

Fluid chemistry and shallow gas hydrate dynamics at active pockmarks of the Vestnesa Ridge, west Svalbard margin

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Abstract

Gas hydrate dynamics and the fluid flow systems from two active pockmarks along Vestnesa Ridge (offshore west Svalbard) were investigated through the pore fluid geochemistry obtained during the 2016 MARUM-MeBo 70 drilling cruise. Based on the pore water chloride concentration profiles from Lunde and Lomvi pockmarks, we estimated up to 47% pore space occupied by gas hydrate in the sediments shallower than 11.5 mbsf. These gas hydrates were formed during periods of gaseous methane seepage, but are now in a state of dynamic equilibrium sustained by a relatively low methane supply at present. We detect a saline formation pore fluid around nine meters below seafloor from one of the seepage sites in Lunde pockmark. This formation pore fluid has elevated dissolved chloride concentrations and B/Cl ratios, higher δO and δD isotopic signatures of water and lower δB signatures, which collectively hint to a high temperature modification of this fluid at great depths. By integrating our findings with the previous work from Vestnesa Ridge, we show that the variable fluid phases (gaseous vs. aqueous fluid) and migration pathways are controlled by the sediment properties, such as buried carbonate crusts, and the state of fluid reservoirs.

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Key Points:

- Up to 47% of gas hydrates from active pockmarks are currently at a dynamic equilibrium state sustained by relatively low methane fluxes.
- We document the migration of a saline formation fluid whose composition is modified by hydrate formation dynamics.
- We propose an evolution model for the Lunde pockmark and emphasize the role of buried seep carbonates in diverting fluids.

Abstract

Gas hydrate dynamics and the fluid flow systems from two active pockmarks along Vestnesa Ridge (offshore west Svalbard) were investigated through the pore fluid geochemistry obtained during the 2016 MARUM-MeBo 70 drilling cruise. Based on the pore water chloride concentration profiles from Lunde and Lomvi pockmarks, we estimated up to 47% pore space occupied by gas hydrate in the sediments shallower than 11.5 mbsf. These gas hydrates were formed during periods of gaseous methane seepage, but are now in a state of dynamic equilibrium sustained by a relatively low methane supply at present. We detect a saline formation pore fluid around nine meters below seafloor from one of the seepage sites in Lunde pockmark. This formation pore fluid has elevated dissolved chloride concentrations and B/Cl ratios, higher $\delta^{18}\text{O}$ and δD isotopic signatures of water and lower $\delta^{11}\text{B}$ signatures, which collectively hint to a high temperature modification of this fluid at great depths. By integrating our findings with the previous work from Vestnesa Ridge, we show that the variable fluid phases (gaseous vs. aqueous fluid) and migration pathways are controlled by the sediment properties, such as buried carbonate crusts, and the state of fluid reservoirs.

1 Introduction

Pockmarks are seafloor manifestations of sub-surface fluid discharge (Hovland et al. 2002, Hovland and Svensen 2006). The presence of pockmarks has been reported from a large depth range comprising continental shelf (Hovland et al. 2002) to deep sea regions (Ondréas et al. 2005, Sahling et al. 2008, Marcon et al. 2014, Sultan et al. 2014). Pockmarks in association with deep water gas hydrate system (~1200 meters water depth) have also been long recognized along Vestnesa Ridge off the west Svalbard margin (Vogt et al. 1994, Vogt et al. 1999). The Vestnesa pockmarks have been recently studied for their sub-surface fluid plumbing systems (Bünz et al. 2012, Knies et al. 2018), history of tectonic stress (Plaza-Faverola et al. 2015, Plaza-Faverola and Keiding 2019), controls of gas hydrate stability zone (Plaza-Faverola et al. 2017), as well as likely sources of light hydrocarbons and the biogeochemical consequence of fluid flow through fractures (Hong et al. 2016, Yao et al. 2019, Pape et al. 2020). Fluids fueling the Vestnesa pockmarks migrate along chimney-like conduits that are vertical zones characterized by brecciation/fracturing of the sediment that result in scattering of the seismic signal (Plaza-Faverola et al. 2015). These conduits have developed under tectonic stress and served as the main pathways for persistent fluid migration since the Pleistocene (Plaza-Faverola et al. 2015, Knies et al. 2018, Plaza-Faverola and Keiding 2019). However, it is not clear how the composition of this long-lasting fluid system evolves during the history of pockmarks along the Vestnesa Ridge as ground truth observations beyond a few meters subsurface are not yet available along the ridge. Specifically, substantial knowledge gaps exist in the geochemical composition of fluids as well as the interplay between pockmark evolution, near-seafloor gas hydrate dynamics and fluid migration at a meter-scale. Such a lack of information hinders the evaluation of the present model about pockmark evolution from Vestnesa Ridge.

Here, we report pore fluid composition (concentrations of dissolved chloride and boron) and isotopic ratios ($\delta^{18}\text{O}$ -H₂O, δD -H₂O, and $\delta^{11}\text{B}$) obtained from sediments recovered during the 2016 MARUM-MeBo drilling campaign (cruise MSM57-1/-2) from Lunde and Lomvi pockmarks (Bohrmann et al. 2017), two of the most active pockmarks in terms of seafloor gas emissions along Vestnesa Ridge (Bünz et al. 2012). Because pore fluid chloride is a conservative tracer whose concentrations is unaffected by biogeochemical activities, downcore chloride concentration profiles have been widely used to infer the in-situ production and consumption of water (such as due to gas hydrate dissociation and formation) as well as physical mixing of water from different

sources (Kastner et al. 1991, Torres et al. 2011, Kim et al. 2013a, Kim et al. 2016, Wallmann et al. 2018, Hong et al. 2019). Especially, positive chloride concentration anomalies could occur when gas hydrate is actively forming and expelling chloride at a rate much faster than chloride diffusion, which results in the accumulation of chloride in the pore fluid (Ussler and Paull 2001). Such anomalies have been successfully applied to infer formation conditions and quantify the rates of gas hydrate formation (Ussler and Paull 2001, Haeckel et al. 2004, Milkov et al. 2004, Torres et al. 2004, Tomaru et al. 2006, Torres et al. 2011, Peszynska et al. 2016, Hong and Peszynska 2018).

To further differentiate the various processes in the pore fluid, $\delta^{18}\text{O}$ and δD signatures of water serve as additional constraints (Kastner et al. 1991, Martin et al. 1996, Hong et al. 2019, Chen et al. 2020). Different diagenetic processes, such as authigenic clay transformation, ion filtration as well as gas hydrate formation and decomposition, result in variable degrees of fractionation on $\delta^{18}\text{O}$ and δD of water (Kastner et al. 1991, Maekawa et al. 1995). Dissolved boron, a minor constituent in the pore fluid but abundant in various silicate minerals (see the review by Marschall 2018 and references therein), is an excellent tracer for water-rock interactions. The diagenetic reactions that involves silicate minerals (such as clays) releases abundant dissolved boron with low $\delta^{11}\text{B}$ values due to the large isotopic fractionation associated with boron desorption under medium to high temperatures (Palmer et al. 1987, Spivack et al. 1987, You et al. 1995, James and Palmer 2000). Repeated observations of these distinct $\delta^{11}\text{B}$ signatures in pore fluid have proven the applicability of the boron proxy to evaluate the origin of fluids generated at greater depths (You et al. 1995, You et al. 1996, Deyhle and Kopf 2001, Kopf and Deyhle 2002, Hüpers et al. 2016). With the information of pore fluid geochemistry from a sediment depth down to 60 meters below seafloor (mbsf), we intend to address the interaction between fluid migration, gas hydrate dynamics and pockmark evolution from the most active pockmarks along Vestnesa Ridge.

2 Materials and Methods

2.1 Drilling/coring sites during cruise MSM57-1/-2

The sediment cores studied herein (Tab. 1) were collected during cruise MSM57-1/-2 onboard 'RV MARIA S. MERIAN' with the seafloor drill rig MARUM-MeBo70 (Freudenthal and Wefer 2013). Coring positions were guided by high resolution bathymetry data (Fig. 1b) collected during a cruise 1606 onboard R/V G.O. Sars a few months before the MSM57 cruise. We combined the results from gravity cores taken close to MeBo drill sites to obtain a better coverage in the uppermost few meters of the sediments (Tab. 1). The three locations investigated from Lunde pockmark include a non-seepage site from the central depression of the pockmark (GeoB21601-1 & GeoB21605-1 & GeoB21610-1) and two sites with high methane fluxes (SW seepage site: GeoB21621-1 & GeoB21637-1 and SE seepage site: GeoB21619-1) (Fig. 1a). As a comparison to the Lunde pockmark, we also report results from two gravity cores recovered from the seepage area of Lomvi pockmark (GeoB21623-1 & GeoB21624-1). In addition, a low methane flux site (GeoB21606-1 & GeoB21613-1) that is outside any pockmark footprint is included as a reference (Fig. 1a). Gas hydrates were only recovered from the seepage sites of both pockmarks (Fig. 1b).

2.2 Pore water sampling and analyses

The procedures for sediment core handling are detailed in Bohrmann et al. (2017). Briefly, sectioning of the sediment cores and sampling for pore water were done at an ambient temperature of ~10 °C. Before splitting into halves, the surfaces of the core liners were scanned with infrared radiation (IR) camera (see Pape et al. 2020) to detect negative thermal anomalies that can be caused by the endothermic gas hydrate dissociation (Trehu et al. 2004). We sampled 2-3 cm sections from the working halve of the gravity cores and 8-10 cm from the working halve of the MeBo cores for pore water extraction by using the GEOMAR argon-gas squeezers. In average, it took 30 to 45 minutes to squeeze 5-10 ml of pore water. Squeezing was performed in a +4 °C refrigerated room. Gas pressure was monitored and never exceeded five bars during the squeezing. Water from completed dissociated gas hydrate, as indicated by the dissipating temperature anomalies, was sampled with acid-washed rhizons and syringes (Seeberg-Elverfeldt et al. 2005) and treated identical to other pore water samples. Three gravity cores were dedicated to recover intact gas hydrate. The gas hydrate samples were preserved within liquid nitrogen for storage at MARUM. Centimeter-sized gas hydrate subsamples were later left to dissociate at room temperature to obtain water samples from gas hydrate for analyses of cation concentrations and stable boron isotopic signatures. The hydrate-bound water was filtered with 0.2 µm disposable in-line syringe filters and preserved with acid-washed vials.

After extraction, pore water was divided into sub-samples for further analysis. Shipboard analyses of dissolved chloride concentrations ([Cl]) were conducted through titration with silver nitrate as documented in Bohrmann et al. (2017). For the analyses of stable oxygen and hydrogen isotopes of water ($\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$, hereafter as $\delta^{18}\text{O}$ and δD throughout the text), pore water sub-samples were filled into 2 ml glass vials without headspace. Sub-samples for cations were acidified with 10 µl of concentrated reagent grade nitric acid. Separated acid-washed 1.5 ml Eppendorf vials were used for the analyses of stable isotopes of boron ($\delta^{11}\text{B}$) in the pore fluid. No nitric acid was added to these sub-samples. $\delta^{18}\text{O}$ and δD signatures were determined with a Delta plus XP isotope ratio mass spectrometer (Thermo Fisher Scientific) as detailed in Wallmann et al.

(2018). These values are reported against the Vienna Standard Mean Ocean Water (V-SMOW) standard. For analysis of $\delta^{11}\text{B}$ in pore water, 10 μl of non-acidified samples was put through boron-specific anionic exchange resin Amberlite IRA 743 (Kiss 1988, Yoshimura et al. 1998) to isolate 2-10 ng of boron, following the protocol described by Foster (2008). Analyses of the isotopic ratios were performed with a Neptune multicollector inductively coupled plasma-mass spectrometer (MC-ICPMS) at the St Andrews Isotope Geochemistry (STAiG) Laboratory of the University of St. Andrews following methods detailed previously (Rae et al. 2011, Foster et al. 2013, Rae et al. 2018) with long-term reproducibility of 0.2‰ (2 σ). Values are reported against the NIST 951 standard.

2.3 Quantification of gas hydrate abundance from pore water chloride concentration profiles

During core recovery, dissociation of gas hydrate releases fresh water into the ambient pore space. Such process results in lower [Cl] as compared to the background [Cl] within the hydrate-bearing sediments (Matsumoto 2000, Ussler and Paull 2001, Hesse 2003, Torres et al. 2004, Tomaru et al. 2006, Kim et al. 2013a). Through calculating the difference, we can estimate gas hydrate saturation (S_h in Figs. 2i, 2n and 2t and Tab. 2). Defining the background profile of [Cl] is critical as the water samples containing or adjacent to gas hydrate are inevitably affected by gas hydrate dissociation. We used the [Cl] from sediment samples without any sign of hydrate presence (*e.g.*, no IR anomaly and visual observation) to establish the background [Cl] profiles. Such an exercise was applied to the seepage sites in the Lomvi and Lunde pockmarks (Tab. 2). For the three gravity cores with less than 5-meter of recovery (GeoB21619-1: Lunde SE seepage site; GeoB21623-1, GeoB21624-1: Lomvi pockmark), we fit the downcore [Cl] with linear regressions and extrapolated to the depth range where gas hydrates were recovered. We fit the [Cl] from hydrate-free samples of Lunde SW seepage site with a 4th order polynomial regression to interpolate the background [Cl] for the two hydrate-bearing intervals. The percentages of gas hydrate in the pore space (S_h) from these cores at various depths were calculated according to:

$$S_h (\% \text{ pore space}) = \frac{\beta \times ([\text{Cl}]_{\text{obs}} - [\text{Cl}]_{\text{fit}})}{[\text{Cl}]_{\text{fit}} + \beta \times ([\text{Cl}]_{\text{obs}} - [\text{Cl}]_{\text{fit}})} \times 100$$

where $[\text{Cl}]_{\text{fit}}$ is the interpolated or extrapolated chloride concentration while $[\text{Cl}]_{\text{obs}}$ is the observed chloride concentrations (Tab. 2). Factor β (1.257) is a dimensionless constant that accounts for the density change during hydrate dissociation (Malinverno et al. 2008).

3 Results

3.1 Downcore distribution of gas hydrate from the seepage sites in Lunde and Lomvi pockmarks

The hydrate-bearing intervals for all the sediment cores investigated were determined by shipboard visual inspection, thermal anomalies with IR measurements, and later confirmed by the freshening observed from pore fluid composition. Much shallower gas hydrate occurrences were documented from Lunde SW seepage site by Pape et al. (2020) with a depth of 0.45 mbsf reported for the gravity core GeoB21609-1. This core is however not investigated for pore fluid

geochemistry. For the two MeBo cores recovered from Lunde SW seepage site, gas hydrates were observed exclusively from two depth intervals: 5.80 to 8.28 mbsf and 10.29 to 11.54 mbsf. Gas hydrates were recovered below 3.30 mbsf from the gravity core in Lunde SE seepage site. Three thin layers of gas hydrates between 1.54 mbsf and 2.62 mbsf were recovered by two gravity cores from Lomvi pockmark. Gas hydrate saturations calculated from [Cl] in the Lunde SW and SE seepage sites as well as the Lomvi seepage site range from <1% to 47% of the pore space (Tab. 2).

3.2 Downcore variation in pore water composition

Illustrations of pore water data from all cores investigated in this study were compiled based on their locations (Fig. 2). We report the downcore concentration profiles of dissolved sulfate and chloride as well as pore water B/Cl ratios, $\delta^{11}\text{B}$, $\delta^{18}\text{O}$, and δD to investigate the sources of fluid and gas hydrate dynamics. Downcore methane and sulfate concentrations were reported by Pape et al. (2020). Dissolved sulfate concentrations decrease rapidly towards the sulfate-methane-transition (SMT) which is defined by the shallowest depth where significant amount of methane can be detected and sulfate concentrations drop to a sub-millimolar (mM) level (Figs. 2a, 2e, 2h, 2m and 2s). SMT depths range from *ca.* 10 mbsf at the reference site, 2.5 mbsf in the non-seepage site and less than one mbsf for the two seepage sites (Fig. 2). A few mM sulfate can still be observed in the deeper sediments, which may be due to the contamination by seawater during core handling and pore water sampling (Bohrmann et al. 2017, Pape et al. 2020).

We report pore water B/Cl ratios, instead of absolute concentrations of dissolved B, to correct for the effect of gas hydrate dissolution and formation. Pore water B/Cl ratio profiles from the reference site and the non-seepage site in Lunde pockmark exhibit downcore decreasing trends in general (Figs. 2c & 2g). In the Lunde SE seepage site, pore water B/Cl ratios are fairly constant with depth except for the two measurements from the hydrate-bearing interval (3.35 to 4.73 mbsf, Fig. 2l). In the Lunde SW seepage site, pore water B/Cl ratios slightly decrease with depth above four mbsf and increase from the two hydrate-bearing horizons (5.80 to 8.28 mbsf and 10.29 to 11.54 mbsf, Fig. 2q). From the Lomvi pockmark, pore water B/Cl ratios decrease with depth for the uppermost three meters of sediments. Only the two samples from 2.56 and 2.62 mbsf show anomalously high pore water B/Cl ratios (Fig. 2w).

The $\delta^{11}\text{B}$ in pore water were measured for samples from the reference and Lunde SW seepage sites as well as from Lomvi pockmark sites. The $\delta^{11}\text{B}$ profile from the reference site shows a slight decreasing trend from the expected seawater value of +39.61 ‰ at seafloor to +37.0 ‰ at five mbsf and an increase with depth to +41.0 ‰ between five mbsf and the bottom of the core (*ca.* 60 mbsf) with a few fluctuations in between (Fig. 2d). From the Lunde SW seepage site, the $\delta^{11}\text{B}$ values also slightly decrease from the expected seawater value at seafloor to +37.0 ‰ at four mbsf (Fig. 2r). The values increase to +39.5 ‰ at 15.11 mbsf with low values (+35.0 ‰ to +37.5 ‰) within the intervals where gas hydrates were recovered (Fig. 2r). A slight decrease in $\delta^{11}\text{B}$ values with depth (from +39.0‰ to +37.0‰) was observed from the four available measurements in the top 2.62 meters in the Lomvi pockmark cores (Fig. 2x). The two gas hydrate samples have $\delta^{11}\text{B}$ values of +26.5‰ and +30.3‰ that are significantly lower than all the values from pore fluid samples investigated.

3.3 Pore water chloride concentrations and stable O and H isotopes of water

Downcore [Cl] at the Lunde reference and the non-seepage sites show small variations ranging between 540 and 560 mM (Figs. 2b & 2f). Larger variations in the [Cl] (424.1 to 890.7 mM) were observed from the Lunde SW and SE seepage sites as well as from Lomvi seepage site (Figs. 2i, 2n and 2t and Tab. 2). The [Cl] at the Lunde SE seepage site show a gradual increase in the uppermost three meters of sediments from 572.4 mM to 618.8 mM. In the hydrate-bearing sediments below three mbsf, [Cl] fluctuate between 376.4 mM and 608.9 mM. The [Cl] profile from the Lunde SW seepage site shows a more complicated structure. The range of [Cl] from the hydrate-free sediments for the uppermost six meters of sediments is fairly narrow (575.4 mM to 591.3 mM) with a pronounced downcore increase observed from ca. 6 mbsf to 15.11 mbsf (528.8 mM to 890.7 mM, respectively). For the samples taken from the two hydrate-bearing intervals of the site, [Cl] fluctuate between 424.1 mM and 607.8 mM. At Lomvi seepage site, [Cl] show a general downcore increasing trend with anomalously low values down to 541.8 mM in the three sediment horizons where gas hydrates were recovered (1.54, 2.38, and 2.62 mbsf; Fig. 2t & Tab. 2).

$\delta^{18}\text{O}$ and δD were analyzed for seepage sites in the Lunde and Lomvi pockmarks. At the Lunde SE seepage site, the values of both isotopes decrease slightly with depth from 0.19‰ to 0.02‰ for $\delta^{18}\text{O}$ and -0.06‰ to -0.51‰ for δD within the uppermost three meters of hydrate-free sediments (Figs. 2j & 2k). Water samples taken from the hydrate-bearing samples deeper than 3.35 mbsf at this site have values up to 1.1 and 7.9‰ for $\delta^{18}\text{O}$ and δD , respectively (Figs. 2j & 2k). At the Lunde SW seepage site, the downcore $\delta^{18}\text{O}$ and δD profiles also exhibit complex structures with relatively little fluctuation in values above six mbsf and high values observed in the two hydrate-bearing intervals (Figs. 2o & 2p). Between six and 10 mbsf the isotopic values gradually increase with depth in the hydrate-free sediments and decrease towards lower values (0.25‰ for $\delta^{18}\text{O}$ and 1.80‰ for δD) in the deepest three samples (14.74 to 15.12 mbsf; Figs. 2o & 2p). In general, there are relatively smaller changes in both $\delta^{18}\text{O}$ and δD signatures from the Lomvi seepage site. Only one sample at 2.38 mbsf show slightly higher $\delta^{18}\text{O}$ (0.5‰) and δD values (2.4‰) as compared to values for bottom seawater (Figs. 2u & 2v).

4 Discussion

4.1 Pore water source inferred from chloride concentration, $\delta^{18}\text{O}$ and δD

We investigate the sources of water and processes that contribute to the observed changes in fluid composition from the Lunde seepage sites by studying the profiles of [Cl], $\delta^{18}\text{O}$ and δD . We compare our data ([Cl]_{obs}, $\delta^{18}\text{O}_{\text{obs}}$ and $\delta\text{D}_{\text{obs}}$) with the values from assigned references ([Cl]_{ref}, $\delta^{18}\text{O}_{\text{ref}}$ and $\delta\text{D}_{\text{ref}}$) to investigate the effect of fluid mixing and gas hydrate dynamics (Fig. 3). We chose two sets of reference composition: modern seawater (Lunde SE seepage site) and the composition of a sample from 8.78 mbsf (Lunde SW seepage site) for reasons discussed below.

Following the approach developed by Tomaru et al. (2006), we defined the normalized chloride concentrations, f , as the ratios between observed and reference dissolved chloride concentrations (i.e., [Cl]_{obs}/[Cl]_{ref}) (Fig. 3). The f values reflect the mixing of fluids with different [Cl]. The f values larger than one indicate consumption of fresh water through processes such as gas hydrate formation, while values smaller than one refer to fresh water addition through processes such as gas hydrate decomposition. We also defined parameters that describe the

differences between observed and reference isotopic signatures of water as $\Delta\delta^{18}\text{O}$ ($= \delta^{18}\text{O}_{\text{obs}} - \delta^{18}\text{O}_{\text{ref}}$) and $\Delta\delta\text{D}$ ($= \delta\text{D}_{\text{obs}} - \delta\text{D}_{\text{ref}}$) (Fig. 3). Gas hydrate formation is known to preferentially concentrate ^{18}O and ^2H in the hydrate lattice and result in lower $\delta^{18}\text{O}$ and δD values in the residual fluids following experimentally determined isotopic fractionation factors ($\alpha_{\text{O}}=1.0023$ to 1.0034 and $\alpha_{\text{H}}=1.014$ to 1.024 ; Maekawa (2004)). During gas hydrate decomposition, the release of ^{18}O - and ^2H -enriched fresh water from hydrate lattice results in higher $\delta^{18}\text{O}$ and δD values of the pore water.

All the data from the Lunde SE seepage site can be well explained when modern seawater values ($[\text{Cl}]_{\text{ref}}$: 574 mM; $\delta^{18}\text{O}_{\text{ref}}$: $+0.2\text{‰}$; $\delta\text{D}_{\text{ref}}$: -0.06‰) were chosen as the reference (Figs. 3a & 3b). The data from hydrate-bearing samples can be explained as the buried seawater modified by gas hydrate dissociation during core recovery. The downcore increase in $[\text{Cl}]_{\text{obs}}$ (up to 633 mM) from the hydrate-free samples at this site may hint to ongoing gas hydrate formation. However, this inference is only marginally supported by the $\delta^{18}\text{O}_{\text{obs}}$ and $\delta\text{D}_{\text{obs}}$ signatures as the pore water sample from 2.53 mbsf, where the deepest hydrate-free sediment sample were obtained, are only slightly depleted in ^{18}O and ^2H . In addition, $\delta^{18}\text{O}_{\text{obs}}$ and $\delta\text{D}_{\text{obs}}$ signatures from samples deeper than 2.53 mbsf were affected by hydrate dissociation during core recovery and thus cannot be used to infer any likely formation of gas hydrate.

In contrast, the changes in $\delta^{18}\text{O}_{\text{obs}}$ and $\delta\text{D}_{\text{obs}}$ from the Lunde SW seepage sites cannot be explained with hydrate dynamics if the composition of modern seawater is assigned as the reference (Suppl. Fig. 1). Instead, the data can be better fitted when the composition of the sample from 8.78 mbsf is used as the reference ($[\text{Cl}]_{\text{ref}}$: 616 mM, $\delta^{18}\text{O}_{\text{ref}}$: $+0.60\text{‰}$, $\delta\text{D}_{\text{ref}}$: $+3.76\text{‰}$) (Figs. 3c & 3d). This composition hints to the presence of a saline formation fluid that, when compared to modern seawater, it has higher $[\text{Cl}]$ by 42 mM as well as higher $\delta^{18}\text{O}$ and δD values by 0.40‰ and 3.76‰ , respectively. Between seafloor and 5.80 mbsf, $[\text{Cl}]$, $\delta^{18}\text{O}$ and δD reflect mixing between this saline formation water and modern bottom seawater (Figs. 3c & 3d). Between 5.80 and 11.54 mbsf, this saline formation water was modified by gas hydrate dissociation during core recovery (Figs. 3c & 3d) which results in $\Delta\delta^{18}\text{O}$ and $\Delta\delta\text{D}$ values up to 1‰ and 7‰ , respectively. Below 11.54 mbsf, the enrichment in chloride concentrations up to 890 mM as well as $\delta^{18}\text{O}_{\text{obs}}$ and $\delta\text{D}_{\text{obs}}$ similar to modern seawater values can be best explained by the saline formation water modified by active gas hydrate formation, even though there is no gas hydrate recovered (Figs. 3c & 3d).

We propose that this saline formation water originated from old evaporated seawater that was buried with the formation at great depths. Though not without uncertainties, this explanation is supported by the overall similar Br/Cl ratios between our pore fluid samples and seawater (Suppl. Fig. 2). An alternative explanation for the high $[\text{Cl}]$, $\delta^{18}\text{O}$ and δD of the proposed saline fluid is the residual fluids after clay ion filtration, which leads to the enrichments of anion as well as high $\delta^{18}\text{O}$ and δD values (Phillips and Bentley 1987). This explanation however fails to explain why the same saline formation water is not observed from other sites investigated (*e.g.*, Lunde non-seep and reference sites, Fig. 2) which should all be situated in a similar clay mineral composition. Authigenic clay formation is also known to result in residual fluids with high $[\text{Cl}]$ (Kastner et al. 1991, Sheppard and Gilg 1996, Dählmann and De Lange 2003). This explanation can however be ruled out as clay formation fractionates $\delta^{18}\text{O}$ and δD in opposite directions (Kastner et al. 1991, Sheppard and Gilg 1996, Dählmann and De Lange 2003) and cannot explain the high values in both $\delta^{18}\text{O}$ and δD of this saline formation fluid from Lunde SW seepage site.

4.2 Modes of gas hydrate formation controlled by methane supply

We estimated S_h up to 35% pore space from the two hydrate-bearing horizons in the Lunde SW seepage site based on the [Cl] (Fig. 2n and Tab. 2). At Lunde SE seepage site and Lomvi seepage site the maximum S_h is 47% and 13%, respectively (Figs. 2i, 2t and Tab. 2). Our estimation is much higher than those derived from waveform inversion modeling of ocean-bottom seismic (OBS) (0-2 % pore space in the first 50 meters of sediments from Singhroha et al. 2019), but similar to the estimation based on controlled source electromagnetic (CSEM) (*ca.* 30 % pore space; Goswami et al. 2017) from Vestnesa Ridge. We acknowledge that part of the differences can be attributed to the different methods used (geophysical vs. geochemical), different geophysical scales focused by these methods, and the locations where these measurements were performed (*i.e.*, ridge crest vs. flank) with the OBS stations located outside the pockmark footprint and the CSEM transmitter being towed along the ridge. Nonetheless, while the OBS estimation may represent a gas hydrate distribution under a diffusive flow system (Singhroha et al. 2019), our results and the CSEM estimation likely represent the saturation from the chimney where gas hydrate formation is actively sustained by focused gaseous methane supplied through fractures. We however noted that these geophysical methods are not able to differentiate free gas from gas hydrate (Singhroha et al. 2020). Direct comparison of hydrate saturation may be problematic.

We are able to differentiate the status of gas hydrate deposits, namely active formation versus dynamic equilibrium under ambient pressure and temperature conditions, based on the [Cl] data. It has been shown from Hydrate Ridge, Cascadia Margin (NE Pacific Ocean), and Ulleung Basin (Sea of Japan or East Sea) that positive chloride concentration anomalies are not necessarily associated with all hydrate deposits (see Hong and Peszynska 2018 for a review of data from these locations). When hydrate formation slows down, deposits of gas hydrate can reach a status of dynamic equilibrium. In other words, there is no net gain or loss of gas hydrate under such status as hydrate formation is as fast as its dissolution. The supply of methane is only high enough to maintain the dissolved methane concentration at a saturation level and compensate for methane loss via diffusion and microbial consumption (*e.g.*, anaerobic oxidation of methane, Boetius et al. 2000), but too low to support additional hydrate formation. Dissolved chloride that is expelled during an early stage of active formation slowly diffuses away under the dynamic equilibrium.

Hong and Peszynska (2018) applied a kinetic model on the data obtained from IODP Site1328 (Cascadia margin). They showed that gas hydrate deposits that are not associated with positive chloride concentration anomalies could be explained by either a slow formation or periodically fast formation with a prolonged relaxation period. In the former explanation, the rates of hydrate formation would be only slightly higher than that under dynamic equilibrium which takes a time scale of 250,000 years (250 thousand years or 250 kyr) to form 40% of gas hydrate. The dissolved chloride that expelled during hydrate formation has sufficient time to diffuse away and results in no accumulation of chloride in the pore water. For the periodically fast formation with a prolonged relaxation period, massive gas hydrate can form in a very short period of time (200 years for 40% of gas hydrate) sustained by pulses of methane gas supply. The rapid formation is followed by a prolonged relaxation stage (40 kyr for the gas hydrates at 233 mbsf from IODP Site1328) that allows sufficient time for the large positive chloride concentration anomalies to diffuse away.

The absence of positive [Cl] anomalies associated with the two hydrate-bearing sediment layers from Lunde SW seepage site (Fig. 2n) suggests that these gas hydrate deposits were likely not actively forming at the time of investigation. The temporal constraints obtained from U-Th dating of seep carbonates from the SW seepage site allow us to further differentiate the two hydrate

formation modes from this site. The U-Th ages allow to reconstruct two major past seepage events at Lunde SW seepage site; 40–50 thousand years ago (ka) (determined from 5–10 mbsf at MeBo drill site GeoB21616-1) and 133–160 ka (determined from >15 mbsf from MeBo drill site GeoB21637-1) (Himmeler et al. 2019). Formation of seep carbonates during defined intervals was interpreted to reflect variable methane fluxes with ubiquitous carbonate precipitation tracking episodes of intensive seepage. Based on these carbonate age inferences, the event-driven rapid hydrate formation is a more likely scenario as the slow hydrate formation requires a minimum formation time that exceeds the ages of seep carbonates and hosting formation (i.e., 250 kyr to built-up 40% of gas hydrates as estimated by Hong and Peszynski (2018)). As the gas hydrate recovered from the Lunde SW seepage site is notably shallower (<11.54 mbsf; Tab. 2) than that at IODP Site1328, the length of time required for the positive chloride concentration anomalies to mix with seawater is expected to be significantly shorter than 40 kyr from this site. To form gas hydrate within a few centuries under the periodically fast hydrate formation condition, a large upward flux of methane gas is required, a conclusion supported by previous studies (Haeckel et al. 2004, Torres et al. 2004, Liu and Flemings 2006, Sultan et al. 2014, Hong et al. 2018), and by the bubble fabric in the gas hydrate pieces recovered (Fig. 1c) (Bohrmann et al. 1998, Sultan et al. 2014).

4.3 Migration of the deep water inferred from stable boron isotopic signatures

In the previous sections, we show that [Cl], $\delta^{18}\text{O}$ and δD signatures from Lunde SW seepage site can be best explained by a saline formation fluid mixed with modern seawater and modified by gas hydrate dynamics. We propose that such a saline formation fluid originated from much greater depths and its flow conduit was intercepted at the SW seepage site, an inference supported by the B/Cl molar ratios and $\delta^{11}\text{B}$ of pore water.

In the hydrate-free sediments from the Lunde SW seepage and reference sites, pore water samples have lower B/Cl ratios (down to 6×10^{-4} mol/mol, Figs. 2c & 2q) and $\delta^{11}\text{B}$ signatures (+38 to +40 ‰, Figs. 2d & 2r) as compared to the seawater values. Pore fluids in these sediments are not influenced by any deep-rooted fluids but were affected by a combination of local diagenetic processes. For example, Hüpers et al. (2016) interpreted the low pore water boron concentrations and $\delta^{11}\text{B}$ signatures observed from Nankai Trough as the results of combined effect from volcanic ash alteration and NH_4 -induced boron desorption from clay surface. Though there is no volcanic ash reported from Vestnesa Ridge, we expect a similar combination of processes to occur and explain the observed profiles. The co-occurrence of high pore water B/Cl ratios (up to 8×10^{-4} mol/mol or 43% higher than that of bottom seawater ratio) and $\delta^{11}\text{B}$ as low as +35.0‰ in the pore fluid observed from the hydrate-bearing samples in SW seepage site indicates a deep-rooted fluid that has received boron desorbed from clay surface under sufficiently high temperature (Palmer et al. 1987). Similar boron signals have been observed along the decollement fault from several accretionary prism systems and used to infer deep fluid migrating (You et al. 1995).

Low $\delta^{11}\text{B}$ values (+15.6 to +22.9‰) were also reported for seep carbonates (Deyhle et al. 2003). Carbonate dissolution or re-crystallization may therefore release boron with low $\delta^{11}\text{B}$ values into the pore water. However, the low B/Ca ratios observed from the seep carbonates recovered from Vestnesa Ridge (in the range of 29.7 to 167.0 $\mu\text{mole/mole}$; Deyhle et al. 2003) make this process unlikely to explain the elevated B/Ca ratios observed in pore water (Fig. 4). In addition, there is no sign of significant calcium carbonate dissolution from the SW seepage site based on the absence of downcore variation in Ca/Cl ratios below the SMT (Suppl. Fig. 2).

Kopf et al. (2000) suggested that water from gas hydrate decomposition is depleted in ^{11}B ($\delta^{11}\text{B} = +30.6\text{‰}$) and may cause low $\delta^{11}\text{B}$ values in the pore fluid. This hypothesis was challenged by later studies (Teichert et al. 2005, Hüpers et al. 2016) that suggested a limited effect of gas hydrate dissociation on $\delta^{11}\text{B}$ of the pore fluid. We evaluate this hypothesis by considering a binary mixing between modern seawater and a gas hydrate end member represented by one of our gas hydrate samples with a $\delta^{11}\text{B}$ value of $+26.5\text{‰}$ (Fig. 4). While the $\delta^{11}\text{B}$ value of the other gas hydrate sample ($+30.3\text{‰}$) can be explained by the mixing of bottom seawater and our assigned gas hydrate end member, the mixing trend fails to explain the values for other pore fluid samples (Fig. 4). It is apparent that pore water B/Ca ratios are insensitive to mixing with water released from dissociating gas hydrate as this solution is characterized by low calcium and boron concentrations (0.4 to 0.7 mM for calcium and 31.3 to 49.5 μM for boron). For example, a *ca.* 34% mixing with the gas hydrate end member is able to explain the lowest $\delta^{11}\text{B}$ value observed from our pore fluid samples (Fig. 4) even though the resulting B/Ca ratios are only 3.4% higher than the modern seawater B/Ca ratio. We can therefore exclude the influence of gas hydrate dissociation on the pore fluid boron signals and conclude that both $\delta^{11}\text{B}$ and pore water B/Ca ratios indicate a deep-rooted fluid under modification of high temperature diagenesis.

4.4 Interaction between fluid flow, shallow gas hydrate dynamics and local geology from Lunde pockmark

We integrate our fluid geochemical findings with previous studies from the Lunde pockmark and propose an evolution model for the fluid pumping systems (Fig. 5). Based on the high resolution 3-D P-cable seismic data, Plaza-Faverola et al. (2015) documented a buried pockmark/seep carbonates at the horizon coinciding with the major seismic reflection H50 (Fig. 5) which was estimated to be *ca.* 60-65 mbsf and 200-300 ka old, based on the average sedimentation rates extrapolated from the nearby Ocean Drilling Program (ODP) Sites 914 & 911 (Knies et al. 2014, Mattingsdal et al. 2014). This buried pockmark/carbonate intervals are located within the main fluid channel referred to as gas chimneys that are *ca.* 500 m in diameter for the ones associated with Lunde and Lomvi pockmarks (Plaza-Faverola et al. 2015). The internal structure of a gas chimney is highly complex with fractures and zones of high density material (e.g., hydrates, carbonates) influencing the migration pathway of ascending fluids (e.g., Pape et al., 2020). The geochemical signatures observed from Lunde pockmark lead us to infer that ascending fluids may have been directed towards the southwest of the main pockmark depression (*i.e.*, the SW seepage site), and likely also towards the SE part of the pockmark (*i.e.*, SE seepage site) (Fig. 5c), a mechanism that has been proposed previously (Aharon et al. 1997, Gay et al. 2011, Pape et al. 2011, Sultan et al. 2014). We propose that while part of the ascending gaseous methane is sequestered by gas hydrates in the shallow sediments of the seepage sites, a fraction of the gaseous methane escapes to the water column forming small seafloor pits within the main pockmark structure, as persistently documented during multi-year on-site investigations (Bünz et al. 2012, Smith et al. 2014).

The accumulation of gaseous methane, under unique circumstances, may result in overpressurized mini fractures in the shallow sediments as documented by Yao et al. (2019). The gaseous methane also constantly replenishes the dissolved methane pool in the fractures and pore space which fuels microbial sulfate reduction through anaerobic methane oxidation (Boetius et al. 2000) as reflected by the large isotopic fractionation in dissolved inorganic carbon (Pape et al. 2020). The carbonate alkalinity produced during the microbial process promotes the precipitation

of seep carbonates, an evident process from pore fluid calcium profiles (Supp. Fig. 1 and Hong et al. 2016), seismic profiles (Plaza-Faverola et al. 2015 and as illustrated in Fig. 6), the occurrence of seep carbonates in several stratigraphic intervals (Himmler et al. 2019 and Fig. 1) and microfossil investigations (Consolaro et al. 2014, Ambrose et al. 2015, Szttybor and Rasmussen 2016, Schneider et al. 2017, Szttybor and Rasmussen 2017, Schneider et al. 2018, Dessandier et al. 2020). We speculate that the relatively well lithified sediment intervals containing abundant seep carbonate cements, in return, also influence the direction of the flow by acting as self-sealed sub-systems that fluids can bypass as new pulses of pore-fluid pressure builds up. For example, the pore fluid profiles from the non-seepage site drilled at the major depression of Lunde pockmark show only low to moderate methane flux (Fig. 2 and quantification from Pape et al. 2020) since the fluid may be diverted by the buried carbonate intervals (Fig. 5a). Similarly, even though the gas hydrates recovered from SW seepage sites were formed during a period with intensive gaseous methane supply (as reflected by the bubble fabric in Fig. 1b and illustrated in Fig. 5a), their currently dynamic equilibrium suggests a decrease in gas supply likely as a result of pore space blockage by carbonate-cemented sediments (Figs. 1c & 5b). A similar conclusion has been made through numerical modeling (Luff et al. 2004, Luff et al. 2005) and the investigations of seep carbonates texture along the Norwegian margin (Hovland et al. 2002, Mazzini et al. 2003). Despite the partly blocked fluid conduit, the same fluid conduit still connects to a deep sourced aqueous fluid, as reflected by the presence of saline formation water and boron anomalies (Fig. 5c).

5 Conclusions

Through the investigation of pore fluid geochemistry from Vestnesa Ridge, we reach the following conclusions:

- 1) Gas hydrates occupying up to 47% pore space were recovered in the sediments shallower than 11.5 mbsf from both Lomvi and Lunde pockmarks.
- 2) At the Lunde SW seepage site, a saline formation water with high [Cl], $\delta^{18}\text{O}$ and δD is identified from the same intervals where gas hydrates were recovered. These saline formation fluids have high B/Cl ratios and low $\delta^{11}\text{B}$ values, suggesting their deep-sourced origin. This deep fluid likely migrates along the same conduits that were used by free gas methane, which stimulated the formation of gas hydrates recovered from this location.
- 3) The absence of positive chloride concentration anomalies (*i.e.*, smooth concentration profiles) associated with gas hydrate deposits recovered from Lunde SW seepage site suggests that they were not actively formed at the time of recovery. They have likely formed during past seepage events tens to hundred thousand years ago as determined via U-Th dating of seep carbonates in a previous study. Such a time scale suggests that the hydrates were formed during brief periods of strong methane gas supply and hints to an even greater methane supply in the past compared to the present.
- 4) We propose that the migration pathways for fluids have been gradually blocked by seep carbonates formed during the seepage events. This might have impeded fluid migration and reduced the rate of gas hydrate formation. This process may explain the low to moderate methane flux from the non-seepage site and the dynamic equilibrium state of the gas hydrate recovered from the SW seepage site from the Lunde pockmark.

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Table 1

Specifics of sediment cores investigated in this study. Refer to Bohrmann et al. (2017) and Pape et al. (2020) for exact positions. Additional data on the sediment cores are made available through the PANGAEA data publisher (<https://www.pangaea.de/>).

Site	Core code [GeoBXXXXX-X]	Tool	Cored/Drilled Depth [mbsf]
Reference Site	21606-1	GC-3	5.84
	21613-1	MeBo-126	62.50
Lunde pockmark non-seepage site	21601-1	GC-1	5.77
	21605-1	GC-2	7.65
	21610-1	MeBo-125	22.80
Lunde pockmark SW seepage site	21621-1	MeBo-128	7.75
	21637-1	MeBo-138	23.95
Lunde pockmark SE seepage site	21619-1	GC-9	4.78
Lomvi pockmark	21623-1	GC-11	1.55
	21624-1	GC-12	2.62

Table 2
Estimation of gas hydrate saturation (S_h in % pore space) from pore fluid chloride concentrations.

Core #	Depth (mbsf)	[Cl] _{obs} (mM)	[Cl] _{fit} (mM)	S_h (%)	Core #	Depth (mbsf)	[Cl] _{obs} (mM)	[Cl] _{fit} (mM)	S_h (%)
SE seepage: GeoB21619-1	3.35	633.5	634.8	<1	SW seepage: GeoB21637-1	5.80	429.6	584.2	31
	3.51	512.3	637.8	24		6.28	454.1	587.1	27
	3.61	591.2	639.7	9		6.42	471.0	588.1	24
	3.90	376.4	645.1	47		6.54	520.9	589.1	14
	4.00	608.9	647.0	7		6.90	514.9	592.1	16
	4.34	483.8	653.3	31		7.11	543.9	594.1	10
	4.43	490.7	655.0	30		7.38	555.9	596.8	9
	4.53	475.9	656.9	32		8.28	534.9	608.3	15
	4.63	417.8	658.7	42		10.29	456.6	648.3	35
	4.73	537.0	660.6	22		10.88	584.8	664.4	15
Lomvi-seepage: GeoB21624-1	2.38	552.5	593.9	13		11.29	556.9	677.4	21
	2.62	578.8	597.3	4		11.54	607.8	685.8	14
GeoB21623-1	1.54	541.8	580.0	8	GeoB21621-1	6.51	424.1	588.9	32

Figure 1

Location maps, seismic data, and core photos from the investigated pockmarks along Vestnesa Ridge. (a) An overview map for Vestnesa Ridge with detailed bathymetry from Lunde and Lomvi pockmarks (see Tab. 1 for core details). The locations of the three study sites from Lunde pockmark (non-seepage, SW seepage, and SE seepage) and the reference site are indicated. (b) High resolution bathymetry of the Lunde pockmark with a NE-SW-trending seismic line across the pockmark shown in (d). (c) Photographs of carbonate-cemented sediments and gas hydrates with bubble fabric recovered from the Lunde SW and SE seepage sites. (d) A seismic profile showing the sub-surface structure of the Lunde pockmark. The dashed white boxes showing roughly the penetration of the drilling from Lunde non-seepage and SW seepage sites. The high reflectance in the seismic data was interpreted as buried carbonate cemented sediment strata (Plaza-Faverola et al. 2015) which is confirmed by the presence of authigenic carbonate formations in the drilled cores that are the results of past methane seepage activities (Himmeler et al. 2019).

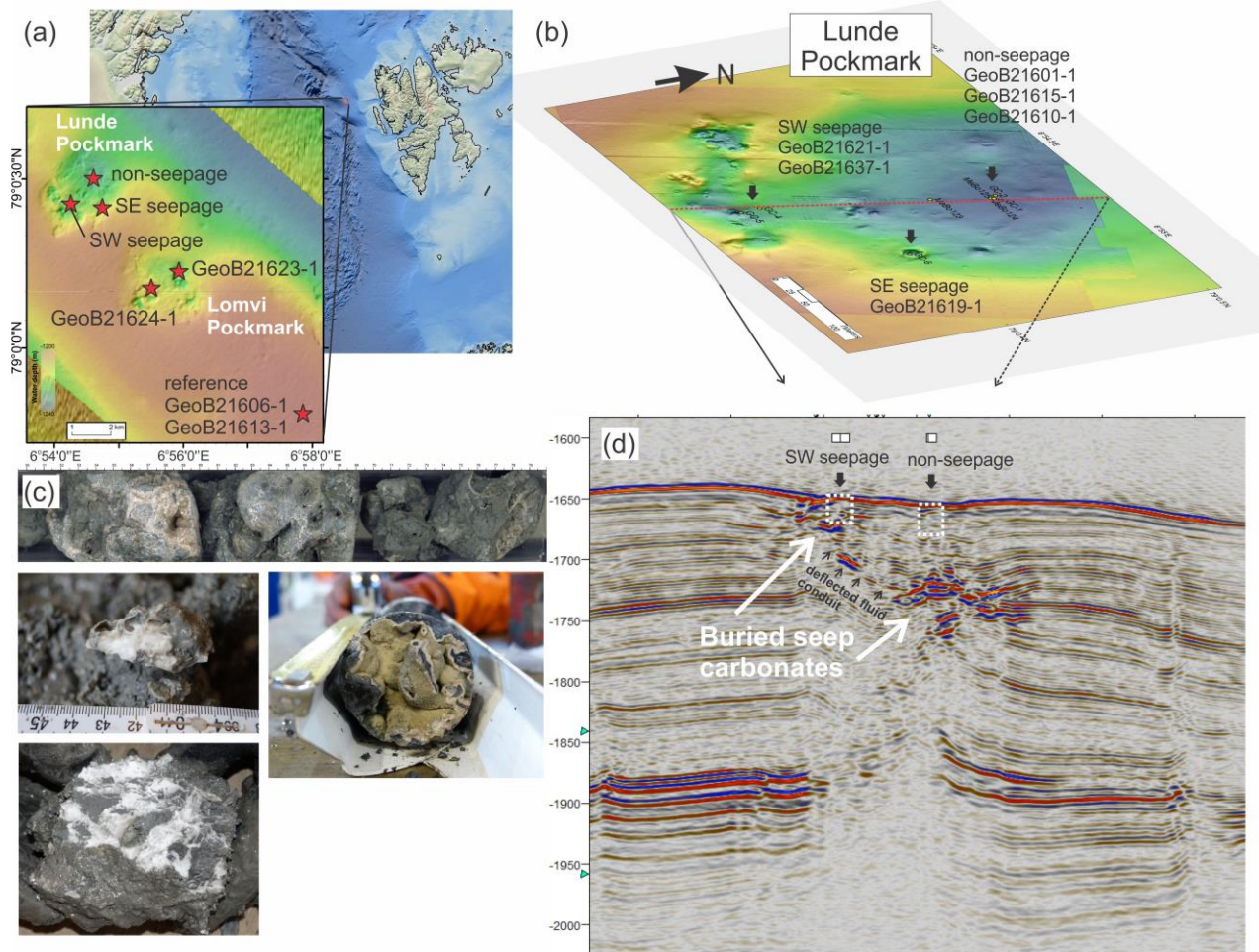


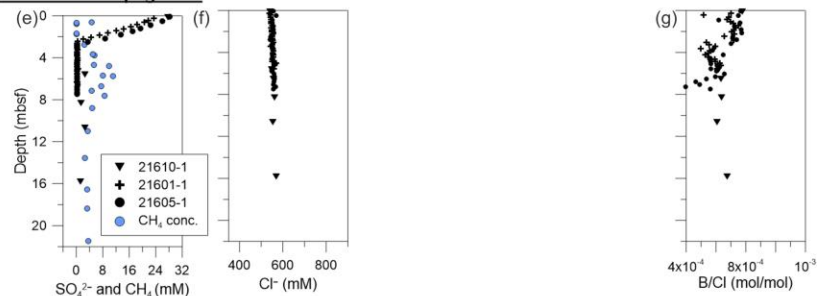
Figure 2

Pore fluid profiles of sulfate, methane, chloride ([Cl]), $\delta^{18}\text{O}$, δD , B/Cl ratio, and $\delta^{11}\text{B}$ in MeBo and gravity cores from the investigated sites in Lunde and Lomvi pockmarks. The abundance of gas hydrate (in % of pore space) was estimated from [Cl] and plotted as horizontal bars along with the chloride concentration profile (see text for detail). The gaps in the geochemical profiles are due to poor recovery of sediments within those intervals. Note the different depth scales for the various sites.

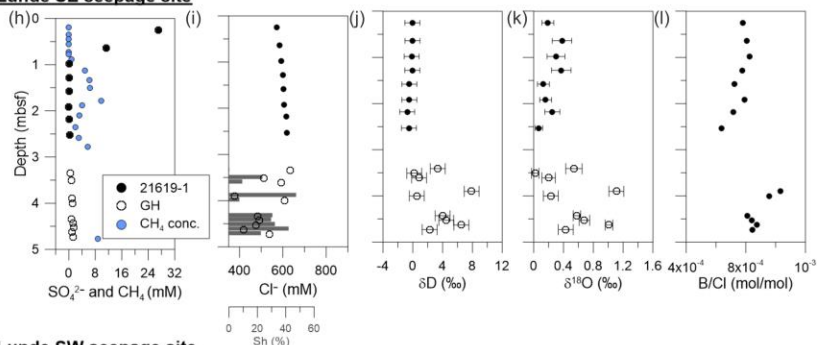
Reference site



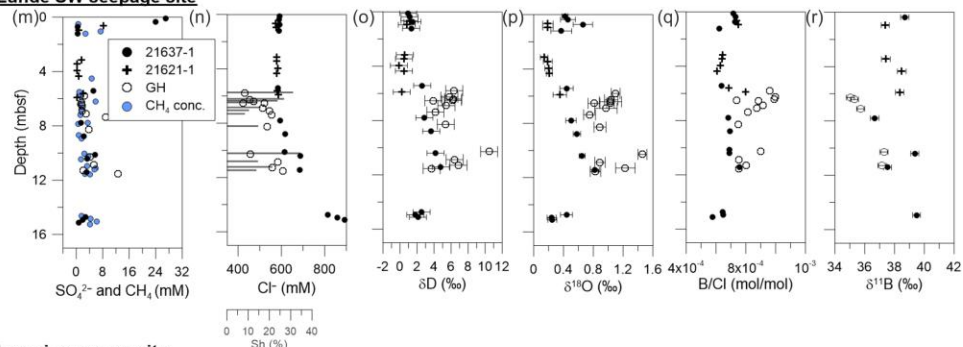
Lunde non-seepage site



Lunde SE seepage site



Lunde SW seepage site



Lomvi-seepage site

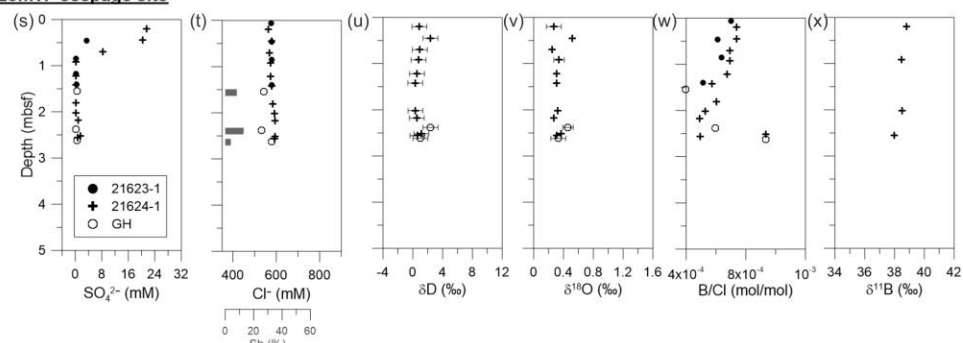
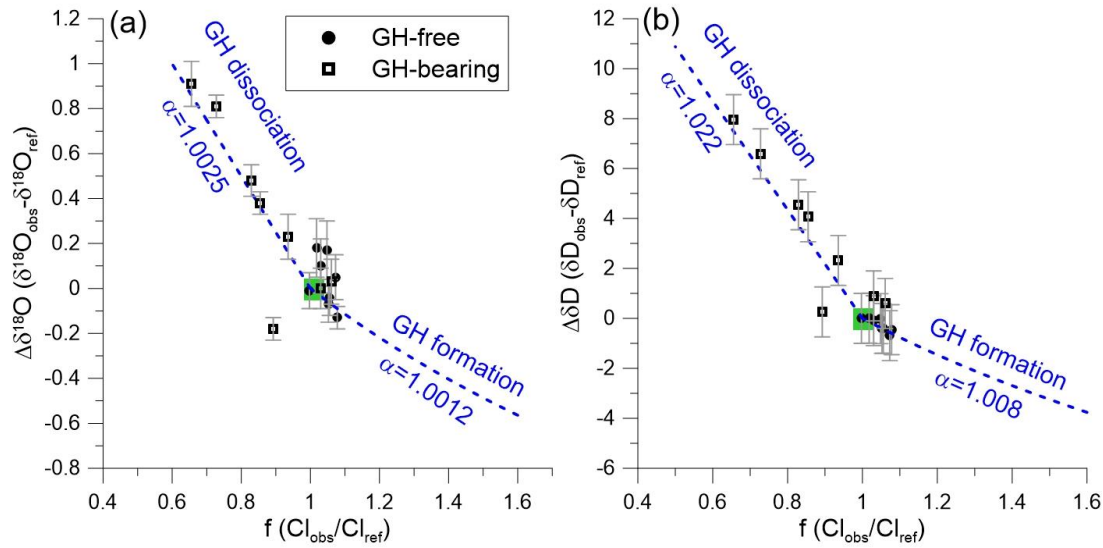


Figure 3

Normalized chloride concentration (f) versus differences in $\delta^{18}\text{O}_{\text{obs}}$ (Figs. 3a & 3c) and $\delta\text{D}_{\text{obs}}$ (Figs. 3b & 3d) relative to the assigned reference composition ($\Delta\delta^{18}\text{O}$ and $\Delta\delta\text{D}$) (GH=gas hydrate). For the Lunde SE seepage site (Figs. 3a & 3b), we chose modern seawater composition as the reference ($[\text{Cl}]_{\text{ref}} = 574 \text{ mM}$, $\delta^{18}\text{O}_{\text{ref}} = +0.20\text{‰}$, $\text{dD}_{\text{ref}} = -0.06\text{‰}$). Most of the data from hydrate-bearing samples can be explained by the expected fractionation factors (α) for gas hydrate dissociation and formation determined from laboratory (e.g., Maekawa 2004). For the Lunde SW seepage site (Figs. 3c & 3d), we chose the composition from a sample at 8.78 mbsf as the reference ($[\text{Cl}]_{\text{ref}} = 616 \text{ mM}$, $\delta^{18}\text{O}_{\text{ref}} = +0.60\text{‰}$, $\delta\text{D}_{\text{ref}} = +3.76\text{‰}$) as modern seawater composition fails to explain the distribution of data (see Suppl. Fig. 1). We propose that the values of sample at 8.78 mbsf represent the composition of a saline formation fluid that, in addition of mixing with local bottom seawater (red dash lines), was modified by hydrate formation at greater depths and gas hydrate dissociation during core recovery.

Lunde SE seepage site-modern seawater



Lunde SW seepage site-saline formation water

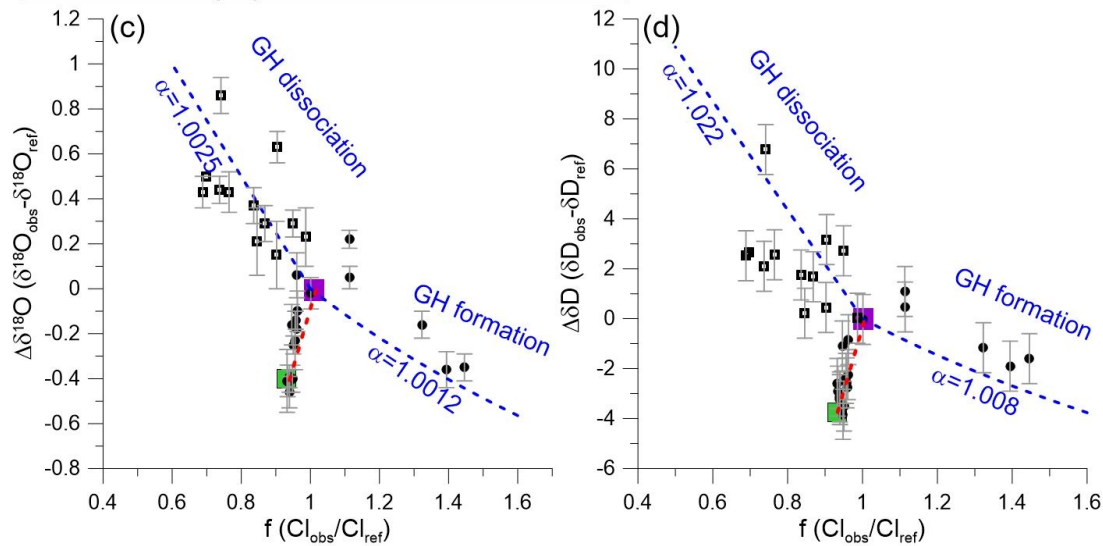


Figure 4

A mixing diagram between local bottom seawater (open green square) and water from gas hydrate as represented by the composition of one of two gas hydrate samples analyzed (open black square). Compositions of pore fluid (cross, solid triangle, and circle) and seep carbonates (blue square). Both gas hydrate dissociation and seep carbonates dissolution cannot explain the observed boron signatures from pore fluid. This observation supports the inference that the pore fluid boron signatures reflect in-situ signal from the deeply-buried fluid source.

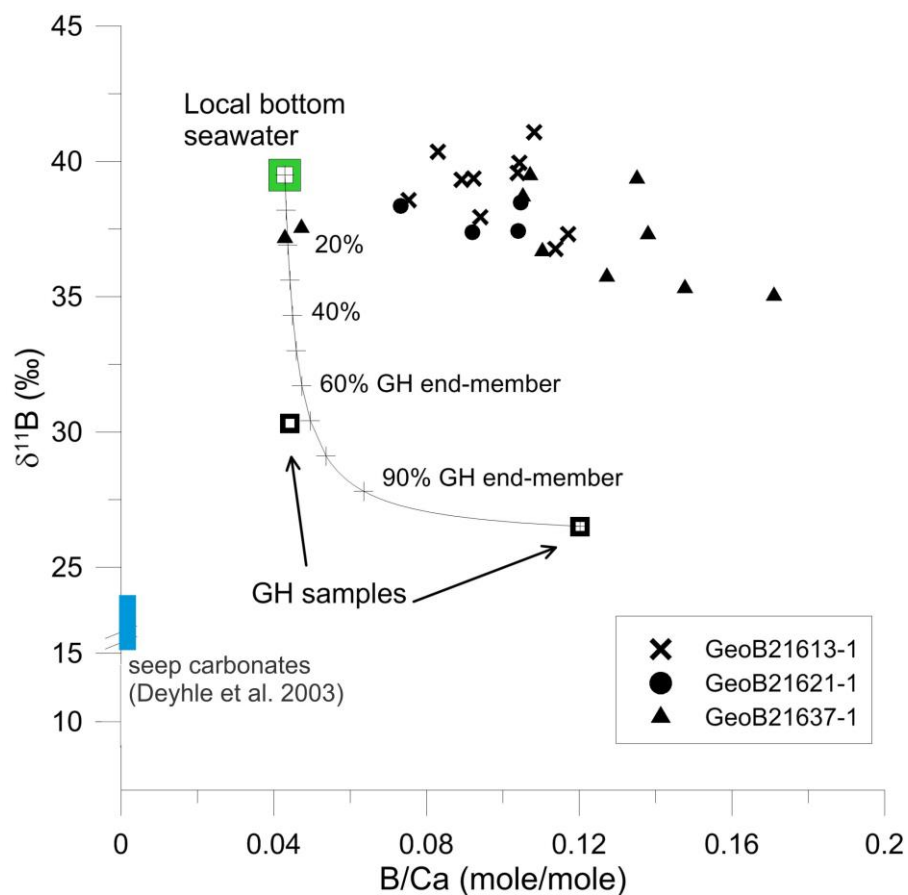


Figure 5

A conceptual evolution model for the fluid pumping system of Lunde pockmark that integrates seismic interpretation, U-Th ages of seep carbonates and the pore fluid geochemistry. (a) When the main fluid channel was blocked by the buried pockmarks/seep carbonate observed from the seismic profile (corresponds to the H50 horizon in Fig. 1d), a deflected fluid conduit was created. Gaseous methane was diverted and forced to flow along this conduit, which triggered active formation of gas hydrate that was recovered during the cruise. (b) The fluid conduit was gradually blocked by the authigenic carbonate cementation, which also decreases the gas discharge on the seafloor. (c) At the present day, the dynamic equilibrium status of the gas hydrates from the SW seepage site suggests a halt of gaseous supply, likely due to the complete blockage by the carbonate cemented sediments that were recovered during drilling (Fig. 1c). The saline formation water is still able to migrate along the same fluid conduit used by gaseous methane in the past. Signs of active hydrate formation can be observed in the pore fluid from the bottom of the soft sediments recovered at SW seepage site. This hints to an active formation of gas hydrate in the lateral or horizontal adjacent sediments. Age data of seep carbonates that are associated with previous methane seepage events were determined by the U-Th method (Himmler et al. 2019) while the age of H50 horizon was determined by local sedimentation rates (Knies et al. 2014, Mattingdal et al. 2014).

