Click to see slides from oral presentation

# [EA]Bound Gas in Near-Surface Sediment – Indication for Thermogenic Hydrocarbons in the Northern Barents Sea?*

**Philipp Weniger[1] and Martin Blumenberg[1]**

Search and Discovery Article #42504 (2020)**
Posted February 24, 2020

*Adapted from extended abstract based on oral presentation given at 2019 AAPG Hedberg Conference, Hydrocarbon Microseepage: Recent Advances, New Application, and Remaining Challenges, Houston, Texas, June 18-20, 2019
 DOI:10.1306/42504Weniger2020

[1]Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany (philipp.weniger@bgr.de)

## Abstract

The northern Norwegian Barents Sea is an under-explored region, for which significant petroleum potential is expected, but little direct geochemical information on petroleum systems is available. The analysis of bound (adsorbed) gas in near-surface sediment, established more than 80 years ago, is a tool frequently applied in hydrocarbon exploration of 'frontier' areas. The method assumes that traces of hydrocarbons that migrated from subsurface petroleum systems to the surface are trapped in near-surface sediment and that their geochemical and stable isotope signature remains unaltered and reflects the genetic origin. Previous studies observed differences between bound gas and interstitial (headspace) gas, caused by alteration or mixing and thus 'classical' interpretation schemes for gas origin based on relative abundance and δ13C of methane may be unreliable. To improve knowledge on petroleum systems in the northern Barents Sea, seismic data and near-surface sediment samples were collected south of Svalbard.

Interpretation of bound gas origin focused on ethane and propane, which are less prone to alteration than methane. Concentration anomalies of bound gas with stable carbon signatures typical for thermogenic gas were found along the Western

Barents Margin and near margins of the Olga Basin. Organic geochemistry of near-surface sediment from locations close to Svalbard showed presence of allochthonous mature organic matter. The amount and composition of bound gas extracted from source rock samples from outcrops on Svalbard indicate that contribution of transported material to near-surface sediment can influence the bound gas. Near-surface sediment from the Olga Basin contains no mature kerogen and concentration anomalies of bound gas correspond to areas where seismic data show sub-cropping Jurassic shales or reactivated faults. The stable carbon isotope composition of bound gas suggests a thermogenic origin. According to seismic data, Middle Triassic shales, which are proven source rocks on Svalbard and in the southern Barents Sea, were sufficiently buried to generate oil and gas and a likely source for bound gas in this area.

## Gas in Near-Surface Marine Sediments

The glaciomarine near-surface sediment from the northern Barents Sea collected by gravity coring in this study is dominated by clay and silt with less than 10% sand, an average water content of 30 wt.%, 1.5 wt.% organic carbon and 0.5 wt.% inorganic carbon. Gas in this sediment can occur in form of free gas (e.g. bubbles), gas dissolved in pore water, gas sorbed on the surface of minerals or organic particles and occluded gas trapped in pores (Figure 1). In practice, it is not possible to separate between these gases and commonly used extraction methods will yield mixtures. For example, the headspace extraction method used for interstitial gas analysis most likely yields free and dissolved gas, whereas the acid extraction method commonly used for bound (adsorbed) gas analysis will yield dominantly sorbed gas but also occluded gas released from closed pores after dissolution or disaggregation of the sediment.

## Bound (Adsorbed) Gas Acid Extraction Revisited

Bound (adsorbed) gas acid extraction is a method introduced for on-shore near-surface prospecting more than 75 years ago (Horwitz, 1972 and references therein). This method was also applied in off-shore areas where it is used by BGR since the late 1970s (Stahl et al., 1981) (Figure 2).

However, differences observed between interstitial gas and bound gas in both concentration and gas composition during the past decades raised concerns on the applicability of the bound gas method for seepage detection and interpretation of gas origin (Abrams, 2017). For example, bound gas plotted on a commonly used “Bernard diagram”, a plot of methane stable carbon isotope composition versus the ratio of methane to the sum of ethane and propane, often resembles thermogenic “wet” gas with

relatively high abundance of ethane and propane. A review of bound gas data from BGR and literature confirms this observation, but also shows that this is not always the case (Figure 3).

These observations led us recently to revisit the bound gas method and address some of the remaining question:

Is the bound gas composition influenced by light hydrocarbons, generated from sedimentary organic matter during the acid extraction procedure (e.g. via acidic hydrolysis)?

Is the bound gas adsorbed, and if so, could it be released by temperature desorption alone?

Can bound gas in near-surface sediments be influenced by gas bound in transported allochthonous sediments?

To address the first question the standard bound gas acid extraction method was used on a peat sample containing immature organic matter. Results show that only minor amounts of light hydrocarbon were released from peat (Figure 4). While the bound gas is dominated by $C_{4+}$ hydrocarbons, typical for a wet gas, the amounts are too low to significantly influence the bound gas composition of near-surface sediment, which mostly has concentrations in the range between 100 and 2000 ppb (Weniger et al., 2019). Whether the light hydrocarbons were desorbed from peat or released by hydrolysis requires further investigation.

To test if bound gas is adsorbed, the standard acid gas extraction method is compared with a series of experiments involving (a) ultrasonication in a heated bath at 80° C for 1.5 hours, (b) ultrasonication in a heated bath at 80° C for 3 hours and addition of 20% hydrochloric acid, and (c) ultrasonication at 80° C for 3 hours and addition of 20% hydrochloric acid followed by addition of phosphoric acid, similar to the standard method (Figure 5). These tests were performed on sub-samples of a near-surface sediment from the Northern Barents Sea (Kveitola Trough). Because adsorption is an exothermal process, physically adsorbed gas can be desorbed by increasing temperature. However, experiments showed that by ultrasonication at 80°C less than 10 ppb gas was released from the near-surface sediment, which is more than two orders of magnitude lower than the amount released by the standard acid extraction method. Heating and addition of hydrochloric acid, which dissolves most carbonates, released significantly more gas, but still less than if phosphoric acid is used.

These experiments show that the majority of gas bound in near-surface marine sediment is only released after the sediment is dissolved or chemically disintegrated, indicating that gas is trapped within sediment particles rather than adsorbed on their surface. Some of the bound gas is released after dissolving carbonates, indicating that it was trapped within carbonate or in pores

sealed by carbonate cements. The majority of the gas, however, is bound in clays or other minerals and only released after treatment with phosphoric acid.

In the Northern Barents Sea iceberg plough marks and presence of ice-rafted debris are frequently observed in seafloor sediment. To investigate whether bound gas in near-surface marine sediment could be influenced or even inherited from gas bound to eroded and ice-transported sediment, samples of three different source rocks from outcrops on Svalbard where subjected to the standard acid extraction procedure. Samples included coal from the Paleocene Firkanten Formation, organic-rich shale from the Jurassic Agardhfjellet Formation, and the Triassic Botneheia Formation. The amount of bound gas extracted from these source rocks was variable, ranging from 200 ppb for the coal to more than 2000 ppb for the thermally mature and oil prone Botneheia Formation shale (Figure 6). Bound gas concentration is not related to source rock TOC, but shows good correlation to thermal maturity and related parameters such as Rock-Eval production index (S1/(S1+S2)) and bitumen index (S1*100/TOC). These results show that the concentration of bound gas in source rocks can be higher than the concentration of bound gas in marine near-surface sediments. If gas bound in source rocks survives erosion and transport, it can influence the concentration and composition of gas in near-surface sediments.

## Origin of Bound Gas in the Northern Barents Sea

The relationship between bound gas concentration and bitumen index (BI) observed in source rocks may indicate presence of allochthonous sediments with mature organic matter and associated bound gas. A comparison of bound gas concentration and bitumen index of source rocks with near-surface sediments from the Northern Barents Sea shows that all near-surface sediments with bound gas concentration anomalies higher than 1000 ppb from Storfjordrenna and the Olga Basin margin have low BI values and are not caused by gas bound in transported sediments (Figure 7). However, some near-surface sediments with anomalous bound gas concentration from the Kveithola Trough also have high BI values (higher than in all studied near-surface sediments from the Northern Barents Sea) and thus may be influenced by transported sediment.

The stable carbon isotope composition of bound gas is often used to identify gas origin (e.g. Faber and Stahl, 1984). Gas generated by thermal cracking of organic matter is characterized by methane $\delta^{13}C$ values larger than -50 ‰, VPDB, whereas values of microbial gas are mostly < -60 ‰, VPDB. Bound methane in near-surface sediment from the Northern Barents Sea indicates a thermogenic origin for areas with concentrations anomalies and mixtures of microbial and thermogenic gas for areas with lower bound gas concentrations (Figure 8).

The carbon isotope composition of ethane and propane is less influenced by microbial gas and reveals differences between areas with concentration anomalies found at Storfjordrenna south of Svalbard and the Olga Basin Margin. It also shows similarities between anomalous near-surface bound gas from the Northern Barents Sea with fields from the Southern Barents Sea that are associated with Jurassic or Triassic source rocks. The isotope composition of thermogenic gas depends on both thermal maturity and isotope composition of precursor organic matter, which is different for different kerogen types, e.g. $\delta^{13}C$ of terrigenous organic matter is mainly larger than of marine organic matter at the same maturity. Thus interpretation of precursor kerogen type and thermal maturity is not possible based on gas composition alone. By integrating bound gas isotope composition with structural information from 2D seismic data and thermal maturity estimated from a simplified 1D basin and petroleum system model, an origin from a Triassic source was found to be most likely for bound gas with anomalous concentration from the Olga Basin, whereas for bound gas from Storfjordrenna and the Kveithola Trough near the Western Barents Margin a Jurassic or younger source rock is more likely (Weniger et al., 2019).

## Conclusions

The bound gas acid extraction method releases only small amounts of gas from immature organic matter (peat); these amounts are negligible compared to amounts of bound gas typically found in near-surface sediments.

Less than 2% of bound gas was released by temperature desorption alone and less than 25% by heating and treatment with hydrochloric acid. Most near-surface bound gas is only released after dissolution and disintegration of the sediment using phosphoric acid. Bound gas is not simply adsorbed on sediment particle surfaces, but instead trapped within the mineral matrix or in closed pores.

Organic-rich source rocks can contain significant amounts of bound gas. The amount of bound gas extracted from source rocks correlates with source rock maturity and Rock-Eval S1. The relationship between bound gas concentration and bitumen index may reveal contribution of bound gas from transported material in near-surface sediments.

Bound gas in the Northern Barents Sea with concentration >1000 ppb is not influenced by transported material.

Stable carbon isotope composition of these bound gases suggests a thermogenic origin and reveals differences between gas from the Olga Basin area and locations near the Western Barents Margin (Storfjodrenna, Kveithola Trough).

Whether these differences are caused by differences in thermal maturity or by differences in precursor source organic matter (kerogen type) cannot be explained using bound gas geochemistry alone. Integration of bound gas composition with structural information from seismic data and 1D petroleum system and basin models suggests an origin from a Triassic source rock for the Olga Basin, whereas for Storfjordrenna and the Kveithola Trough a Jurassic or younger source of bound gas is more likely.

## Acknowledgements

We thank Karsten Piepjohn and Lutz Reinhard for support during the CASE 17-2 expedition and Malte Jochmann and Store Norske AS for valuable help during field work and sample collection in Mine 7.

Kai Berglar and BGR's PANORAMA team and the crews and onboard scientific parties of RV OGS Explora and RV Polarstern are thanked for support during marine expeditions BGR13-2, BGR15-2 and PS99.1. We thank Dietmar Laszinsky and Jürgen Poggenburg for assistance with gas analyses and isotope measurements, Daniela Graskamp and Philipp Grosche for assistance with sample preparation and bound gas extraction, Monika Weiß, Petra Adam, Sylvia Kramer and Georg Scheeder for assistance with bulk geochemical analyses of sediment samples and Jolanta Kus for vitrinite reflectance measurements.

We thank Eckhard Faber and Michael Abrams for valuable discussions on near-surface gas geochemistry.

## References Cited

Abrams, M., 2017, Evaluation of Near-Surface Gases in Marine Sediments to Assess Subsurface Petroleum Gas Generation and Entrapment: Geosciences, v. 7, p. 35.

Blumenberg, M., R. Lutz, S. Schlömer, M. Krüger, G. Scheeder, K. Berglar, I. Heyde, and P. Weniger, 2016, Hydrocarbons from near-surface sediments of the Barents Sea north of Svalbard – Indication of subsurface hydrocarbon generation?: Marine and Petroleum Geology, v. 76, p. 432-443.

Faber, E., and W. Stahl, 1983, Analytic Procedure and Results of an Isotope Geochemical Surface Survey in an Area of the British North Sea: Geological Society, London, Special Publications, v. 12, p. 51-63.

Faber, E., and W. Stahl, 1984, Geochemical surface exploration for hydrocarbons in North Sea: AAPG Bulletin, v. 68, p. 363-386.

Hinrichs, K.-U., J.M. Hayes, W. Bach, A.J. Spivack, L.R. Hmelo, N.G. Holm, C.G. Johnson, and S.P. Sylva, 2006, Biological formation of ethane and propane in the deep marine subsurface: Proceedings of the National Academy of Sciences, v. 103, p. 14684-14689.

Horvitz, L., 1972, Vegetation and Geochemical Prospecting for Petroleum: AAPG Bulletin, v. 56, p. 925-940.

Knies, J., E. Damm, J. Gutt, U. Mann, and L. Pinturier, 2004, Near-surface hydrocarbon anomalies in shelf sediments off Spitsbergen: Evidences for past seepages: Geochemistry, Geophysics, Geosystems, v. 5, p. Q06003.

Stahl, W., E. Faber, and D.L. Kirksey, 1981, Near-surface evidence of migration of natural gas from deep reservoirs and source rocks: AAPG Bulletin, v. 65, p. 1543-1550.

Weniger, P., M. Blumenberg, K. Berglar, A. Ehrhardt, P. Klitzke, M. Krüger, and R. Lutz, 2019, Origin of near-surface hydrocarbon gases bound in northern Barents Sea sediments: Marine and Petroleum Geology, v. 102, p. 455-476.

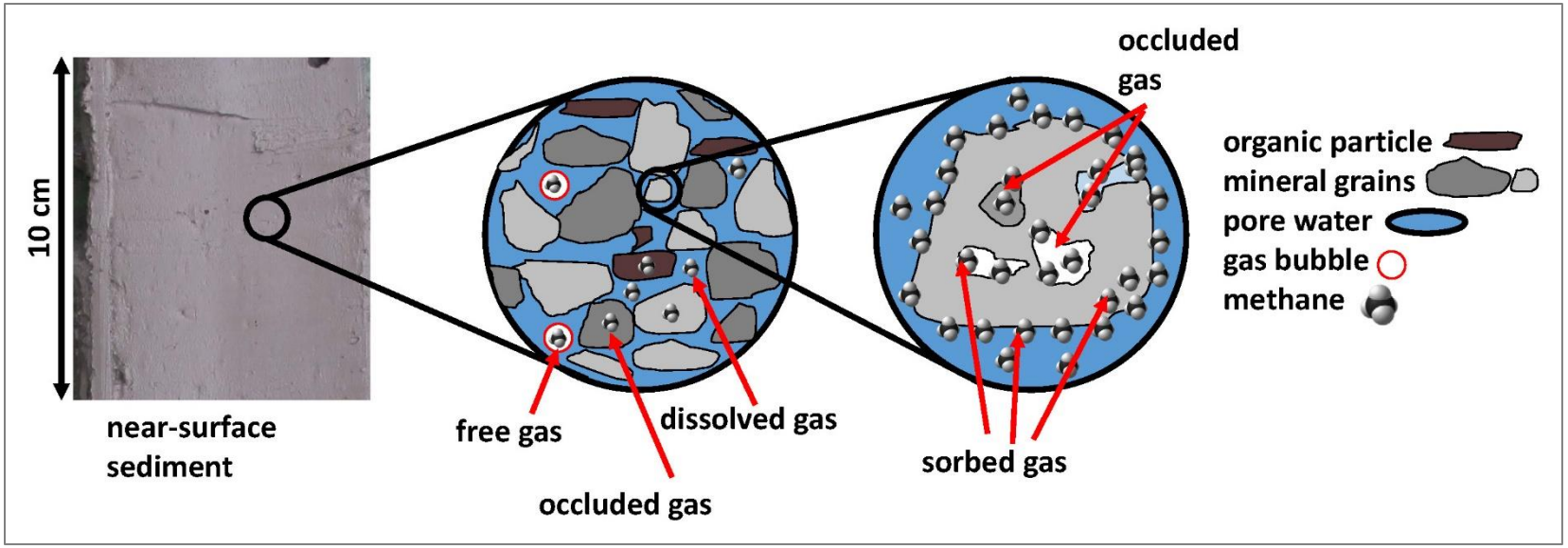


Figure 1. Sketch illustrating possible occurrence of gas in near surface sediment.

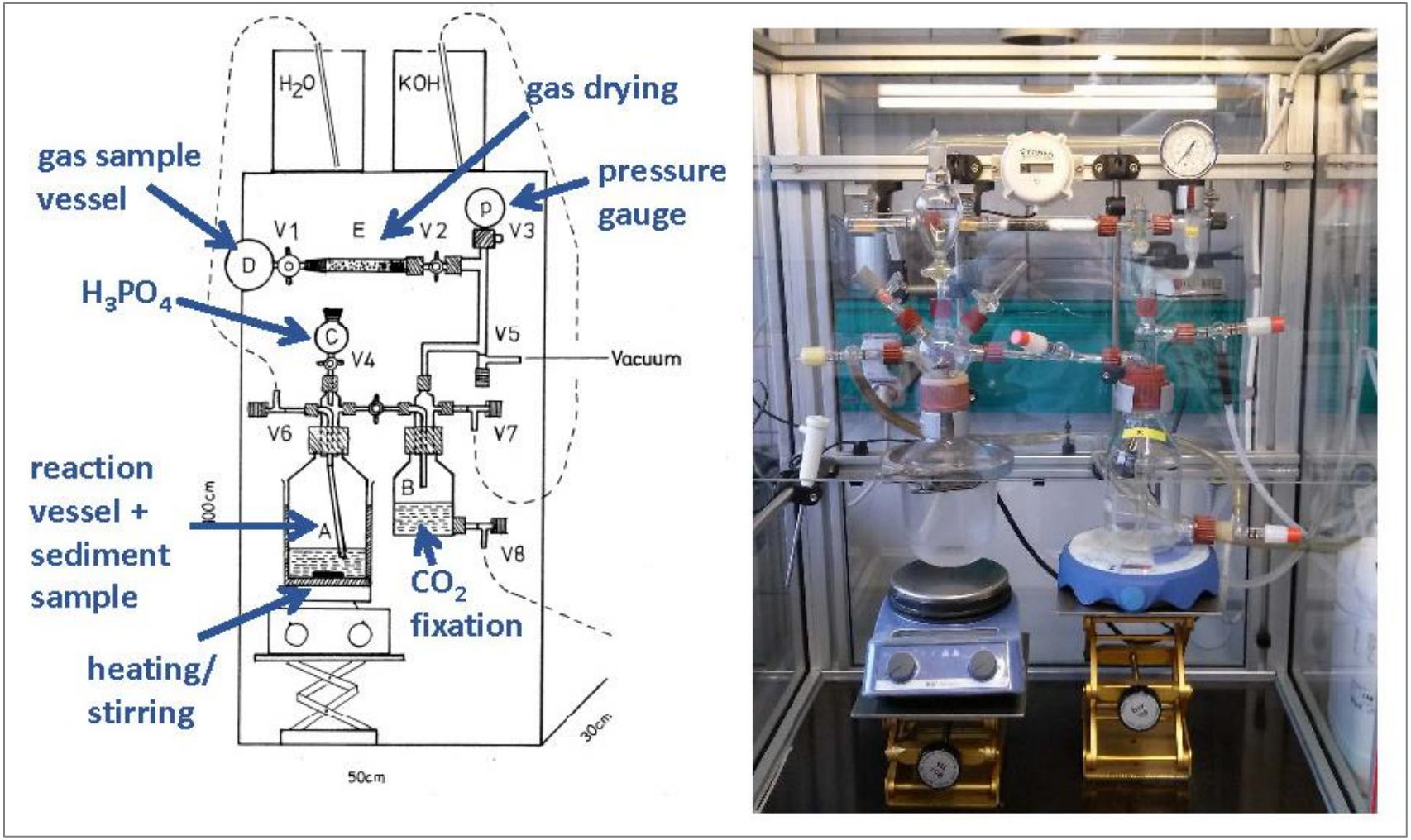


Figure 2. Modified Horwitz method for bound gas acid extraction used at BGR (schematic modified after Stahl and Faber, 1978, in Faber and Stahl, 1983).

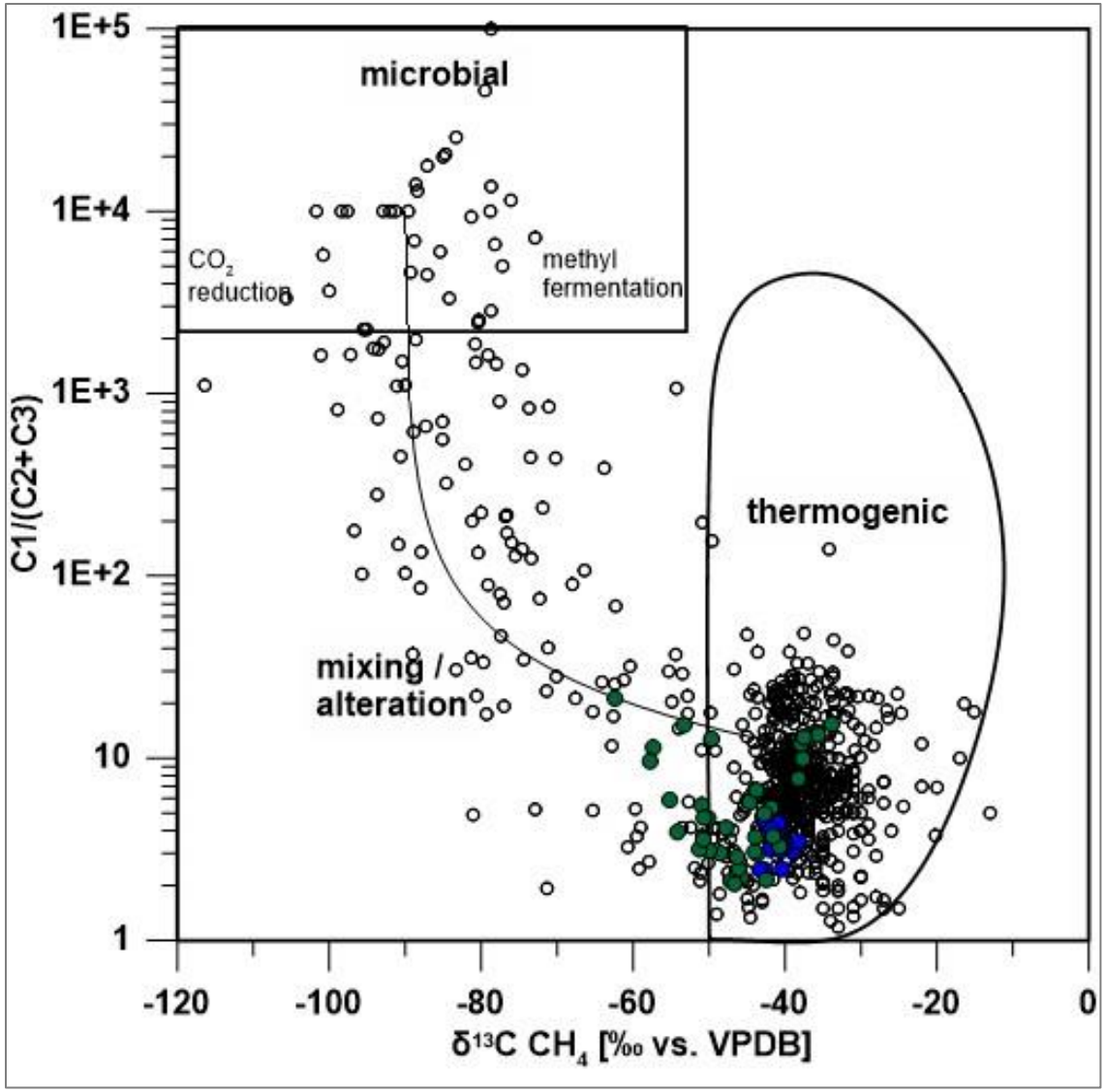


Figure 3. Compilation of bound gas data from the Northern Barents Sea (filled symbols) and various other locations (open symbols) (for details and references see Weniger et al., 2019).

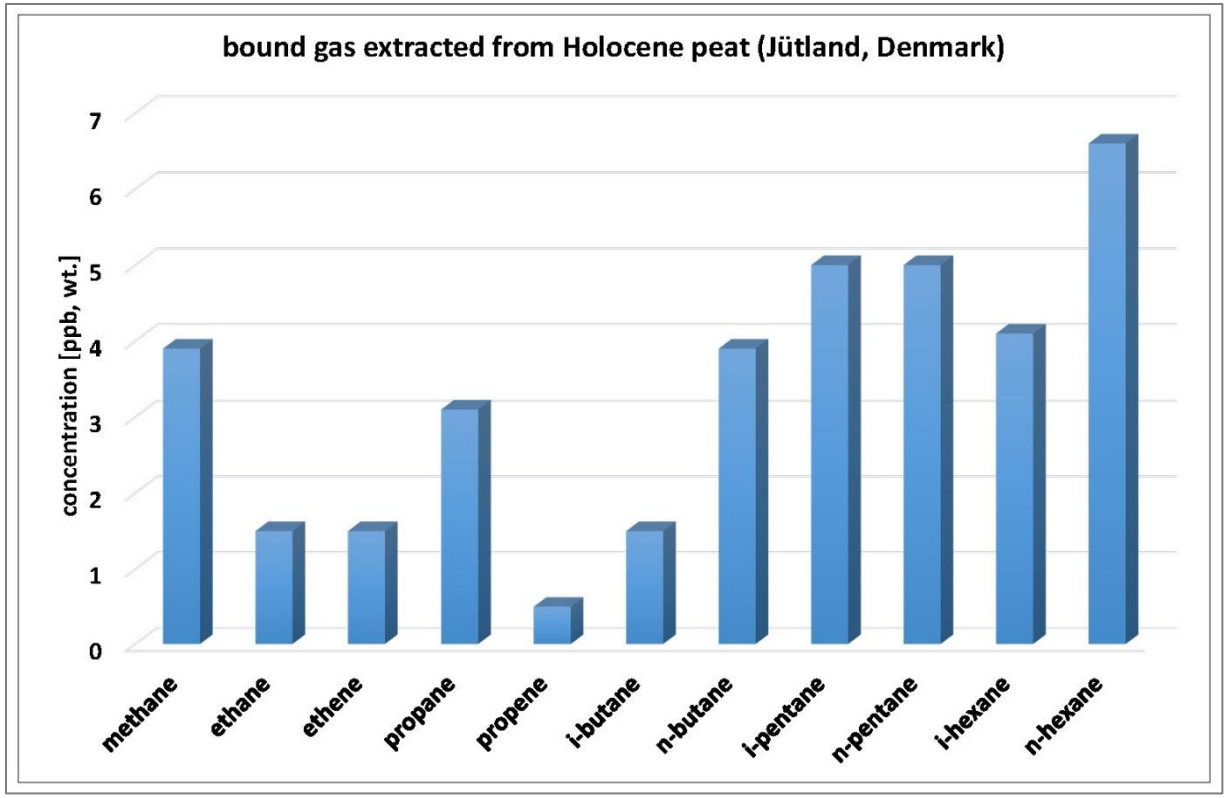


Figure 4. Bound gas released from a Holocene peat sample (North Jütland, Denmark, TOC 50.1%).

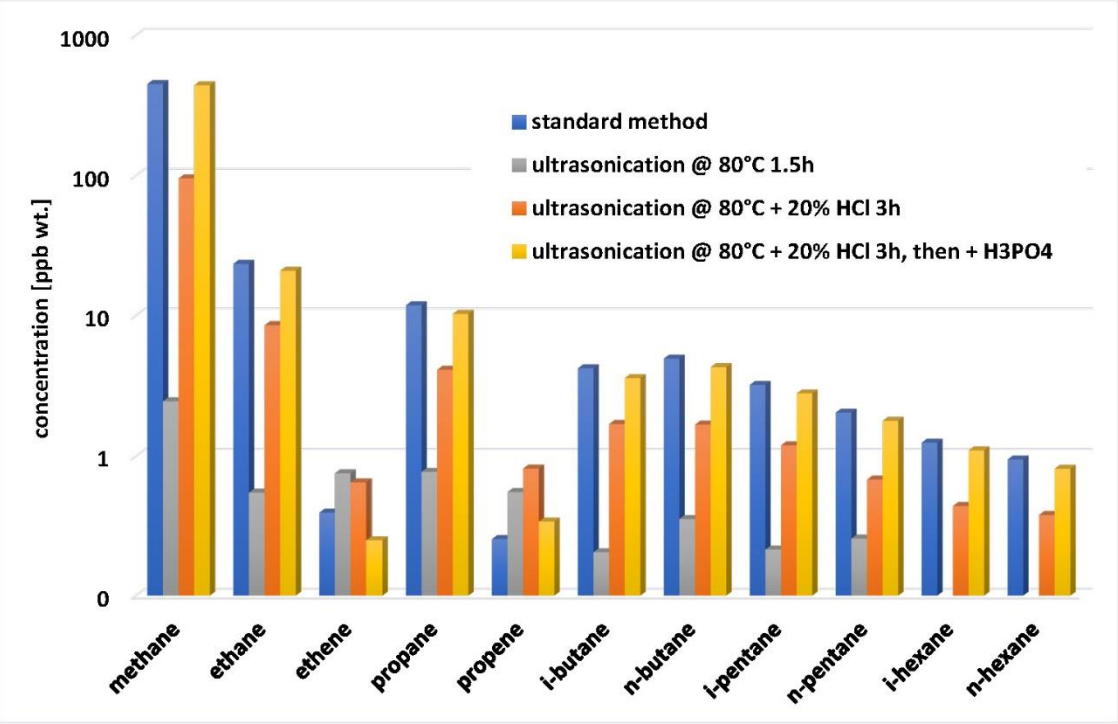


Figure 5. Results of bound gas extraction tests using ultrasonication, heating and different acid treatments.

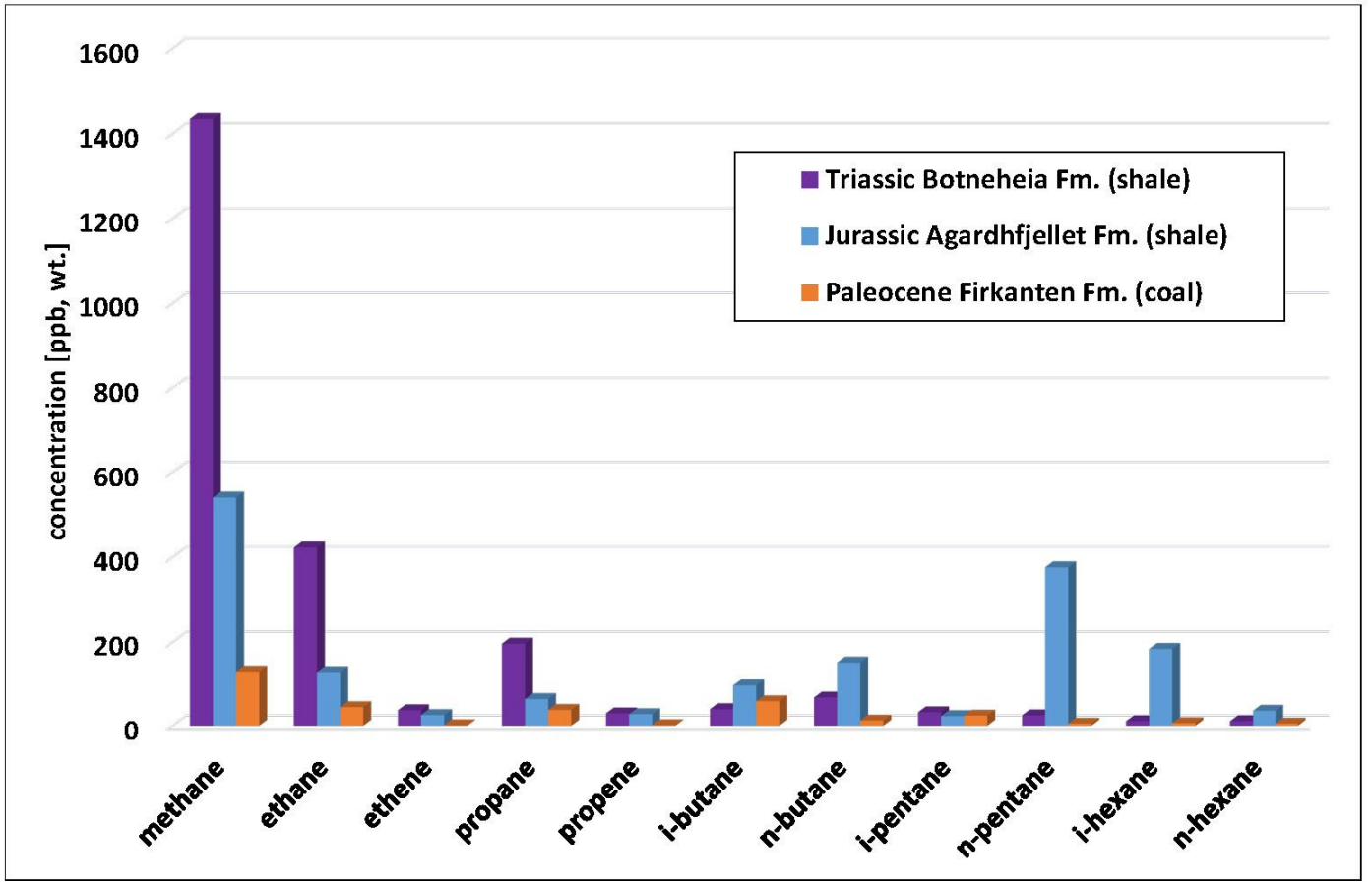


Figure 6. Bound gas extracted from different source rock samples from Svalbard.

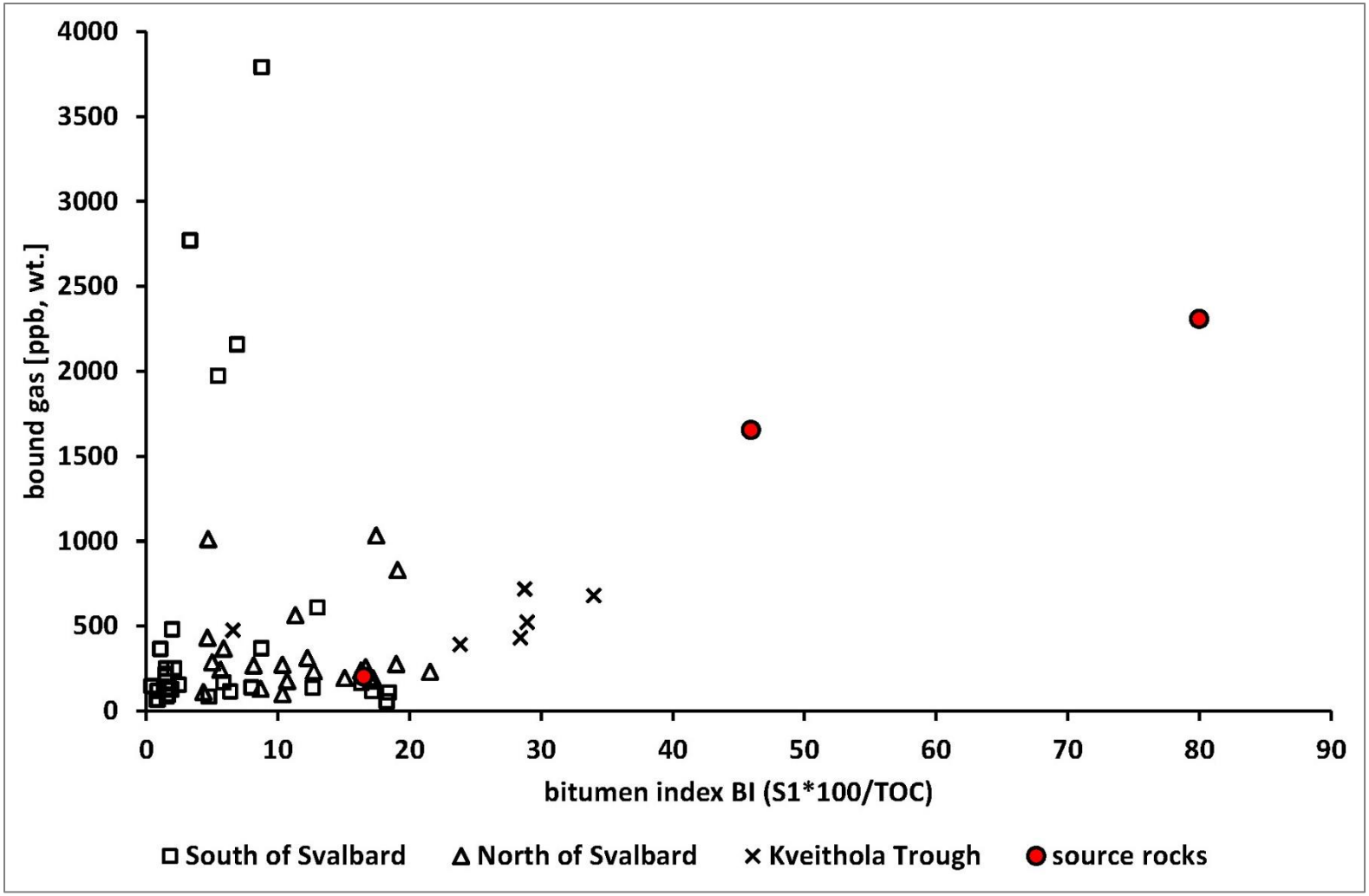


Figure 7. Comparison of bitumen index and bound gas concentration of source rock samples and near-surface sediments from the Northern Barents Sea collected north of Svalbard (Blumenberg et al., 2016) and at the Kveithola Trough and other areas south of Svalbard (Weniger et al., 2019).

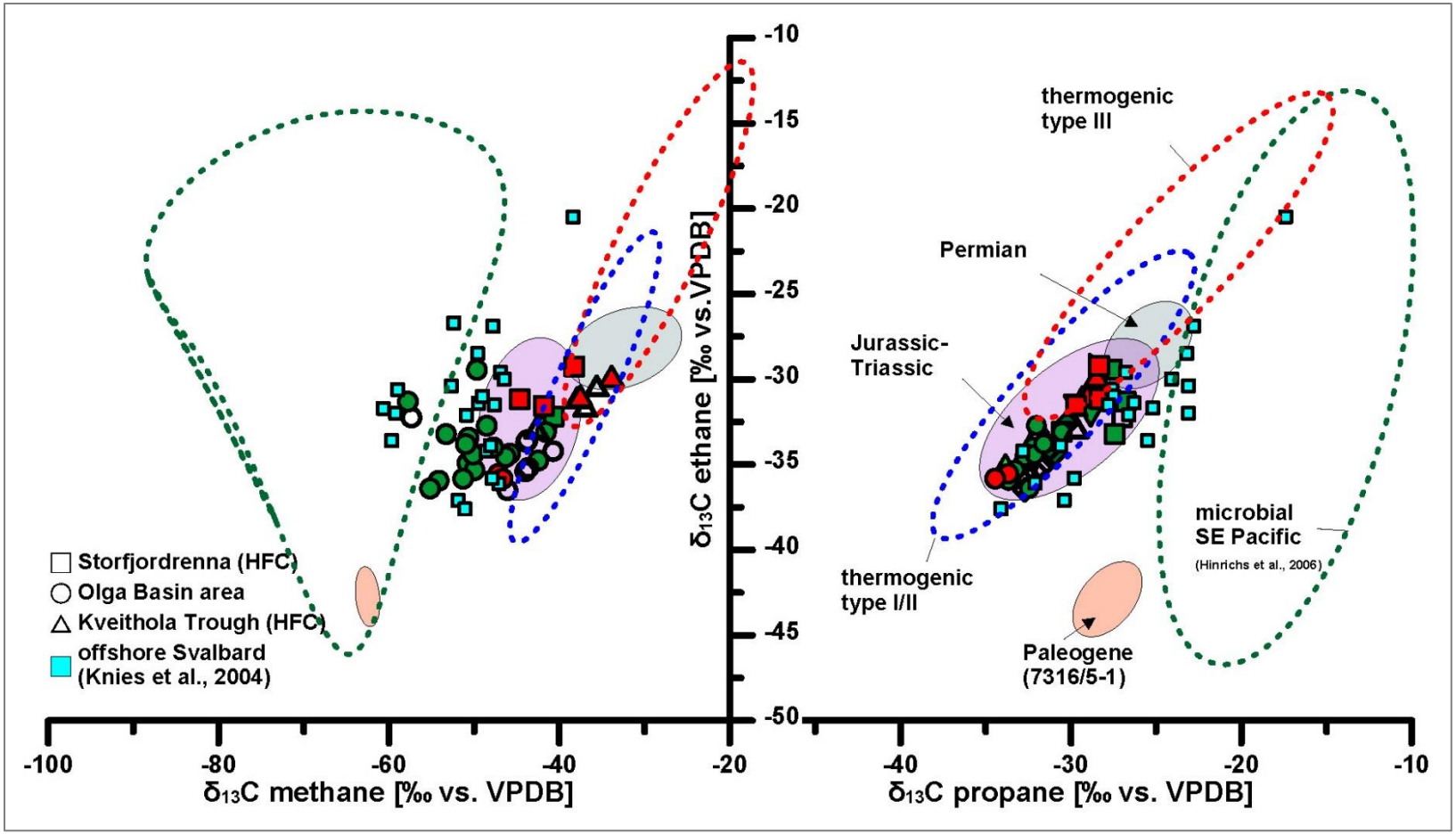


Figure 8. Stable carbon isotope composition of methane, ethane and propane of bound gas from the Northern Barents Sea. Shaded areas indicate gas reservoirs of different sources in the Southern Barents Sea (created using data published at www.npd.no). The dashed blue and red outlines indicate thermogenic gas generated during pyrolysis experiments of marine source rocks and coal, respectively.