1 A Climatic Trigger for the Giant Troll Pockmark Field in

2 the Northern North Sea

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13 Abstract

- 14 Pockmarks are seafloor craters usually formed during methane release on continental
- margins. However, the mechanisms behind their formation and dynamics remain elusive.
- Here we report detailed investigations on one of the World's largest pockmark fields located
- in the Troll region in the northern North Sea. Seafloor investigations show that >7000
- pockmarks are present in a ~600 km² area. A similar density of pockmarks is likely present
- over a 15,000 km² region outside our study area. Based on extensive monitoring, coring,
- 20 geophysical and geochemical analyses, no indications of active gas seepage were found. Still,
- 21 geochemical data from carbonate blocks collected from these pockmarks indicate a
- methanogenic origin linked to gas hydrate dissociation and past fluid venting at the seafloor.
- We have dated the carbonates using the U-Th method in order to constrain the pockmark
- formation. The carbonates gave an isochron age of 9.59 ± 1.38 ka BP, i.e. belonging to the
- 25 initial Holocene. Moreover, radiocarbon dating of microfossils in the sediments inside the
- 26 pockmarks is consistent with the ages derived from the carbonates. Based on pressure and
- temperature modelling, we show that the last deglaciation could have triggered dissociation

of gas hydrates present in the region of the northern part of the Norwegian Channel, causing degassing of 0.26 Mt_{CH4}/km² at the seafloor. Our results stress the importance of external climatic forcing of the dynamics of the seafloor, and the role of the rapid warming following the Younger Dryas in pacing the marine gas hydrate reservoir.

- 33 Keywords: Norwegian North Sea; Troll; pockmarks; gas hydrates dissociation; deglaciation;
- 34 modelling

1. Introduction

Despite several decades of research on pockmarks, many features and mechanisms controlling their activity remain poorly understood. Key aspects such as 1) timing of formation and 2) external (climatic) versus internal (overpressure) forcing are still debated.

Part of the reason for this is the limited availability of large-scale high resolution bathymetry

and monitoring data from continental margins, and the lack of accurate pockmark ages.

Pockmarks often display gas flares, gas-rich sediments, gas hydrate deposits or contain carbonates originating from the seepage of thermogenic or microbial methane (e.g. Mazzini et al., 2005; Haas et al., 2010; Nickel et al., 2013). They have been found in a large variety of geological settings at continental margins (e.g. Gontharet *et al.*, 2007; Greinert *et al.*, 2010; Kocherla *et al.*, 2015). Although exceptions exist, it is commonly accepted that the driving force for pockmark formation is linked to methane migration and degassing. The methane may ultimately be sourced from deep hydrocarbon-rich reservoirs or from dissociating shallow gas hydrate deposits (e.g. Solheim and Elverhøi, 1993; Naehr *et al.*, 2000; Smith *et al.*, 2014). A common assumption is that some of the pockmarks offshore Norway were formed at some stage after the Last Glacial Maximum (e.g., about 21 ka ago), maybe even

quite recently (e.g. Jung and Vogt, 2004; Paull *et al.*, 2008; Hustoft *et al.*, 2009; Plaza-Faverola *et al.*, 2011). Cremiere *et al.* (2016) recently published a study on pockmarks in the Barents Sea, where methanogenic carbonates from pockmarks were dated. The results suggest methane seepage between 17-2 ka, linked to initial gas hydrates dissociation after the deglaciation of the southwest Barents Sea (~18–16 ka).

By investigating one of the World's largest pockmark fields offshore Norway, located above a giant gas reservoir (Fig. 1A), we aim at resolving if the degassing was driven by deep or external forcing, and if the last deglaciation was the ultimate pockmark trigger. The main difference between this study and those previously done in the same region (e.g. Vogt *et al.*, 1994; Bunz *et al.*, 2005; Mazzini *et al.*, 2006; Ivanov *et al.*, 2010; Reiche *et al.*, 2011; Chand *et al.*, 2012), is that we have access to petroleum industry data including seismic profiles and bathymetry, ROV video observations and cores and sea floor carbonate samples, providing the necessary regional coverage, and statistical analyses in addition to stratigraphic details from a selection of pockmarks.

2. Study area and Quaternary geology

The Norwegian Channel is a distinct trough separating the Norwegian mainland from the shallower parts of the North Sea Shelf to the south and west. The water depths in the central part of the trough increase gently from around 305 m in the Troll area to about 400 m at the shelf break. Fast flowing ice streams are believed to have given The Norwegian Channel its characteristic physiography (Sejrup et al., 2003; Ottesen et al., 2005). During the LGM, ice streams probably extended all the way to the shelf edge where the North Sea Trough Mouth Fan was deposited (Nygard *et al.*, 2007). The Troll area was thus situated below an ice

stream, about 200 km from its terminus during these periods. Present day Antarctic ice
streams show that analogous settings have subglacial water pressures that are approximately
equivalent to the glacial overburden (e.g. Alley et al., 1989) and that the ice rides on a layer
of deforming sediments (deformation till). The temperature and pressure regime imposed by
the presence of the ice streams provides an important constraint for understanding the
possible contribution of gas hydrates to the formation of pockmarks in the Norwegian
Channel.

Following the break-up of the Norwegian Channel Ice Stream, the pressure history is determined by the interaction of eustatic sea level changes and isostatic rebound. Relatively rapid Late Glacial, glacial marine sedimentation has allowed the determination of a detailed seafloor temperature history for the Troll area (Sejrup *et al.*, 2003; Sejrup *et al.*, 2004).

The base of the sediments from this period is separated from the underlying gravelly and sandy sediments (Unit L3; Saalian age) by a glacial erosion surface at 74 m depth (i.e. 8903/8904 borehole in Sejrup et al., 1995; Sejrup et al., 2003). The sediments above consist of tills, probably deformation tills, deposited by the latest Norwegian Channel Ice Stream (NCIS). The top of the till at 16.9 mbsf is crenulated by iceberg plough marks and overlain by glacial marine deposits that merge into Holocene marine deposits at ~3 mbsf.

3. Methods

3.1 Marine expeditions, petrography, and geochemical and geotechnical analyses

During the period 2005-2007 large seismic and multibeam echo-sounder surveys and several sampling campaigns were conducted over the Troll gas field in the Norwegian Channel to better understand the gas transfer processes from deeper levels to the seafloor (Fig.1A). Additional high-resolution multibeam lines, video stills, and subbottom profiler (SBP) records were later acquired during several ROV dives (some examples in Fig. 1B-C). Forty-five cores and a large collection of sea floor carbonate blocks were collected from three selected pockmark complexes (Septagram, Arch, Peanut) and the surrounding areas (e.g. Fig. 1D). The data collected at these localities is used for a broader interpretation of the whole area. Carbonates were studied using optical and electron microscopy, carbon and oxygen isotope analyses and complemented with the data presented by Mazzini *et al.* (2016). The composition of the pore waters extracted from the sediment cores was also analysed. Cone penetration tests (CPT) were performed at six locations respectively outside, on the sloping edge and inside the targeted pockmarks.

3.2 Statistical analyses

of data analysis methods using PAST, v. 3.04 (Hammer *et al.*, 2001) and in-house software. Point pattern analysis can give information about the mode, timing and structural control of pockmarks (e.g. Hammer et al., 2009; Cartwright et al., 2011; Moss et al., 2012; Hillman et al., 2015). The analysis was limited to a rectangular region south of Troll A with relatively stationary point density (3189 pockmarks). Nearest-neighbour analysis (Clark and Evans,

A selected region of 296 km² from high-resolution bathymetric data was subjected to a range

1954) is a simple technique using the distance from each point to its nearest neighbour. The

average neighbour distance is compared with the one expected for Complete Spatial

Randomness (CSR). Donnelly's edge correction (Donnelly, 1978) was applied. The average nearest neighbour distance is 173.0 m, compared with 152.4 expected from CSR. CSR can thus be rejected at p<0.0001 (t test). This indicates a lateral inhibition mechanism where points tend to avoid each other. Nearest neighbour analysis only gives information on the local scale. To investigate point density at a range of scales, Ripley's K analysis was applied (Ripley, 1976). The number R(d)of points within circles of radius d centred on one point is computed, and averaged over all points. For CSR, a quadratic R(d) is expected, as the number of points is proportional to area. A normalized function L(d), square root of R(d), is expected to follow L(d)=d for CSR. The function L(d)-d thus represents departure from CSR at any scale d. An estimate of fractal dimension was obtained from the asymptotic linear slope in a log-log plot of R(d). The main feature of the Ripley's K curve (Fig. 2A) is a dip at small scales (up to ca. 250 m), indicating local lateral inhibition. At larger scales, the pattern drifts towards CSR. A region of elevated values, corresponding to clustering, occurs at scales from 1000 to 1500 m. The estimated fractal dimension value of D=2.0 coincides with that of CSR (Fig. 2B), and thus does not give any indication of fractal geometry as might be expected from an underlying fractal pattern of faults or cracks. Local alignment of points along straight lines was assessed following Amorese et al. (1999). A rectangular blade with length 1.6 km was centred on each point, and rotated through a full revolution. Point counts within these blades were compared with the expected count for CSR and tested using a binomial distribution with a significance level of 0.05 (not corrected for multiple comparison). The alignments were filtered using the dispersion index, mean index and butterfly bow criteria of Amorese et al. (1999). The linear alignment analysis is shown in Fig. 2C. A strong preference for NNW-SSE orientation is evident in the rose plot, with an

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average orientation of 347 degrees (geographical), random orientation rejected at p<0.01 (Rayleigh test).

Morphological parameters were computed as follows. For each position in the N=7243 data set, a square with sides 150 m was extracted from the grid data, and smoothed with a Gaussian filter. The local regional depth was estimated from the median depth of the corners. The depth of the pockmark was estimated as the difference between the local depth and the largest depth in the square. Automatic delineation of pockmarks is difficult, because the depression continues gradually into the surrounding plain. For robustness, we simply defined the pockmark as the area deeper than a threshold value set to 1.3 m below the local depth. The diameter/depth calculations are summarized in Fig. 2D. The pockmark was edge-detected using the Canny algorithm and least squares fitted to an ellipse. Diameter was computed as the geometric mean between the major and minor axes. The average orientation of the major axes (Fig. 2E) is 347 degrees, the same value as for the lineaments described above. Random orientation can be rejected at p<0.0001 (Rayleigh test).

3.3 Preparation and TIMS U-Th analysis of carbonates

The carbonate blocks collected from the pockmarks contained a large fraction of detrital material and were not suitable for regular U-Th dating. We performed TIMS U-Th analysis to obtain isotopic ratios of ²³⁰Th/²³²Th, ²³⁸U/²³²Th and ²³⁴U/²³²Th for isochron plotting.

Sample preparation and TIMS U-Th analysis (Table 1 I) was performed at the Department of Earth Science, University of Bergen. Bulk carbonate samples were crushed to <5 mm and washed with water to remove clay and shell fragments. Further cleaning was done by repeated treatment with an EDTA and ascorbic acid solution for gentle leaching of the outer

surface of the sample fragments. For TIMS analysis sub-samples of 1-3 g were incinerated at 500 and 900°C prior to dissolution to decompose organic matter. The material was dissolved in HNO₃ and spiked with 233 U, 236 U, and 229 Th. Chemical separation and purification included scavenging with Fe-precipitation, two sets of ion-exchange columns (AG-1x 8 chloride forms, 200-400 mesh) and final evaporation with H_3 PO₄. U and Th were loaded separately on single filaments (5x zone refined rhenium) with graphite and measured as U⁺ and Th⁺ on a Finnigan MAT 262 mass spectrometer, through three different experiments with SEM ion counter jumping mode acquisition. Mass calibration was done routinely when switching from lighter elements to U, as well as an initial run of the in-house standard (B-018, Eemian speleothem). All U-Th ages are reported with 2 σ uncertainties. A standard algorithm was used to calculate the ages using the program 'TIMS-Age4U2U' (Lauritzen and Lundberg, 1998). Results include activity ratios, U and Th concentrations, and U-Th ages (Fig. 3).

3.4 Radiocarbon dating of foraminifera

Radiocarbon dating was performed on foraminifera and molluscs picked from samples selected from the different cored units, both within and outside the pockmarks (Table 2, Fig. 1D). Samples were prepared by picking monospecific sub-samples of benthic foraminifera where possible from the sand fraction. Both a mollusc and foraminifera (mostly *Nonionellina labradorica*) samples were dated at BH 102 tube 6E. Samples were analysed by Beta Analytic Inc. (Florida, USA) using AMS analyses. The 2σ error in the ages of the AMS radiocarbon dates is \pm 40–50 years, where σ is the standard deviation.

3.5 Gas hydrate stability modelling at Troll

The TEMP/W (®-TEMP/W) software was used to model the hydrate stability at the Troll location in the local uppermost 450 m of the sedimentary succession. TEMP/W is a finite element software that can be used to model the thermal variations in the ground related to environmental changes. The formulation allows to analyse both simple and highly complex geothermal problems, with or without temperatures that result in freezing or thawing of sediment moisture. For this work parameters representative of gas hydrates substituted the properties of ice thus allowing to determine the stability of gas hydrates for given conditions. Environmental conditions, i.e. temperature and pressure, were applied to the model for a time period ranging from the LGM (22 ka b2k) until 8 ka b2k (Tables 3-4). The water pressure was calculated from either subglacial conditions assuming wet based ice or, following deglaciation, from a combination of eustatic sea level from Deschamps et al. (2012) and an isostatic depression of about 110 m (also used by Sejrup et al., 2003 in the Troll area) that decayed logarithmically until present. The subglacial temperature was assumed to be 0°C. After the time of the glacial breakup, from the Norwegian Channel, seafloor temperatures were based on Sejrup et al. (2004). However, inspection of the species contributing to the earlier part of this curve may indicate that the temperatures provided by these authors are too high due to the influence of reworked warm water foraminifera on the transfer functions. The temperature history we used is shown by the orange curve in Fig. 4A. The sedimentation history was divided into 18 discrete events since the used software did not allow a continuous sedimentation history. The hydrostatic pressure at the time of deposition was used to define the corresponding hydrate stability vs temperature curves (Dickens and

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Quinby-Hunt, 1994). The seafloor temperature was applied as a boundary condition to the

topmost layer that had been deposited at the appropriate time step. The depositional history

213 from Lehman and Keigwin (1992) was converted to calendar years using CALIB REV7.1.0 (Stuiver and Reimer, 1993) and the Marine 13 calibration curve (Reimer et al., 2013). 214 The heat flux was kept constant but tuned to give a thermal gradient as found at present with 215 the present day stratigraphy and a temperature at the sea floor of 7°C and 13.8°C at 200 mbsf 216 (from unpublished borehole data). 217 The thermal conductivities were calculated as a function of quartz content, porosity and 218 hydrate content. The latter was limited to 10 % of the pore volume which is similar to 219 contents found by seismic refraction experiments (i.e. Bunz et al., 2005; Westbrook et al., 220 2008 and refs therein) in hydrate bearing areas. Table 4 shows the latent heat of formation 221 and thermal conductivity of hydrate respectively. 222 The model output does not compute the migration of gas, so the hydrate content was solely 223 224 based on the propagation of the appropriate thermal conditions that are controlled by the heat flux, thermal conductivity and the latent heat of formation of hydrate (up to a default 225 maximum of 10% of the pore volume). The model therefore indicates whether or not there is 226 a possibility for hydrate formation and also gives the time history for temperature changes to 227 propagate through the sediment. 228

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4. Results

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4.1 Mapping and statistical analyses

A total of 7,243 pockmarks have been mapped from the high resolution bathymetry data collected in the area above the Troll field (Fig. 1A). Statistical analyses from the selected

region of bathymetric data show that the pockmarks (Fig. 1B) have an average density of 10.8 /km². The structures range in size from 10 to 100 meters in diameter and are typically 6 meters deep but can exceptionally be deeper than 20 meters. Three groups can be distinguished with respect to diameter/depth ratio: deep (shafts), regular (bowls) and shallowlarge (saucers) (Fig. 2D). Bathymetric data also show that there is no evidence of structural control on the location of the pockmarks. This conclusion is in agreement with statistical analysis of the pockmark distribution that shows neighbour avoidance up to a scale of hundreds of meters and no indication of fractal geometry (Fig. 2C). Statistical analyses also reveal a very pronounced NNW-SSE orientation of elongated pockmarks (Fig. 2E). This orientation coincides with the main N-S currents sweeping the area. Linear alignments of pockmarks have a similar NNW-SSE trend (Fig. 2C). Industrial data (courtesy of Statoil) show that the pockmarks field extends over a broad region of 15,000 km² (215 km by 70 km) in the northern part of the Norwegian Channel. The pockmark density may varies from east to west, reaching a maximum of 20/km². By using the measured average pockmark density of 10 to 20 per square kilometre we obtain a total number of pockmarks in the range of 150,000 to 300,000 in the region, making this one of the largest pockmark fields in the World.

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4.2 Sea floor observations and analytical results

In addition to the data reported by Mazzini *et al.* (2016), further observations on pockmark activity are summarized below. Sea floor images and sampling revealed the presence of broadly distributed, exhumed carbonate blocks in the pockmarks. These carbonates have bulk δ^{13} C as low as -59.7% V-PDB and δ^{18} O up to 4.5% V-PDB. These values indicate methanogenic origin, possibly linked to gas hydrate dissociation (Mazzini *et al.*, 2016) as similarly concluded from carbonate studies collected at other comparable sites (Bohrmann *et*

- al., 1998; Mazzini et al., 2006; Ivanov et al., 2010; Cremiere et al., 2016). The origin of the 259 pockmarks can therefore be linked to methane seepage. We argue that the pockmarks in the 260 Troll area are currently inactive based on:
- a) No evidence of bubbles, fluid seepage, microbial colonies or other typical living 262 chemosymbiotic assemblages observed during seafloor video dives or reported by the 263 hydrocarbon industry surveys. 264
- b) No free *in situ* gas has been found in any layer of the cores collected from the pockmarks. 265
- c) Extended exposure of carbonates to sea floor resulting in abundant outer surface alteration, 266 267 corrosion and pyrite oxidation.
- d) Water analyses extracted from cores sampled inside and outside the pockmarks show no 268 difference between pockmark and background pore water sulphate concentrations (Mazzini et 269 al., 2016). 270
- e) No evidence of gas charged sediments or defined conduits is observable from the seismic 271 data through the pockmarks. 272
- 273 f) Metagenomic studies of pockmark sediments do not show overabundance of methanotrophic organisms compared to normal sediments (Havelsrud et al., 2012). 274

4.3 Dating the pockmark activity

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In order to determine the timing and mechanisms for pockmark formation, TIMS U-Th dating 277 278 was performed on ten authigenic carbonates samples from the Troll pockmark field. The TIMS results show high levels of ²³²Th (Table 1A), and the individual U-Th analyses cannot 279 provide reliable ages because of the detrital contamination. To resolve the contamination 280

issue we used isochron plotting to obtain the detrital-free 230 Th/ 234 U and 234 U/ 238 U ratios (Fig. 3, Table 1B). The best-fitted isochron plot for the Troll samples (n=5) gives a U-Th age of 9.59 ± 1.38 ka (Fig. 4A Table 1C). This shows that the timing of methane seepage and thus carbonate formation took place shortly after the end of the Younger Dryas (YD) temperature anomaly (Clark *et al.*, 2012; Deschamps *et al.*, 2012). As seep carbonates typically form by rapid precipitation during methane release (e.g. Luff and Wallmann, 2003), the carbonate age is virtually identical to the age of the pockmark field.

Further support for the new age of the pockmarks formations comes from microfossil radiocarbon dating of samples from units identified with the ROV sub-bottom profiler that imaged sediments down to 20-35 m (Fig. 1D, Table 2). We have identified four different units adjacent to the pockmarks (Fig. 1C), and these are representative for the study area (Haflidason *et al.*, 1998). These are: Unit a (marine deposit 3-4 m thick, fairly transparent, with a well-defined base up to 10,000 ¹⁴C years BP old - 11.5 cal ka BP); Unit b (10-15 m thick and well-stratified glacial marine deposit); Unit c (6-7 m thick, transparent and structureless deposit, with some signal-scattering intervals > 15,000 ¹⁴C years BP old - 17.8 cal ka BP, glacial marine, perhaps reworked by iceberg ploughing); Unit d (a probable deformation till giving high-amplitude reflection which inhibits deeper imaging). Units a, b and c correspond to Unit L1, whereas Unit d corresponds to Unit L2 in Sejrup *et al.*, (2003) and Nygard et al. (2007) that overlies Unit L3, a sandy gravelly deposit from the penultimate glaciation. The pockmarks clearly cross-cut the reflections in Unit b, including the boundary between Unit a and Unit b. The radiocarbon-dated foraminifera from the bottom of the Septagram pockmark gives it a maximum age of about 13 ¹⁴C ka BP (~15 cal ka b2k).

Geotechnical cone penetration tests (CPTs) show that the sediments inside the pockmarks are over-consolidated compared to those present outside where normal hemipelagic compaction

occurs. Calculations indicate that up to 7 meters of sediments have been eroded from inside the pockmarks and can account for the missing part of Unit b that were likely removed during pockmark formation (Fig. 5). Analogue and modelling studies (e.g. Pau et al., 2014 and refs therein) show that currents similar to those measured on the seafloor at Troll (i.e. up to 25 cm/s) trigger substantial turbulence inside pockmarks and are capable of preventing the sedimentation of particles up to fine sand. This process also clarifies why the pockmarks are not filled and still present on the seafloor although they are inactive. The ice-rafted clasts inside the pockmarks are interpreted to be lag deposits winnowed from Unit b (a glacial marine unit) during pockmark formation.

Besides giving an indication for the time of the pockmark formation, the calculated initial $^{234}\text{U}/^{238}\text{U}$ activity ratios (Table 1A) suggest that the carbonates precipitated from pore waters with a composition different from seawater, and that the Troll samples thus have ratios more characteristic of fresh water or evolved pore waters. Waters with fresh signatures could potentially be derived from shallow aquifers in sand-silt horizons loaded with ice-derived melt water, and/or from dissociation of gas hydrates and release of low salinity waters. The latter is more consistent with the presence of methane-derived carbonates, the broad distribution of pockmarks, and the $\delta^{18}\text{O}$ values of the carbonates.

4.4 Gas hydrate stability

The regional pressure and seafloor temperature histories since the LGM were used to model the gas hydrate stability and show that changes in seafloor temperature propagate downwards within a few hundred years affecting the hydrate stability. The model shows that the gas hydrates stability zone extended down to ~300 mbsf when the area was covered by an ice stream, but that the stability zone was limited to Unit L3 (~75-110 mbsf) following glacial breakup mainly due to the drop in pressure due to loss of subglacial water pressure. This unit, consisting of coarse sand and gravels, can potentially host a significant amount of hydrates and remained within the stability zone until the Holocene warming of the seafloor water masses (11.5 cal ka; Sejrup *et al.*, 2004) with the possible exception of a period during the Allerød-Bølling period. Fig. 4B summarizes the hydrate stability in this unit. If only a few percent of CO₂ is present in the methane, the whole period prior to the Holocene warming is well within the stability zone. Hughes *et al.* (2016) demonstrate that the deglaciation of the most of the North Sea and the Norwegian Channel occurred very quickly between 19 and 18 cal ka BP. The sudden drop in pressure (points 2 to 3, Fig. 4B) reflects this rapid breakup of the Norwegian Channel ice stream. Even without a glacially induced elevated water pressure, Unit L3 remains within the stability zone.

The present gas concentrations in Unit L3 and below are relatively high whereas those in the overlying units are very low (Statoil unpublished data). This piece of evidence combined with modelled history of hydrate stability (Fig. 4B), supports that Unit L3 was a pre Holocene reservoir for gas hydrates.

5. Discussion

5.1 Scenario for pockmark formation

The observations and the multidisciplinary data collected in the Troll region provide solid data to constrain the pockmark activity and formation scenario. Rapid changes in water temperature occurred during the last deglaciation with shifts in seafloor temperatures of more

than 5°C within a time period of a few decades (Lehman and Keigwin, 1992; Sejrup et al., 2004; Hughes et al., 2016). The numerical modelling supports the concept that abrupt climatic changes that influenced global and local ice-sheet melting histories triggered the gas hydrate dissociation and methane release to seafloor. This resulted in the rapid formation of pockmarks and extensive precipitation authigenic carbonate in the conduits close to the sea floor. This sequence of events is supported by all the available data and the formation scenario involving broad clathrate dissociation is consistent with the large number of pockmarks evenly distributed over a large flat area. This situation would unlikely result from sporadic gas seepage from deeper seated reservoirs. Further supporting evidence comes by the statistical calculations and in particular by the application of the "drainage cell" model of Moss et al. (2012). According to these authors, neighbour avoidance may indicate a relatively shallow source and that the pockmarks formed over a relatively short period of time. The suggested 75 m deep Unit L3 is indeed a shallow candidate that was capable of releasing significant amounts of gas from clathrates dissociation. The fact that the gas release was synchronous throughout the area is supported by the vast regional seismic survey. The data shows no evidence of buried pockmarks other than on the

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The fact that the gas release was synchronous throughout the area is supported by the vast regional seismic survey. The data shows no evidence of buried pockmarks other than on the horizon associated with the Younger Dryas (YD), thus ruling out the possibility of earlier stages of gas venting in the region. Instead, all the pockmarks are located at the same stratigraphic level. This timeframe not only matches the output of the applied numerical model but also the U-Th dating (9.59 \pm 1.38 ka BP) of the precipitated carbonates and defines a time window for the methane seepage. Additional matching evidence is provided by the dating of the sediments around and inside the pockmarks revealing the same age of the pockmarks formation.

Our results show that the gas hydrate dissociation was completed after the YD, during a period when rapid warming is broadly documented (e.g. Alley, 2000; Alley, 2004 and refs. therein). Indeed there is no evidence of gas hydrates being currently present in the Troll area, which is now outside the hydrate stability zone and showing very low methane concentrations in the sediments between 0-75 m below the sea floor. No active pockmarks are reported in the area although numerous surveys have been performed for the oil and gas industry during the development of various hydrocarbon fields. This finding is consistent with the absence of post-YD methane concentration peaks in the ice cores and with the short residence time (~10 years) of methane in the atmosphere (WG1, ICCP_Report 2013). We conclude that the hydrate dissociation and pockmark-derived methane release represent a climate-induced pacing of the seafloor temperature. Such a scenario is relevant for understanding the consequences of the current warming of the oceans.

5.2 Gas hydrates volumes

For a conservative calculation of the gas volume released from the pockmarks above the Troll field, we use a 30 % porosity and a 10 % saturation of the pore volume by hydrate volume present before the last deglaciation in the sand and gravel rich Unit L3 over the Troll region. This is consistent with values documented by various authors (i.e. Bunz et al., 2005; Westbrook et al., 2008 and refs therein). Unit L3 is on average ~7 m thick, and mapped to be laterally extensive in all of the Troll region and further over a large flat area of at least 15,000 km² in the northern part of the Norwegian Channel (e.g. Rise et al., 2004). The bathymetry changes by only ~100 meters from Troll to the shelf edge and pockmarks are present throughout the area. Using these parameters we assess a potential volume of 3.15 km³ of gas hydrates that presumably dissociated from Unit L3 in a relatively short period of time (~150).

to 300 yrs). This conservative estimate would generate \sim 0.26 Mt_{CH4}/km². The released methane was likely partly oxidized in the water column. However, if rapidly released from the pockmarks, a significant fraction would have reached the atmosphere.

6. Conclusions

- Based on a multidisciplinary study from the Northern North Sea, we conclude that:
- One of the World's largest pockmark fields is located in the Norwegian Channel in the
 Northern North Sea. More than 7000 pockmarks have been found at the sea floor in a
 broad region above and around the Troll gas field. The pockmark density is ~10/km².
 - The pockmarks do not show clustering, but rather neighbor avoidance, suggesting a regional and well distributed sub-surface source of gas.
 - Carbonate geochemistry and gas hydrate stability modelling shows that gas hydrate dissociation is a likely triggering mechanism for the pockmarks. None of the investigated pockmarks showed evidence for present-day activity and gas seepage.
 - U-Th dating of the carbonates shows a formation during the initial Holocene, thereby indicating that the pockmarks formed as a consequence of the rapid climatic changes following the Younger Dryas.
 - We conclude that external forcing was responsible for the formation of one of the World's largest pockmark fields.

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Figure captions

Fig. 1 (A) Fragment of Troll field multibeam coverage where more than 7,000 pockmarks (2.5 m gridding resolution) have been mapped. Indicated are the Troll A platform and the pockmark areas more intensively studied. Inset map offshore Norway. UTM Zone 31,WGS84 datum. (B) Example of high-resolution bathymetry (0.2 m resolution) of the Septagram pockmarks showing a 15 m deep circular depression with a flat interior For location refer to Fig. 1A. (C) Example of ROV sub-bottom profile through the Septagram pockmark. Indicated are the four imaged units (a-d). Fir size refer to Fig. 1B. The pockmarks typically cross-cut the reflections of Unit b. See text for geochronology of these units. (D) Multibeam line across the Septagram region and locations of the cores available that were collected in the area for radiocarbon dating and CPT (pink triangles). The scale for the maps in the manuscript are in meters or kilometers, UTM Zone 31, WGS84 datum.

Fig.2 (**A**) Ripley's K analysis. (**B**) Log-log plot of Ripley's R(d). The asymptotic linear slope gives a fractal dimension close to D=2.0. (**C**) Lineaments found with the blade method and rose plot of the orientations over the survey area (scale in kilometers). (**D**) Diameter and depth of the analysed pockmarks highlights three distinct groups of pockmarks: deep (shafts), regular (bowls) and shallow-large (saucers). (**E**) A pockmark with its fitted ellipse. Grid cells are 2.5 m square. Rose plot of major axis orientations (N=6834). The mean pockmark orientation coincides with the main N-S currents swiping the area.

Fig. 3 U-T raw data isochron plots for the Troll samples. The slopes of the regression lines provide the detrital Th-free ratios of ²³⁰Th/²³⁴U and ²³⁴U/²³⁸U. The intercept with the y-axis in the left diagram gives the un-contaminated ²³⁰Th/²³²Th activity ratio.

Fig. 4 (A) Single age data and isochron data from all the samples compared to 1) the Greenland temperature data (GISP2 core, Alley, 2000; Alley, 2004); 2) the (GISP2 core, Alley, 2000); 2) temperature history for the hydrate stability modelling (orange curve) with some adjustments in the older parts where the transfer functions may be influenced by reworked warm species.). The orange curve is derived from 3) the seafloor temperature history from Sejrup *et al.* (2004) (black curve). The Troll carbonate ages follow the Younger Dryas rapid warming event. Carbonate formation (and hence pockmark formation) could be related to the deglaciation and the resulting changes in sea floor pressures and temperatures that followed. (B) The pressure-temperature development from Table 3 (point numbers in blue) plotted in a diagram showing the stability zone of methane hydrate (light blue area to

- 463 the upper left). The point numbers in Table 3 are shown in blue. The dashed red line indicates
- the hydrate stability curve for methane with 10 % CO2.

- 466 Fig. 5 Results of CPT tests performed in the study area. The results are adjusted to same
- depth below sea level (i.e. elevation). The shaded area shows the range of CPT measurements
- previously performed in the Troll area. Fig. 1D shows location of CPT stations.

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References

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- 472 ®-TEMP/W, https://www.geo-slope.com/products/temp-w.
- 473 Alley, R. B., 2000, The Younger Dryas cold interval as viewed from central Greenland: Quaternary Science Reviews, v. 19, p. 213-226.
- 475 Alley, R. B., 2004, GISP2 Ice Core Temperature and Accumulation Data: IGBP PAGES/World Data
 476 Center for Paleoclimatology Data Contribution Series #2004-013. NOAA/NGDC
 477 Paleoclimatology Program, Boulder CO, USA.
 - Alley, R. B., Blankenship, D. D., Rooney, S. T., and Bentley, C. R., 1989, Water-pressure coupling of the sliding and bed deformation: III. Application to Ice Stream B, Antarctica: Journal of Glaciology, v. 35, p. 130-139.
 - Amorese, D., Lagarde, J.-L., and Laville, E., 1999, A point pattern analysis of the distribution of earthquakes in Normandy (France): Bulletin of the Seismological Society of America v. 89, p. 742-749.
 - Bohrmann, G., Greinert, J., Suess, E., and Torres, M., 1998, Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability: Geology, v. 7, p. 647-650.
 - Bunz, S., Mienert, J., Vanneste, M., and Andreassen, K., 2005, Gas hydrates at the Storegga Slide: Constraints from an analysis of multicomponent, wide-angle seismic data: Geophysics, v. 70, p. B19-B34.
 - Cartwright, A., Moss, J., and Cartwright, J., 2011, New statistical methods for investigating submarine pockmarks: Computers & Geosciences, v. 37, p. 1595-1601.
 - Chand, S., Thorsnes, T., Rise, L., Brunstad, H., Stoddart, D., Bøe, R., Lågstad, P., and Svolsbru, T., 2012, Multiple episodes of fluid flow in the SW Barents Sea (Loppa High) evidenced by gas flares, pockmarks and gas hydrate accumulation: Earth and Planetary Science Letters, v. 331–332, p. 305-314.
- Clark, P. J., and Evans, F. C., 1954, Distance to nearest neighbour as a measure of spatial patterns in biological populations.: Ecology v. 35, p. 445-453.
- Clark, P. U., et al., 2012, Global climate evolution during the last deglaciation: Proceedings of the National Academy of Sciences, v. 109, p. E1134-E1142.

- Cremiere, A., et al., 2016, Timescales of methane seepage on the Norwegian margin following collapse of the Scandinavian Ice Sheet: Nat Commun, v. 7.
- Deschamps, P., Durand, N., Bard, E., Hamelin, B., Camoin, G., Thomas, A. L., Henderson, G. M., Okuno, J., and Yokoyama, Y., 2012, Ice-sheet collapse and sea-level rise at the Bolling warming 14,600 years ago: Nature, v. 483, p. 559-564.

- Dickens, G. R., and Quinby-Hunt, M. S., 1994, Methane hydrate stability in seawater: Geophysical Research Letters, v. 21, p. 2115-2118.
 - Donnelly, K., 1978, Simulations to determine the variance and edge-effect of total nearest neighbour distance., *in* Hodder, I., ed., Simulation Methods in Archaeology, Cambridge University Press, London.
 - Gontharet, S., Pierre, C., Blanc-Valleron, M. M., Rouchy, J. M., Fouquet, Y., Bayon, G., Foucher, J. P., Woodside, J., and Mascle, J., 2007, Nature and origin of diagenetic carbonate crusts and concretions from mud volcanoes and pockmarks of the Nile deep-sea fan (eastern Mediterranean Sea): Deep Sea Research Part II: Topical Studies in Oceanography, v. 54, p. 1292-1311.
- Greinert, J., Bialas, J., Lewis, K., and Suess, E., 2010, Methane seeps at the Hikurangi Margin, New Zealand: Marine Geology, v. 272, p. 1-3.
 - Haas, A., Peckmann, J., Elvert, M., Sahling, H., and Bohrmann, G., 2010, Patterns of carbonate authigenesis at the Kouilou pockmarks on the Congo deep-sea fan: Marine Geology, v. 268, p. 129-136.
 - Haflidason, H., King, E. L., and Sejrup, H. P., 1998, Late Weichselian and Holocene sediment fluxes of the northern North Sea Margin: Marine Geology, v. 152, p. 189-215.
 - Hammer, Ø., Harper, D. A. T., and Ryan, P. D., 2001, PAST: Palaeontological Statistics software package for education and data analysis: Palaeontologia Electronica v. 4, p. 9.
 - Hammer, Ø., Webb, K., and Depreiter, D., 2009, Numerical simulation of upwelling currents in pockmarks, and data from the Inner Oslofjord, Norway: Geo-Marine Letters, v. 29, p. 269-275.
 - Havelsrud, O. E., Haverkamp, T. H. A., Kristensen, T., Jakobsen, K. S., and Rike, A. G., 2012, Metagenomic and geochemical characterization of pockmarked sediments overlaying the Troll petroleum reservoir in the North Sea: Bmc Microbiology, v. 12.
 - Hillman, J. I. T., Gorman, A. R., and Pecher, I. A., 2015, Geostatistical analysis of seafloor depressions on the southeast margin of New Zealand's South Island Investigating the impact of dynamic near seafloor processes on geomorphology: Marine Geology v. 360, p. 70-83.
 - Hughes, A. L. C., Gyllencreutz, R., Lohne, Ø. S., Mangerud, J., and Svendsen, J. I., 2016, The last Eurasian ice sheets a chronological database and time-slice reconstruction, DATED-1: Boreas, v. 45, p. 1-45.
 - Hustoft, S., Dugan, B., and Mienert, J., 2009, Effects of rapid sedimentation on developing the Nyegga pockmark field: Constraints from hydrological modeling and 3-D seismic data, offshore mid-Norway: Geochemistry, Geophysics, Geosystems, v. 10, p. Q06012.
- Ivanov, M., Mazzini, A., Blinova, V., Kozlova, E., Laberg, J.-S., Matveeva, T., Taviani, M., and Kaskov, N., 2010, Seep mounds on the Southern Vøring Plateau (offshore Norway): Marine and Petroleum Geology, v. 27, p. 1235-1261.
- Jung, W.-Y., and Vogt, P. R., 2004, Effects of bottom water warming and sea level rise on Holocene
 hydrate dissociation and mass wasting along the Norwegian-Barents Continental Margin: J.
 Geophys. Res. Solid Earth, v. 109, B06104.
- Kocherla, M., Teichert, B. M. A., Pillai, S., Satyanarayanan, M., Ramamurty, P. B., Patil, D. J., and Rao,
 A., 2015, Formation of methane-related authigenic carbonates in a highly dynamic
 biogeochemical system in the Krishna–Godavari Basin, Bay of Bengal: Marine and Petroleum
 Geology, v. 64, p. 324-333.

- Lauritzen, S.-E., and Lundberg, J., 1998, TIMS-Age4U2U. Program for data reduction of TIMS U-series Dating. Code and algorithms, Version 2.3: Department of Geology, University of Bergen, Norway.
- Lehman, S. J., and Keigwin, L. D., 1992, Sudden Changes in North-Atlantic Circulation during the Last Deglaciation: Nature, v. 356, p. 757-762.

- Luff, R., and Wallmann, K., 2003, Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: numerical modeling and mass balances: Geochimica et Cosmochimica Acta, v. 67, p. 3403-3421.
- Mazzini, A., Aloisi, G., Akhmanov, G. G., Parnell, J., Cronin, B., and Murphy, P., 2005, Integrated petrographic and geochemical record of hydrocarbon seepage on the Vøring Plateau: Geological Society, v. 162, p. 815-827.
- Mazzini, A., Svensen, H., Hovland, M., and Planke, S., 2006, Comparison and implications from strikingly different authigenic carbonates in a Nyegga complex pockmark, G11, Norwegian Sea: Marine Geology, v. 231, p. 89-102.
 - Mazzini, A., Svensen, H. H., Planke, S., Forsberg, C. F., and Tjelta, T. I., 2016, Pockmarks and methanogenic carbonates above the giant Troll gas field in the Norwegian North Sea: Marine Geology, v. 373, p. 26-38.
- Moss, J. L., Cartwright, J., Cartwright, A., and Moore, R., 2012, The spatial pattern and drainage cell characteristics of a pockmark field, Nile Deep Sea Fan: Marine and Petroleum Geology v. 35, p. 321-336.
- Naehr, T. H., Rodriguez, N. M., Bohrmann, G., Paull, C. K., and Botz, R., 2000, Methane-derived authigenic carbonates associated with gas hydrate decomposition and fluid venting above the Blake Ridge Diapir, *in* Paull, C. K., Matsumoto, R., Wallace, P. J., and Dillon, W. P., eds., Proc. ODP Scientific Results, Volume 164, College Station, TX (Ocean Drilling Program), p. 286-300.
- Nickel, J. C., di Primio, R., Kallmeyer, J., Hammer, Ø., Horsfield, B., Stoddart, D., Brunstad, H., and Mangelsdorf, K., 2013, Tracing the origin of thermogenic hydrocarbon signals in pockmarks from the southwestern Barents Sea: Organic Geochemistry, v. 63, p. 73-84.
- Nygard, A., Sejrup, H. P., Haflidason, H., Lekens, W. A. H., Clark, C. D., and Bigg, G. R., 2007, Extreme sediment and ice discharge from marine-based ice streams: New evidence from the North Sea: Geology, v. 35, p. 395-398.
- Ottesen, D., Rise, L., Knies, J., Olsen, L., and Henriksen, S., 2005, The Vestfjorden-Trænadjupet palaeo-ice stream drainage system, mid-Norwegian continental shelf: Marine Geology, v. 218, p. 175-189.
- Pau, M., Gisler, G., and Hammer, Ø., 2014, Experimental investigation of the hydrodynamics in pockmarks using particle tracking velocimetry: Geo-Marine Letters, v. 34, p. 11-19.
- Paull, C., et al., 2008, Origin of pockmarks and chimney structures on the flanks of the Storegga Slide, offshore Norway: Geo-Marine Letters, v. 28, p. 43-51.
- Plaza-Faverola, A., Bünz, S., and Mienert, J., 2011, Repeated fluid expulsion through sub-seabed chimneys offshore Norway in response to glacial cycles: Earth and Planetary Science Letters, v. 305, p. 297-308.
- Reiche, S., Hjelstuen, B. O., and Haflidason, H., 2011, High-resolution seismic stratigraphy, sedimentary processes and the origin of seabed cracks and pockmarks at Nyegga, mid-Norwegian margin: Marine Geology, v. 284, p. 28-39.
- Reimer, P. J., et al., 2013, Intcal13 and Marine13 Radiocarbon Age Calibration Curves 0-50,000 Years Cal Bp: Radiocarbon, v. 55, p. 1869-1887.
- Ripley, B. D., 1976, The second-order analysis of stationary point processes: Journal of Applied Probability v. 13, p. 255-266.

- Rise, L., Olesen, O., Rokoengen, K., Ottesen, D., and Riis, F., 2004, Mid-Pleistocene ice drainage pattern in the Norwegian Channel imaged by 3D seismic: Quaternary Science Reviews, v. 23, p. 2323-2335.
- Sejrup, H. P., Aarseth, I., Hafiidason, H., Løvlie, R., Bratten, Å., Tjøstheim, G., Forsberg, C. F., and Ellingsen, K. L., 1995, Quatemary of the Norwegian Channel: glaciation history and palaeoceanography: Norsk Geologisk Tidsskrift, v. 75, p. 65-87.
- Sejrup, H. P., Birks, H. J. B., Kristensen, D. K., and Madsen, H., 2004, Benthonic foraminiferal distributions and quantitative transfer functions for the northwest European continental margin: Marine Micropaleontology, v. 53, p. 197-226.
- Sejrup, H. P., et al., 2003, Configuration, history and impact of the Norwegian Channel Ice Stream: Boreas, v. 32, p. 18-36.

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618 619

620

- Smith, A. J., Mienert, J., Bunz, S., and Greinert, J., 2014, Thermogenic methane injection via bubble transport into the upper Arctic Ocean from the hydrate-charged Vestnesa Ridge, Svalbard: Geochemistry Geophysics Geosystems, v. 15, p. 1945-1959.
- Solheim, A., and Elverhøi, A., 1993, Gas-related sea floor craters in the Barents Sea: Geo Marine Letters, v. 13, p. 235-243.
- Stuiver, M., and Reimer, P. J., 1993, Extended 14C database and revised CALIB radiocarbon calibration program: Radiocarbon v. 35, p. 215-230.
- Vogt, P. R., Crane, K., Sundvor, E., Max, M. D., and Pfirman, S. L., 1994, Methane-Generated (Questionable) Pockmarks on Young, Thickly Sedimented Oceanic-Crust in the Arctic Vestnesa-Ridge, Fram Strait: Geology, v. 22, p. 255-258.
 - Westbrook, G. K., et al., 2008, Estimation of gas hydrate concentration from multi-component seismic data at sites on the continental margins of NW Svalbard and the Storegga region of Norway: Marine and Petroleum Geology, v. 25, p. 744-758.
- WG1, ICCP_Report 2013, Climate change 2013, The Physical Science Basis: ICCP_Report, v. Fifth Assessment Report.

Figure1
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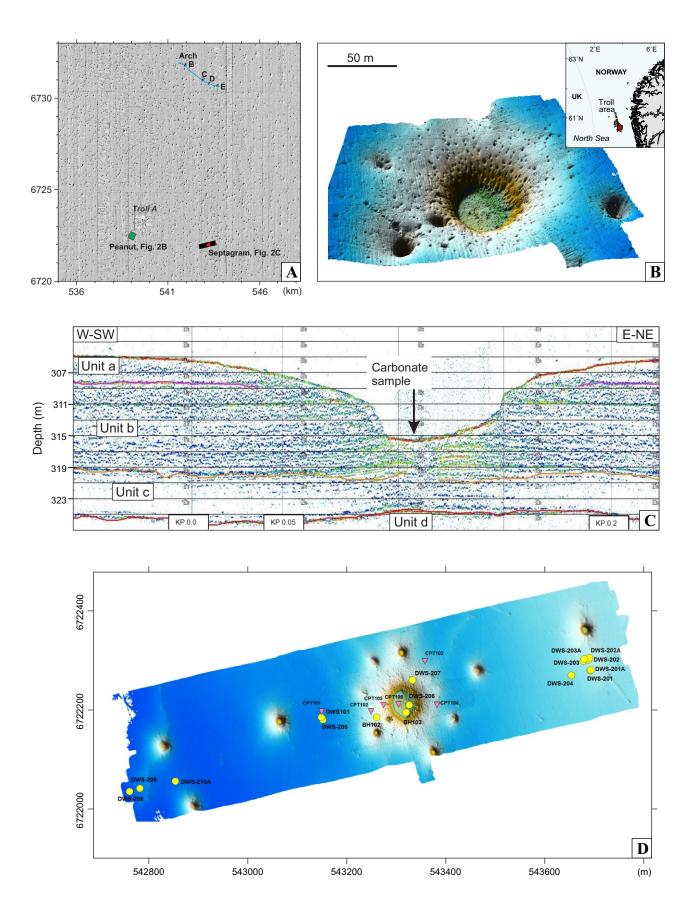


Figure2
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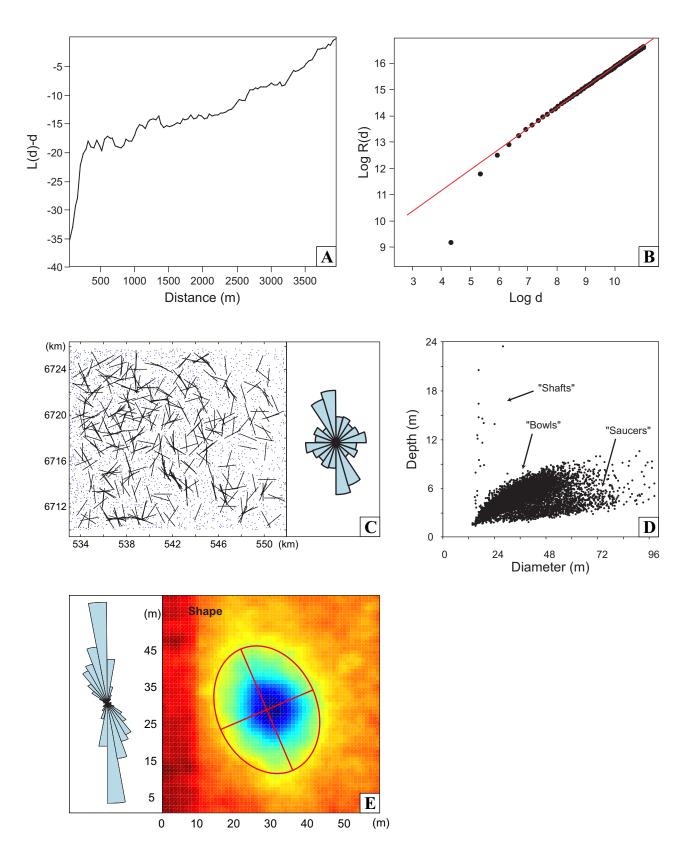
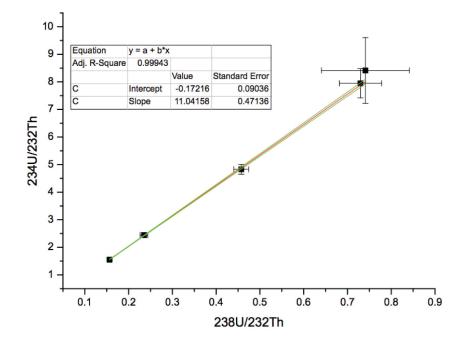


Figure3
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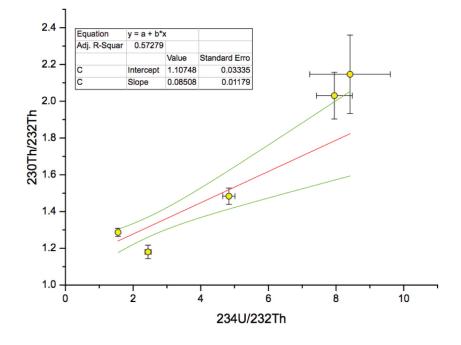
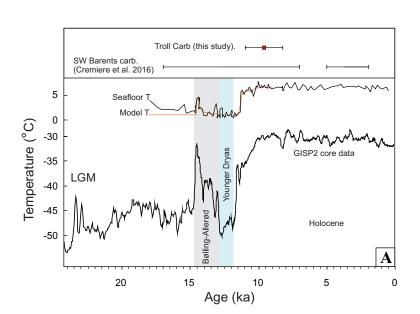
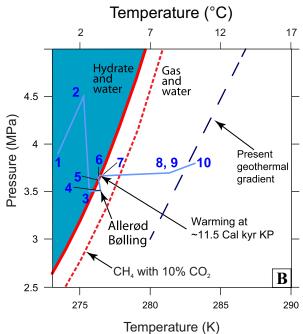


Figure4
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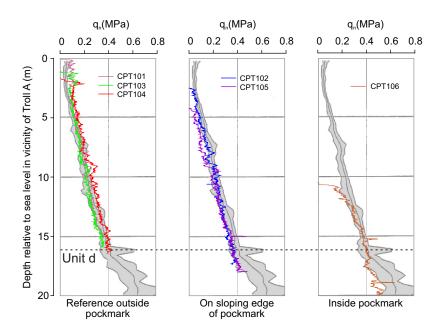


Table1

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Table 1. I - Summarised output of TIMS U-Th analysis of pockmark carbonates from Septagram, Troll. All errors are 2σ .

Lab.No.	Sample ID	ppm ²³⁸ U	ppm ²³² Th	$^{234}U/^{238}U_{(act)}$	$^{230}\text{Th}/^{234}\text{U}_{(act)}$	²³⁰ Th/ ²³² Th (act)	$^{234}\mathrm{U}/^{238}\mathrm{U}$ (init act)	Age $\pm 2\sigma$ (ka)	Corrected age (ka)*
716	B53-2 mørk	4.128 ± 0.019	154	1.126 ± 0.018	0.255 ± 0.006	2.030 ± 0.127	1.14 ± 0.02	31.89 ± 0.89	9.31 ± 1.92
717	B53-2 lys	3.986 ± 0.078	147	1.173 ± 0.081	0.255 ± 0.026	2.147 ± 0.213	1.19 ± 0.08	31.80 ± 3.90	10.65 ± 3.79
732	B67-4	1.024 ± 0.003	182	1.026 ± 0.010	0.828 ± 0.012	1.289 ± 0.022	1.04 ± 0.01	188.3 ± 8.8	Negative [§]
733	B67-6	1.527 ± 0.005	178	1.073 ± 0.011	0.483 ± 0.010	1.180 ± 0.037	1.09 ± 0.01	71.18 ± 2.18	Negative [§]
734	B610-8	2.438 ± 0.008	145	1.091 ± 0.009	0.307 ± 0.007	1.484 ± 0.044	1.10 ± 0.01	39.67 ± 1.08	Negative [§]

^{*} Correction factor used by TIMS Age4U2U (Lauritzen and Lundberg, 1998) is 1.5. § Negative because correction factor is larger than present-day measured value

II-Ratios for isochron plotting calculated from TIMS U-Th analysis. All errors are 2σ .

Lab.No.	²³⁰ Th/ ²³² Th	$^{238}\text{U}/^{232}\text{Th}$	$^{234}U/^{232}Th$
716	2.0303 ± 0.1268	0.7298 ± 0.0482	7.9493 ± 0.5300
717	2.1468 ± 0.2132	0.7410 ± 0.1005	8.4132 ± 1.1927
732	1.2868 ± 0.0223	0.1565 ± 0.0034	1.5546 ± 0.0355
733	1.1803 ± 0.0369	0.2352 ± 0.0088	2.4414 ± 0.0916
734	1.4835 ± 0.0441	0.4575 ± 0.0171	4.8314 ± 0.1790

III – Activity ratios for calculating 230 Th ages and resulting ages ($\pm 1\sigma$).

Group	$^{234}U/^{238}U$	$^{230}\text{Th}/^{234}\text{U}$	Age $\pm 1\sigma$ (ka)
Troll – Septagram	11.042 ± 0.471	0.08508 ± 0.01179	9.587 + 1.378 - 1.366

Table2
Click here to download Table: Table 2 14C_age_table_26.02.2016_v3-1.pdf

Table 2: Results of radiocarbon analyses and core coordinates.

Name	Sample	Northings	Eastings	Depth (m)	Dated material	¹⁴ C Age (yrs)	St.dv. (1 s)	d ¹³ C ‰ (V-PDB)	Cal age b2k	Cal age (1 s)
BH102	BH 102 tube 6E	6722185	543260	5.80	Molluscs	12 430	40	-0.8	13 960	70
BH102	BH 102 tube 6E	6722185	543260	5.80	N. labradorica	12 960	50	-4.8	14 955	150
BH103	BH 103 tube 7	6722195	543320	6.40	N. labradorica	14 290	50	-2.4	16 890	130
DWS101	DWS 101 tube 7	6722185	543149	10.00	N. labradorica	13 180	40	-10.4	15 270	70
DWS-201A	DWS 201A-2-D	6722280.8	543691.8	0.64	U. mediterranea	6 020	40	-0.3	6 490	55
DWS-201A	DWS 201A-5-B/C	6722280.8	543691.8	3.39	U. mediterranea	9 950	40	-1.8	10 980	95
DWS-201A	DWS 201-A-Shoe B	6722280.8	543691.8	5.43	N. labradorica	11 160	40	-2.4	12 710	45
DWS-204	DWS 204-4-F	6722269.7	543653.1	2.90	N. labradorica	11 140	40	-3.4	12 700	45
DWS-204	DWS 204-6-B	6722269.7	543653.1	4.47	Sp. Undetermined	11 790	40	-0.8	13 320	55
DWS-206	DWS 206-2-D	6722210.2	543326.4	0.45	N. labradorica	12 980	40	-3.2	14 995	130
DWS-209	DWS 209-3-F	6722041.7	542782.8	1.25	U. mediterranea	7 300	40	-0.2	7 810	55
DWS-209	DWS 209-6-B	6722041.7	542782.8	3.75	N. labradorica	10 940	40	-4	12 570	60
DWS-209	DWS 209-6H	6722041.7	542782.8	4.55	N. labradorica	12 130	40	-3.2	14 205	75
DWS-209	DWS 209-6H	6722041.7	542782.8	4.55	N. labradorica	12 090	40	-1.4	13 575	70

Table 3: Pressure and temperature development for moraine layer (Unit L3) at 90 mbsf. The temperatures have been extracted from model. The pressure was calculated from a combination of water depth (Fleming et al, 1998) and estimated isostatic depression for points 3 to 7. For points 1 and 2 a subglacial water pressure corresponding to a head of water of 200 m water above sea level was used. All hydrate had melted for points 8, 9 and 10. Point no. refers to blue number in Fig. 4B.

Point	Тетр.	Pressure	Cal Age	Rel. Sea level	Isostasy	'Seafloor'' temp	Burial depth	Comment
No.	(°K)	(MPa)	(ka BP)	(m)	(m)	(°K)	(m)	
1	273.5	3.9	22	-110	100	273	6	Ice Stream: 200 m head of water
2	275.4	4.5	18.5	-93	100	273	62	Burial by till: 200 m head of water
								Cold seafloor water at site. Ice breaks up – no sub glacial
3	275.7	3.5	16.5	-93	63	274	62	pressure.
4	276.6	3.55	14.3	-73	48	274	64	Allerød warming
5	276.35	3.62	13.5	-63	45	274	72	Burial, rising sea level
6	276.35	3.67	11.5	-45	32	274	76.5	End of ice age
7	276.64	3.67	11.3	-45	32	277	76.5	Influx of warm water
8	281.35	3.9	8.5	-13	23	277	77.8	Rising sea level
9	281.35	3.9	8.5	-13	23	280	77.8	Warmer water
10	283.14	3.8	0	0	0	280	80	Present

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Table 4. Properties of water and hydrate used to calculate the thermal properties of the sediments.

Parameter	Value	Unit
Seawater density	1027	kg·m ⁻³
Hydrate density	915	kg⋅m ⁻³
Grain matrix density	2793.44	kg⋅m ⁻³
Thermal conductivity of seawater	49.68	$kJ \cdot days^{-1} \cdot m^{-1} \cdot K^{-1}$
Thermal conductivity of hydrate	42.34	$kJ \cdot days^{-1} \cdot m^{-1} \cdot K^{-1}$
Thermal conductivity of quartz	664.42	$kJ \cdot days^{-1} \cdot m^{-1} \cdot K^{-1}$
Thermal conductivity of non-quartz minerals	216	$kJ \cdot days^{-1} \cdot m^{-1} \cdot K^{-1}$
Quartz fraction of grains	0.2	-
Specific heat capacity of seawater	3.87	$kJ \cdot kg^{-1} \cdot K^{-1}$
Specific heat capacity of hydrate	2.08	$kJ \cdot kg^{-1} \cdot K^{-1}$
Specific heat capacity of grains	0.71	$kJ \cdot kg^{-1} \cdot K^{-1}$
Volumetric heat capacity of seawater	3974.49	$kJ \cdot m^{-3} \cdot K^{-1}$
Volumetric heat capacity of hydrate	1903.2	$kJ \cdot m^{-3} \cdot K^{-1}$
Volumetric heat capacity of grains	1983.34	$kJ \cdot m^{-3} \cdot K^{-1}$
Latent heat of hydrate	430	$kJ \cdot kg^{-1}$
Volumetric latent heat of hydrate	393450	kJ·m ⁻³