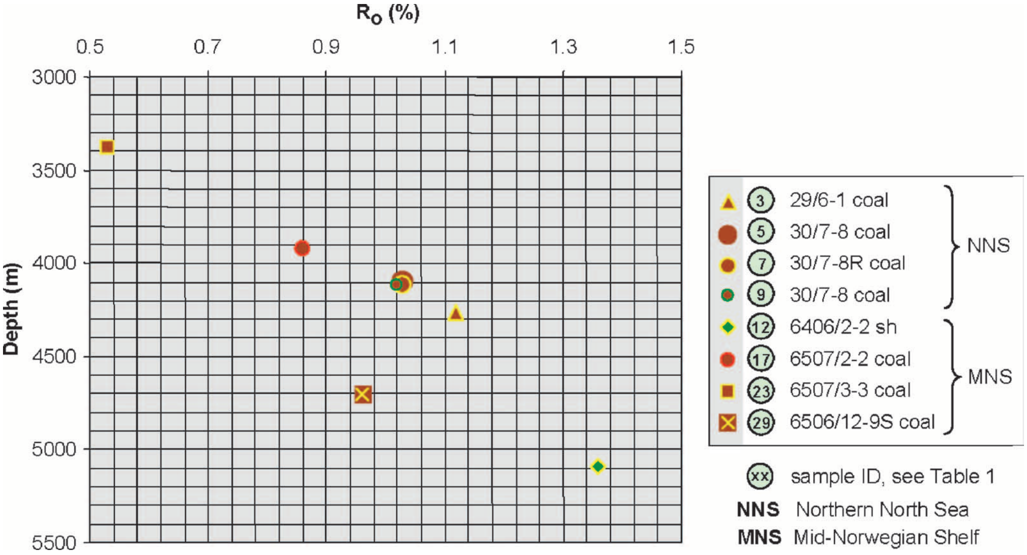


Figure 6. Vitrinite reflectance versus depth of coal and shale samples.

interesting to note that the liberated C_4 from the shale sample (6406/2-2), which had the appearance of a coal but petrographically was a shale, and the corresponding C_4 from the nearby sandstone fluid inclusions are not isotopically separated (Figure 9B) as was the case for C_1 (Figure 9A). This can be explained by the C_4 isotope values more closely reflecting that of the precursor kerogen (see discussion below). The broadly similar $\delta^{13}C_4$ values measured in the gas released from the mid-Norwegian shelf coals and from the mid-Norwegian shelf shale suggest that the organic input on the mid-Norwegian shelf was homogenous over the time interval represented by the age of the samples. The similarly isotopic light C_1 released from all the fluid-inclusion samples of this study possibly tells a different story reflecting a common and yet not well understood mechanism of formation and expulsion. It is in this context that the percentage of C_1 in the fluid inclusions, by far, exceeds the heavier homologs (Table 6), indicating the C_1 to be volumetrically much more significant.

In summary, different types of organic materials are interpreted to have been deposited in the mid-Norwegian shelf and northern North Sea, explaining the difference in $\delta^{13}C_4$ value between these two areas.

Can Our Observations Contribute to Our Understanding of the Origin of Gas on the NOCS?

Most of the recent work addressing the origin of the petroleum on the mid-Norwegian shelf agrees that the source is the Upper Jurassic Spekk Formation shale, both for the light and heavy fraction (Karlsen et al., 1995; Dale, 1997; Odden et al., 1998; Patience, 2002). Our data, however, showing similarly isotopic light C_1 being released from the crushed coals and sandstone fluid inclusions, suggest the coals to be the source of the C_1.

Schoell et al. (2005) artificially matured samples of the prolific Spekk Formation shale (Upper Jurassic) and the Åre Formation coals (Lower Jurassic) from the mid-Norwegian shelf. For each temperature step, they extracted the generated gas and analyzed it for $\delta^{13}C$. Figure 10 summarizes their results, and it is observed that the $\delta^{13}C$ of Åre coal and Spekk shale follow two distinctly different trends with increasing maturity. The findings of Schoell et al. (2005) are in contrast to earlier published kerogen types II and III isotope maturity trends (Faber, 1987; Berner, 1989; Whiticar, 1990, 1994), which are also illustrated in Figure 10. Reservoired gas data from our NOCS isotope database are seen to plot mostly along the coal trend of Schoell et al. (2005). This trendline suggests that most of this gas was generated in the maturity range 0.75–1.5% R_o. Schoell et al. (2005) concluded that the gases associated with Spekk oils are derived from coal. According to the previous trendlines, these gases fit the kerogen type II trendline best and are indicated to have been generated from a source rock in the maturity range 0.95–1.5% R_o. None of the gases in the isotope database have isotope values showing any relation to the humic type III kerogen trend in Figure 10.

The Spekk, kerogen type II trendline suggests that isotopically light C_1 is generated by thermogenic processes at low maturities (R_o = 0.5 associated with $\delta^{13}C_1 \sim -66‰$). This isotopically light C_1 value could,

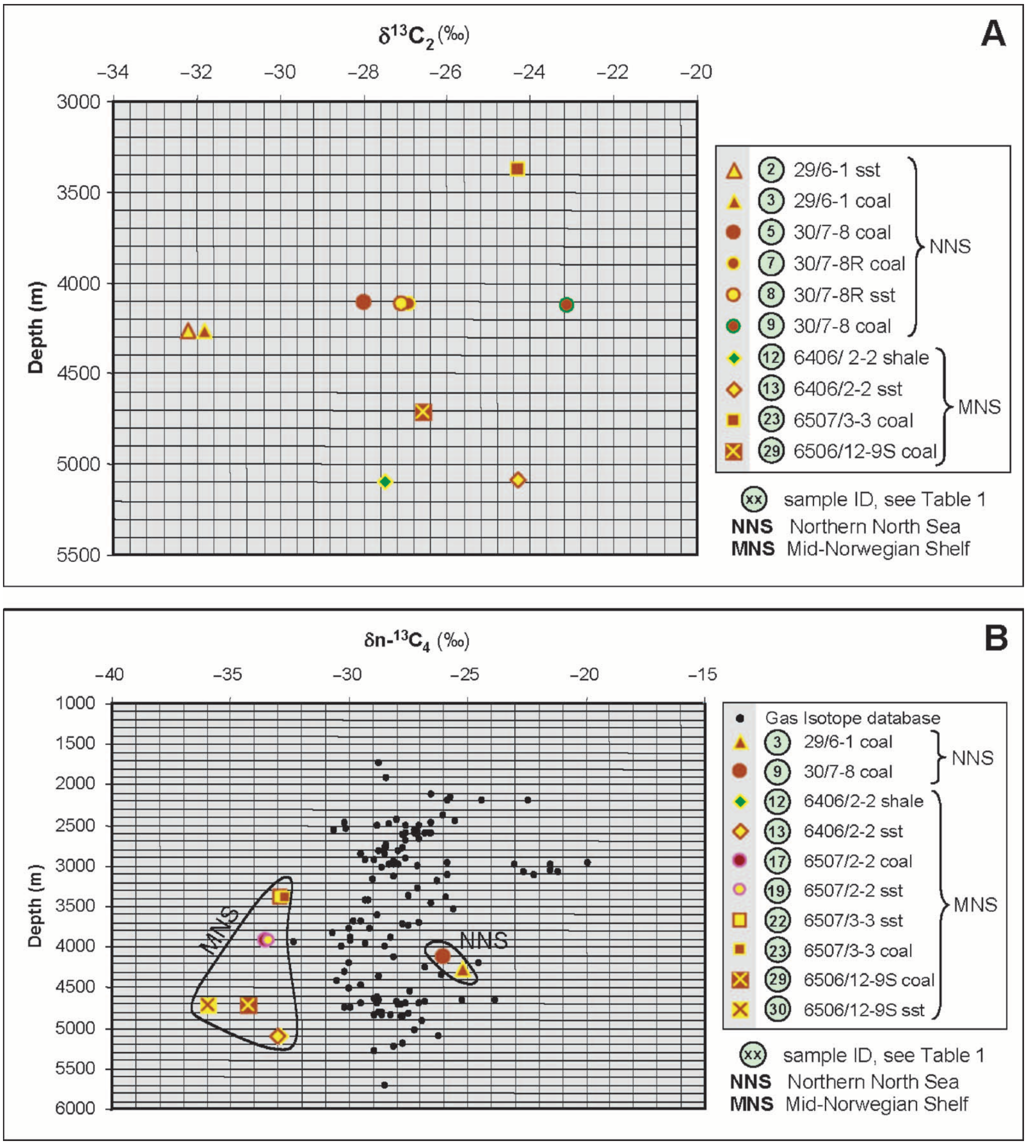


Figure 7. Carbon isotope values of C_2 (A) and n-C_4 (B) versus depth. No trends with depth exist, suggesting the gases were trapped at shallower depths. (B) The δC n-$^{13}C_4$ of the northern North Sea coals are much heavier than those from the mid-Norwegian continental shelf coals of our data set, suggesting different physical properties between these coals. The small difference between the mid-Norwegian continental shelf coals, despite them coming from different formations, indicates that these coals consist of the same organic matter type.

however, also partly be caused by earlier biogenic produced gas resting in the shale matrix. Extrapolating the Åre coal trendline to lower maturities shows the possibility for the isotopically light C_1 from our study to have originated from early mature coals. Volumetrically, however, C_1 generation from coal is reported to be insignificant at maturities lower than 1.0% R_o (Welte et al., 1984; Smith, 1994). If this is correct, the Spekk shale is the likely source of the gas. The similarly isotopically light C_1 realized both from the crushed coals and from fluid inclusions in adjacent sandstones as shown previously suggests, however, that the coals are the source of this C_1. In this case, significantly more C_1 is expelled from low-maturity coals than earlier accounted for, which is a consequence of the isotopically light C_1 being released from all the analyzed fluid inclusions in this study representing two geographically different areas potentially also containing different types of organic material.

The $\delta^{13}C$ values from our inclusion and coal gases are also shown in Figure 10. They all have much lighter C_1 isotope values than the isotope database, suggesting a biogenic and/or an early thermogenic origin. If we assume that the C_2 isotope values are real, then the C_1 isotope values must be altered for our data to fit the trendlines in Figure 10. In this situation, the trendlines suggest maturities ($R_o \sim 0.75–2.5\%$) mostly above that optically measured (average range 0.8–1.0% R_o) for the coals. We therefore disregard this possibility. Alternatively, if the C_1 isotope values are real with the C_2 being altered, then thermogenic processes from an early mature source rock or possibly from methanogens could

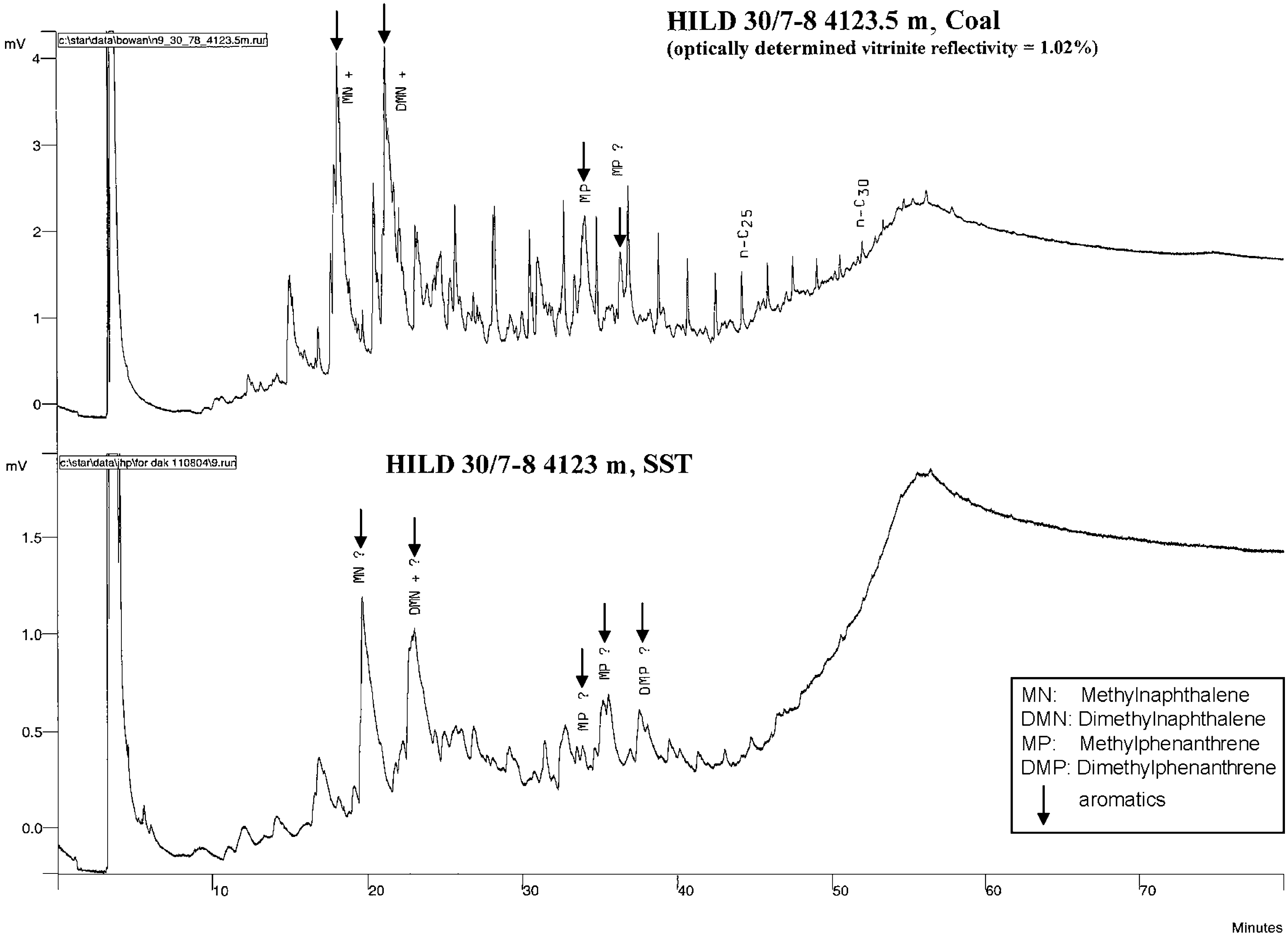


Figure 8. Gas chromatography–flame ionization detector chromatograms of extract from coal (upper) and adjacent fluid-inclusion sandstone (lower) from well 30/7-8, Hild field. Trace amounts of the same type of aromatic compounds as extracted from the coal are found in the fluid inclusions. This suggests that the inclusions are water-gas containing trace amounts of water-soluble aromatics and no alkanes despite the high maturity.

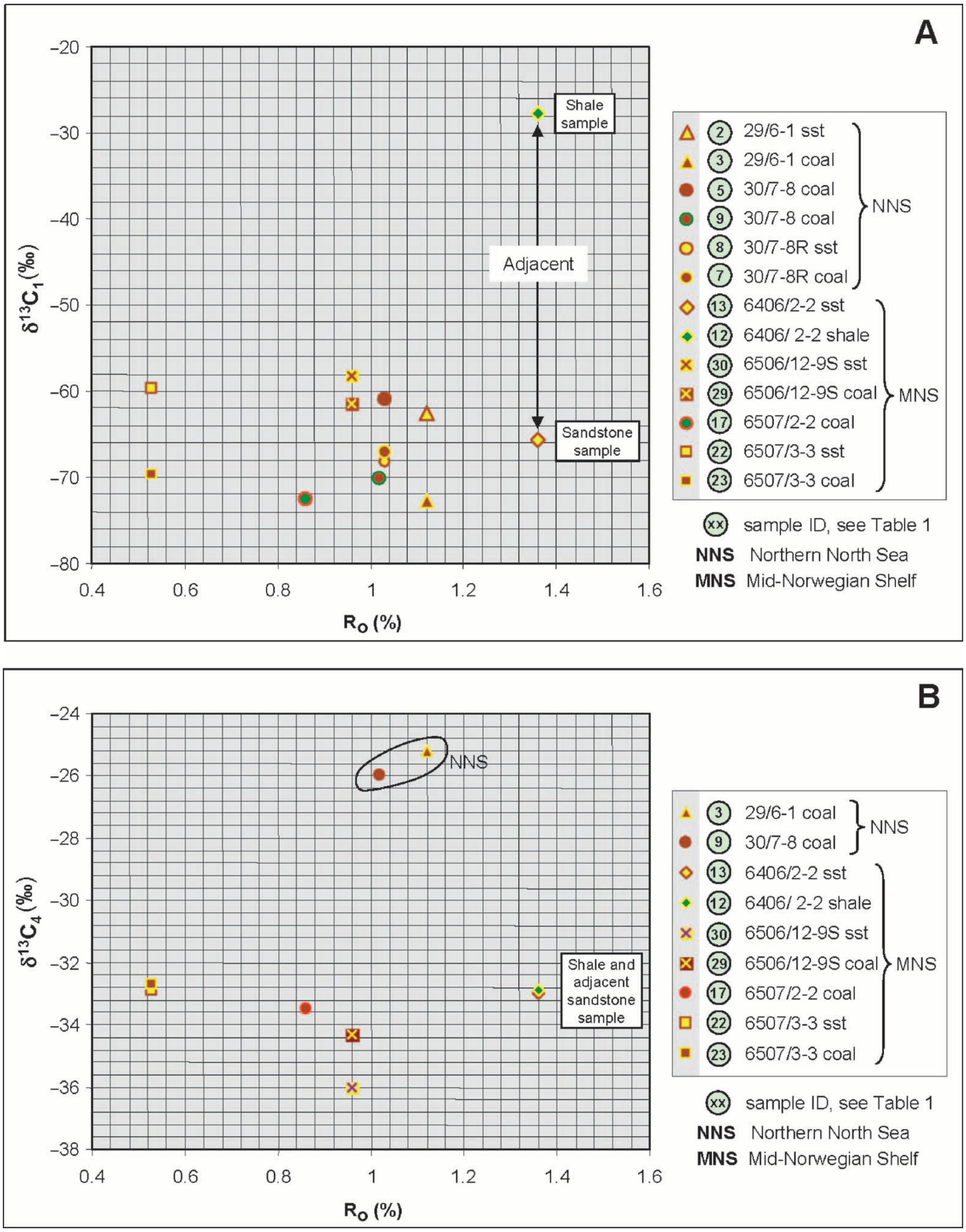


Figure 9. Carbon isotope values of C_1 (A) and n-C_4 (B) versus vitrinite reflectance. No trends with increasing maturity exist, suggesting the gases to have been trapped at shallower depths. (A) The isotopically much heavier C_1 value of the shale sample compared to the coal-related samples suggest the former to have been generated through thermogenic mechanisms and the latter to be biogenically derived. (B) Isotope values of C_4 resemble most closely those of the kerogen-bound precursor hydrocarbon molecule (James, 1983). However, coals from the northern North Sea and the mid-Norwegian shelf plot separately, suggesting that they consist of different organic material (see also Figure 6B).

have generated the C_1. In this scenario the C_2 isotopes are relatively heavy, which should be explained. Biodegradation of the coal-generated gases would drive the isotope values of the C_{2+} fraction toward heavier (enriched in ^{13}C) values. In this situation, C_3 is initially affected (James and Burns, 1984; Head et al., 2003), followed closely by n-C_4 and n-C_5, whereas C_2 and the iso-alkanes are reported to be more resistant (Boreham et al., 2001). C_3 in our data set is, in all but one case, isotopically heavier than C_4 where measured (Table 3), and therefore, we believe that biodegradation has affected the gases and possibly also resulted in the heavy C_2. The C_2 is, however, seen to be isotopically heavier than the C_4 and is not likely to be accounted for by biodegradation (Boreham et al., 2001). Based on the results of this study, biodegradation is, however, not ruled out as a possible mechanism to have generated the isotopically slightly heavier C_2.

Several NOCS gases are shown to have lighter C_1 isotope values than predicted by any of the trendlines (e.g., Troll, Frigg, and Draugen) (Figure 10). This suggests that these gases are a mixture of normal thermogenic and biogenic and/or early thermogenic gases. Accordingly, the Troll gas could result from mixtures

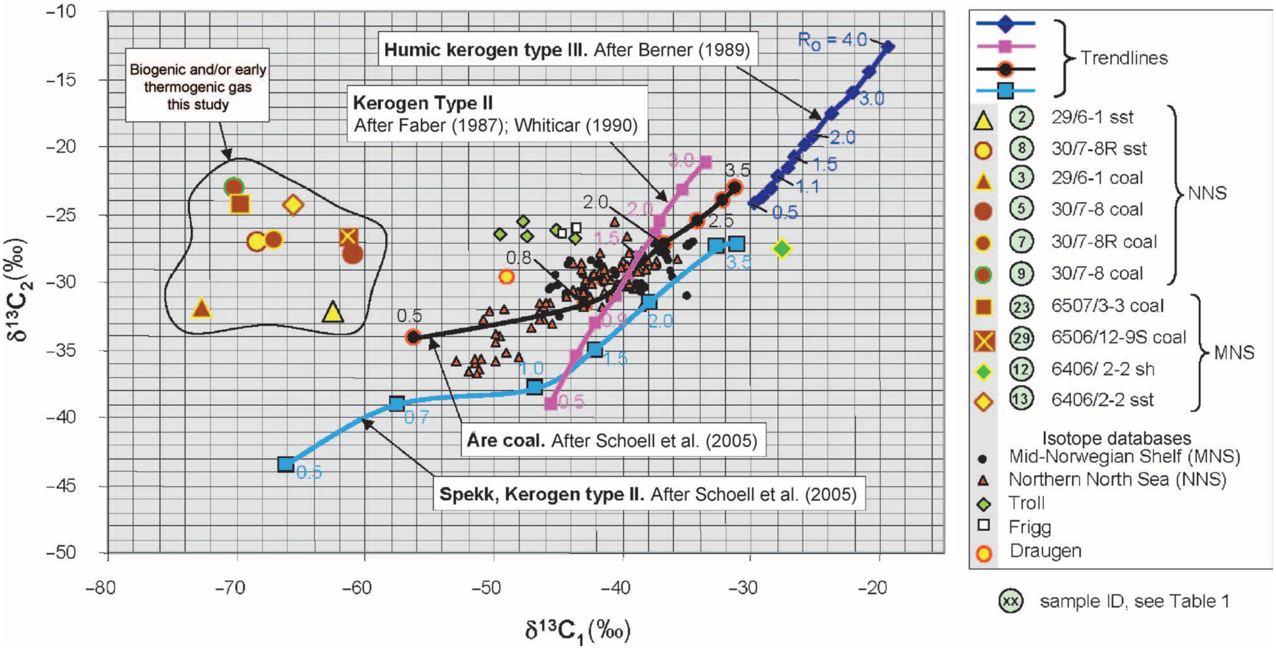


Figure 10. Various published trends of $^{13}C_1$ and $^{13}C_2$ with thermal maturity. The in-house ConocoPhillips isotope databases from the mid-Norwegian shelf and from the North Sea are illustrated. The C_1 isotope values from released gases from the quartz inclusions and coals suggest biogenic origin, whereas the C_2 isotope values suggest maturities of the coals that exceed the actual optically measured values. This could be an artificial effect of the analyzed gases being biodegraded to various extents. The Troll gas appears to be a mixture of biogenic and thermogenically generated gases.

of the following: $^{13}C_1$ of Troll = X% biogenic and/or early thermogenic $^{13}C_1$ + [100 − X]% normal thermogenic $^{13}C_1$, where biogenic and/or early thermogenic gas =– 66‰, i.e., average $^{13}C_1$ of this study; and normal thermogenic gas = $^{13}C_1$ from the three source rock candidates (values seen on trendlines in Figure 10). The percentage of biogenic and/or early thermogenic gas (X) that would have to mix with normal thermogenic generated gas following the kerogen type II trendline is 30%, with the Åre coal trendline 35% and with the Spekk shale trendline 43% following the relationship above. As noted, in all cases, the fraction of biogenic and/or early thermogenic gas is high.

Based on our data, we cannot positively determine the source(s) of the C_1. By extrapolating the trendline for the Åre coal to lower maturity, only a small change in C_2 isotope value is needed to obtain the observed values, suggesting that light biodegradation of the gas could be sufficient. For a Spekk shale kerogen type II to be the source of the C_2, the needed isotopic change is much higher, suggesting severe biodegradation of the gas (Figure 10). We therefore suggest low-maturity coals to be the main source of the gas.

Several authors have discussed the filling history and, thus, the origin of the gas in the Troll field (cf. Horstad and Larter, 1997, and references therein). Horstad and Larter (1997) could not positively identify the source for the gas in Troll, but suggest that the composition is a result of in-situ biodegradation of the gas and the oil leg below. Our study opens the discussion for an alternative explanation, which is mixing of thermogenic and biogenic and/or early thermogenic coal-derived gas.

In summary, the isotope gas data from this study contribute to our understanding of the origin of gas on the NOCS by suggesting that relatively high volumes (35% in Troll) of biogenic and/or early thermogenic isotopically light coal-derived C_1 have been expelled and trapped. This gas has mixed with thermogenic generated isotopically heavier C_1 from mature source rocks, thus skewing the bulk $\delta^{13}C_1$ to lighter values (e.g., Troll, Frigg, and Draugen).

What Are the Quantities of Isotopically Light Gas Released in the Temperature Range 80–100°C (176–212°F) Where Quartz Fluid-Inclusion Formation Is Initiated?

As previously referred, Walderhaug (1994) reports the formation of quartz fluid inclusions with a diameter of 4 μm in the temperature range 80–120°C (176–248°F) to take between 40 and 6 m.y. respectively. The isotope values of the released fluid inclusions represent averages of the total gas released from all the individual disintegrated fluid inclusions in each sand grain from each sample. These fluid inclusions did not form simultaneously. They are a result of quartz overgrowth, which again is controlled by temperature and pressure solution and dissolution. Consequently, fluid inclusions may have been formed throughout the whole temperature range from 80°C (176°F) at roughly 70 Ma (Figure 2) until present. The release of isotopically light C_1 from all the disintegrated sandstone samples suggests that this type of gas with a biogenic and/or early thermogenic signature has been present in the sandstone for a considerable time. We therefore speculate that significant volumes of isotopically light C_1 have been expelled from the analyzed coals over the same time interval.

Because gas is demonstrably trapped in several fluid inclusions, which may have sealed at considerably different times (Figure 4), gas must have been available for trapping over a long time span. Because of the small kinetic diameter of C_1, the gas is unlikely to have resided in the sandstones long before migrating on. We therefore expect that C_1 supply must have kept pace with C_1 loss, and consequently, that the cumulative expelled volumes of isotopically light C_1 over geologic time must have been significant.

This can be illustrated by the previously discussed mixing rates at the Troll field (35% biogenic and/or early thermogenic coal-derived C_1 and 65% thermogenic C_1 from a mature source). The total recoverable dry-gas reserves on Troll are 1250×10^9 m^3 (44.6 tcf) (Horstad and Larter, 1997). If 35% of this is generated through biogenic and/or early thermogenic processes, this amounts to 437.5×10^9 m^3 (15.6 tcf) dry gas, which indeed is significant.

What Could Be the Implications of These Findings to Our Understanding of the Total Gas Budget in the Petroleum System of the NOCS and Elsewhere?

If it is correct that significant volumes of biogenic and/or early thermogenic gas are being expelled from coals at temperatures where quartz inclusions form (>80°C; >176°F), corresponding to depths greater than 2.3 km (7500 ft) (given a temperature gradient of 35°C/km), this will have an important impact on the total petroleum budget and means that much more gas is available to the system than earlier accounted for. Coal, as previously sited, expels huge amounts of biogenic gas and water during the peatification and coalification processes (Hunt, 1979; Faiz, 2004). The C_1 related to these mechanisms is isotopically light as is coalbed C_1 generated through secondary biogenic processes (Scott et al., 1994; Price, 1995; Boreham et al., 1998, 2001; Smith, 1999; Faiz, 2004). Isotopically light C_1 released from early mature coal by thermogenic mechanisms is described from northern West Siberia (Galimov, 1988), whereas isotopically heavy released C_1 is common from oil-mature coals (Schoell, 1983; Whiticar, 1994, 1996).

Similar isotopically light C_1 released from fluid inclusions in this study suggest that the gas has been generated by the same mechanism and over a very long time interval (millions of years). This indicates that the cumulative volumes of C_1 expelled from these processes are significant. Data from this study add on to the earlier described mechanisms for C_1 generation from coal and suggest that coal can be a significant gas expeller over a much wider temperature range than earlier accounted for.

CONCLUSIONS

1. Coals with oil-window thermal maturities liberate isotopic light C_1 upon crushing.
2. Aqueous gas inclusions formed in sandstones in contact with the analyzed coals also contain isotopic light C_1.
3. The liberated C_1 is interpreted to be biogenic and/or early thermogenic.
4. Equally light C_1 has been measured in this study from sandstone-coal pairs deposited far from each other, suggesting a common yet unknown expulsion mechanism from the coals.
5. The disintegrated fluid inclusions of this study were formed over millions of years (<70 m.y.), and the released isotopically light C_1 may potentially have been available over the same time range.
6. Cumulatively significant volumes of C_1 may have been expelled from the coals. This may upgrade exploration for gas in areas containing coal in the subsurface.
7. Our finding may explain the occurrences of isotopic lighter than expected C_1 accumulations worldwide by being mixtures of thermogenic gas from mature source rocks and biogenic and/or early thermogenic produced coal gases.
8. C_1, C_2, and C_3 have been expelled from the analyzed coals without any carbon isotope fractionation.
9. The data from the coals suggest that C_1 and C_2, which have small and very identical kinetic diameters, are preferentially lost from the coals during core retrieval and storage compared to higher homologs.

APPENDIX: PROCEDURE

Techniques

The sandstone samples were disintegrated into single sand grains, washed with dichloromethane/methanol, cleansed with chromic acid and hydrogen peroxide before crushing to liberate gas contained in the inclusions (refer to Karlsen et al., 1993; George et al., 1997, for a detailed description of the method and the uncertainties related to it). The coal samples were subjected to the same procedure to release interstitial gas. The inclusion gas was injected into a GC-FID, and the gas composition was determined. Samples holding sufficient gas were crushed again to liberated hydrocarbon gas for $\delta^{13}C$ measurement. This allowed a direct comparison between the gas in the inclusions and in the traps. Gas released from the coals by crushing was similarly analyzed on GC-FID and for its $\delta^{13}C$ values.

Standard Iatroscan thin-layer chromatography–FID, GC-FID, and gas chromatography–mass spectrometry (GC-MS) methods were used to evaluate the quality of the sandstone and coal extracts and to check for contamination, particularly by drilling mud and also other fluids, which can infiltrate both sandstones, siltstones, and coals.

Coal maceral composition and vitrinite reflectance (R_o) by optical methods were provided by the laboratory of J. M. Jones, Newcastle-upon-Tyne, United Kingdom.

Analytical Methods

For bulk quantification of the extracts, an Iatroscan TH-10 TLC/FID Analyzer from Iatron Laboratories Inc. (Tokyo) was used by applying the procedures described by Karlsen and Larter (1991). For GC-FID analysis of the gas phase in the inclusions and coals, a Varian Capillary Gas Chromatograph Model 3500 with a Chrompack PLOT fused silica CP-Al_2O_3 chromatographic column was used. The column was 25 m (82 ft) long, with an inner diameter of 0.32 mm (0.012 in.) and a film thickness of 5 μm. The detector temperature (FID) was 300°C (572°F), with an initial column temperature of 40°C (104°F) and an initial hold time of 2 min. The injector temperature was 150°C (302°F). The temperature gradient was 23°C/min (73°F/min), with a final column temperature at 180°C (356°F) and a final hold time of 3 min.

For GC-FID analysis of the extracts, a Varian Gas Chromatograph Model 3500 and a 50-m (164-ft) Hewlett Packard Ultra 2 cross-linked 5% phenyl methylsilicone Gum column (inner diameter 0.2 mm [0.007 in.], chromatographic film thickness 0.33 μm) were used. The detector temperature (FID) was 330°C (626°F), with an initial column temperature of 40°C (104°F) and an initial hold time of 2 min. The temperature gradient was 4°C/min (39°F/min), with a final column temperature of 325°C (617°F) and a final hold time of 20 min. Nitrogen was used as carrier gas for both types of GC-FID analysis.

Before GC-MS analysis, the samples were sieved with a 5-Å molecular sieve to remove n-alkanes from the samples. The GC-MS column was a Chrompak CP-SIL 5CB-MS FS 50X.32(.40) WCOT fused silica-type column, with a CP-SIL 5CB Low Bleed/MS stationary phase. The film thickness was 0.40 μm, the column length was 50 m (164 ft), and the inner diameter was 0.32 mm (0.012 in.). The initial column oven was programmed from 80 to 180°C (176 to 356°F) at 10°C/min (50°F/min) then to 310°C (590°F) at 1.7°C/min (35°F/min), with a final hold time of 30 min. Helium was used as carrier gas for GC-MS analysis.

The $\delta^{13}C$ determination on gases was undertaken at Hall Analytical, Manchester, United Kingdom. An inclusion sample from the Idun field earlier analyzed at Kjeller/Applied Petroleum Technology/Institute for Energy Techniques was included as a control sample.

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