



Occurrence, characteristics and formation mechanisms of methane generated micro-pockmarks in Dunmanus Bay, Ireland



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ABSTRACT

A small gas pockmark field in Dunmanus Bay, SW Ireland was surveyed and ground-truthed to assess its activity, geomorphology, explore its formation mechanisms and to investigate its potential influence on the benthic community. The field consisted of 121 circular, shallow units ranging from 5 to 17 m in diameter and not exceeding 1 m in relief. Sub-bottom profiles revealed broad acoustic signatures typical of shallow gas accumulation in the subsurface in addition to vertically elongated signals of ascending bubbles captured in the echo sounder data. The pockmarks show strong correlation with the depth of sub-surface gas fronts. However methane concentrations in the water column and directly above the features were close to typical marine, background values and did not exceed 15 nM. This suggests a very mild, periodic venting scenario. Sediment core samples revealed permeable sandy layers with slightly elevated methane concentrations indicative of stratified, diffusive flow. Pore-water sulphate and chloride data show no sign of pore water freshening and thus suggest that methane gas is the sole fluid responsible for formation of these pockmarks. Benthic infauna distributions showed reduced diversity in pockmarked regions, primarily influenced by the sediment composition. Few species utilising chemo-symbiotic associations were identified, and there was little indication of a community influenced by methane venting in Dunmanus Bay.

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1. Introduction

Fluid flow in the marine subsurface is a known but poorly understood and difficult to observe phenomenon. Pockmarks are sub-circular, shallow depressions formed predominantly in soft, fine-grained substrates, and are widely considered as geo-morphological expressions of fluid expulsion through the sediment (King and MacLean, 1970). They occur in the majority of aquatic environments including lakes, deltas and estuaries (e.g. Berkson

and Clay, 1973; Hovland et al. 1997; Brothers et al. 2012). In most reported cases of pockmarks around the globe the fluid involved is methane gas and thus they are frequently referred to as 'gas pockmarks' (Judd and Hovland, 2007). Although gas expulsion is the most common formation mechanism of these features, compacted pore water (Harrington, 1985) and groundwater expulsions (Christodoulou et al., 2003), iceberg scouring (Pilcher and Argent, 2007), as well as anthropogenic activities such as trawling (Fader, 1991) have also been proposed as viable alternatives. The presence of pockmarks often indicates an active fluid system and thus, they are frequently targeted by the oil and gas industry (Hedberg, 1980). However, seeps are also considered geo-hazards and obstacles for underwater installations as they weaken the sediment structure and alter the morphology of the seabed. A comprehensive understanding of these marine seepage features and their contributions to the food web (Straughan, 1982), local fauna (Dando et al., 1991), nutrient cycles (Wildish et al., 2008), and the carbon cycle in particular (Judd, 2003, 2004) remains elusive.

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Development of Ireland's Marine Resources (INFOMAR) and its predecessor, the Irish National Seabed Survey (INSS), over the past 10 years have revealed pockmarks and other seepage related structures in numerous locations in the Irish Exclusive Economic Zone, i.e. on the Malin Shelf (Monteys et al., 2008, 2009) and in the Irish Sea (Croker et al., 2005; O'Reilly et al., 2014). Pockmarks in Dunmanus Bay were identified in 2007 during a multibeam mapping survey carried out by the RV Celtic Voyager as part of the INFOMAR programme. However, the relatively low resolution of the data precluded detailed insight into the morphology of these features. In April 2009 the RV Celtic Voyager acquired very high resolution bathymetry data that permitted better insight into the morphology and distribution of the Dunmanus Bay pockmarks (Szpak et al., 2009; Monteys et al., 2010). In this paper, we report findings of the first ground-truthing survey of this pockmark field, the activity and nature of these features, and investigate their influence on benthic communities.

2. Study area

Dunmanus Bay is located off the South-West of Ireland, south of the larger and better known Bantry Bay (County Cork). The bay is 7 km wide from Sheep's Head to Three Castles Head and 25 km

long from its mouth. It is a rias setting with only one small river, the Durrus, and several streams draining into the bay. Water depth ranges from below 20 m in the inner bay to over 70 m at its mouth (Fig. 1). The area is strongly influenced by coastal upwelling but tidal activity is low as Dunmanus Bay is out of the main tidal flow (Edwards et al., 1996).

Favourable thermal fronts and adequate nutrient concentrations support high levels of phytoplankton production in these waters and seasonal blooms are common (Raine et al., 1990). Notably, blooms of *Gyrodinium aureolum* (dinoflagellate responsible for the so called "red tides") are frequent in these waters affecting local aquaculture (Jenkinson and Connors, 1980; Roden et al., 1980, 1981). The benthic fauna of Dunmanus Bay remains largely unstudied, with only intertidal species such as sea lettuce (*Ulva lactuca*), snails (*Nucella lapillus*), barnacles (*Semibalanus balanoides*, *Chthamalus montagui*), mussels (*Mytilus* spp.) and limpets (*Patella vulgata*, *Patella aspera*) documented (Cross and Southgate, 1983).

The bedrock geology of Dunmanus Bay has not been studied per se but inferred from the geology of bordering landmasses in the 1850s by Jukes (1864) and Jukes et al. (1861) and more recently by Naylor (1975), Naylor and Sevastopulo, (1993) and MacCarthy (2007). Both Bantry and Dunmanus Bay lie in the South Munster Basin separated by the Sheep's Head anticline. The major

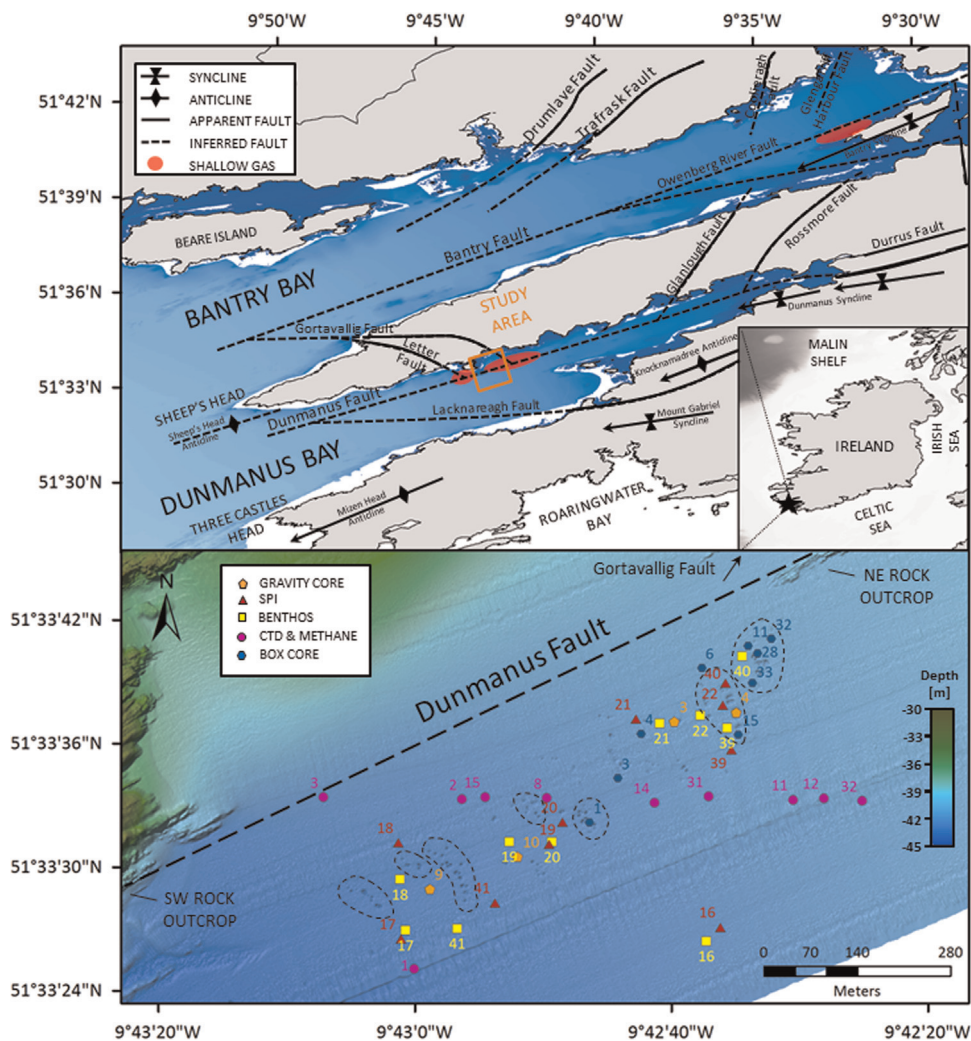


Fig. 1. MBES shaded relief bathymetry of Dunmanus and Bantry Bays with major structural features and index map with site location (top panel). Major fault in this area, the Dunmanus Fault crosses just north of the pockmark field with minor Gortavallig Fault branching out just 250 m north-west from the pockmark field. Detailed sampling map (bottom panel) shows the location of sediment and water column sampling stations. Dashed shapes delineate major pockmark clusters. (DOUBLE COLUMN).

sedimentation controlling fault in this area is the Dunmanus Fault (DF) crossing the entire Bay parallel to the landmass (Fig. 1). Two major branchings off this fault occur in the vicinity of a pockmark field area: the Gortavallig Fault (GVF) and the Letter Fault (LF). Moreover, there are several minor faults in the northern part of the Dunmanus syncline separate from the DF, notably the Rossmore Fault (RF) and the Glanlough Fault (GF). Faults are often associated with fluid migration provided that source rocks are present and thermal conditions favour hydrocarbon generation (e.g. Kutas et al., 2004). Early Carboniferous formations are abundant in the area and contain, in places, organic-rich shales, so called “marine bands” and “Alluvium, Peat-bog” (Jukes, 1864 and Hunt, 1858). The surface sediments in Dunmanus Bay are predominantly muddy sands with a small gravel component. Sub bottom and discrete sediment core data suggests that near surface sediments consist of mainly fine to coarse sands with varying contribution of clays and silts (Szpak et al., 2009). These recent sediments overlie a prominent seismic signature similar to that discovered in Bantry Bay. Plets et al. (2014) interpreted it as transgressive surface, developed pre-11 ka, underlying intertidal-estuarine sediments. As Dunmanus and Bantry Bays have likely experienced the same recent environmental history and share numerous similarities in acoustic data sets, typical of drowned valleys, we suspect that signatures observed in data presented herein represent the extension of the palaeo beach identified in their work.

3. Materials and methods

3.1. Bathymetry

Two Bathymetric datasets have been used in this study. The first, covering the entire bay was acquired in 2007 as part of the INFOMAR programme on-board the RV Celtic Voyager using a Kongsberg-Simrad EM1002 multibeam echo-sounder, with an operational frequency of 93–98 kHz and pulse length of 0.2 ms. The second dataset was acquired in 2009, focusing around the pockmark field, using a Kongsberg-Simrad EM3002D multibeam echo-sounder, with an operational frequency of ca. 240 kHz and low survey speed (2–3 knots). Resulting bathymetric terrain models were gridded at 1×1 m. Pockmark density was calculated using ArcGIS 10.1 with Spatial Analyst Tool add-on (ESRI) (Silverman, 1986).

3.2. Pockmark morphology

Pockmarks were manually delineated using Fledermaus software package (Quality Positioning Services B.V.). Craters were measured along N–S (width), W–E (length), NW–SE and SW–NE axes. Pockmark edge was determined by measuring the slope of the side walls with cut-off point at 2.0° . The depth was calculated by subtracting averaged wall edge depths from the deepest point within the crater. Shared walls of composite pockmarks were not included in calculations. Perimeter and surface area were calculated as for ellipsoids. Volume was calculated as for half-spheroids.

3.3. Sub-bottom profiler

Sub-bottom profile data were acquired using a heave-corrected SES Probe 5000 3.5 kHz transceiver in conjunction with a hull-mounted $4^\circ \times 4^\circ$ transducer array. Acquisition parameters, data logging and interpretation were carried out using the CODA Geokit suite. Both Raw Navigation string and Heave Compensation string were fed into the Coda DA200 system.

3.4. Water column sampling

Water column samples were collected with Niskin bottles mounted on a SBE 32 Carousel Water Sampler (Sea-Bird Electronics Inc., USA). During descent the Conductivity, Temperature and Depth (CTD) profiles were recorded to identify oceanographic background conditions and allow sampling of the water column in a more informative manner. Upon retrieval, samples were transferred immediately to 125 mL serum bottles and crimp sealed with a gas-tight, thick, butyl rubber septum. All water samples were poisoned with a saturated mercuric chloride (HgCl_2) solution to inhibit microbial activity and stored at $2\text{--}4^\circ\text{C}$ until analysis. Samples were analysed according to the modified head-space method with salting-out as described by Gal'chenko et al. (2004). Briefly, samples were boiled in a water bath for 1 h on the day of analysis to ensure full desorption of methane. The methane content from head-space was determined on shore after the cruise on a Carlo Erba gas chromatograph equipped HP-PLOT Q capillary column ($30\text{ m} \times 0.32\text{ mm i.d.}$, $20\ \mu\text{m}$ film thickness) and flame ionisation detector (GC-FID). The detector temperature was set to 225°C and He was used as carrier gas. Samples were quantified based on the methane gas standard response as described in Gal'chenko et al. (2004). Method robustness was tested with methane standards across a range of concentrations and yielded with a precision of $\pm 0.5\text{ nM}$, $n=4$ for concentrations $< 25\text{ nM}$. Chlorophyll *a* concentrations were derived from fluorescence measurements recorded during all CTD casts. The fluorescence sensor was calibrated for Chlorophyll *a* concentrations ranging from 0.04 to $200\ \mu\text{g/l}$.

3.5. METS sensor

A METS sensor (Franatech GmbH, Germany) was mounted on the Sea-Bird 911 CTD (Sea-Bird Electronics Inc., USA) unit. The CTD's water pump feeding tubes were modified to ensure that both sensors analysed the same representative water sample. The sensor was calibrated by the manufacturer for methane concentrations ranging from 2 to 200 nM in a temperature range from 2 to 20°C . An equilibration test was performed to assess the minimal time necessary to reach baseline signal after saturation. Lag time varied between 200 and 300 s depending on saturation conditions (350 and 700 nM respectively). The sensor was deployed with the CTD and held 5 m above the seabed until the signal stabilized. Between deployments the sensor was kept powered on and immersed in running surface water to minimise humidity and temperature variability.

3.6. Sediment sampling

Sediment samples for benthos analysis were collected with a Day Grab sampler (0.1 m^2). Five replicate samples were taken per site. Sediment samples for bulk parameters analysis were collected using box and gravity corers. Samples locations are shown in Table 1. Vessel position was determined using DGPS with horizontal accuracy of $< 1\text{ m}$. Sample position was recorded when the sampler contacted with the seabed to account for vessel drift. Final sample coordinates were corrected for the offset between DGPS antenna and sampling equipment position. Cumulative vessel and sampling uncertainty is estimated to be $\pm 10\text{ m}$.

3.7. Bulk parameters

Upon retrieval, box and gravity core samples were transferred to an argon-purged glove box and a redox potential (E_h) measurement was taken with the use of a temperature compensated push-in Pt electrode with Ag/AgCl reference junction (SCHOTT).

Table 1
Position and parameters measured of samples collected in the Dunmanus Bay. SPI – Sediment Profile Imagery, WS – water sampler, PSA – particle size analysis, TC – total carbon, PW – pore water analysis, DM – dissolved methane, R – redox potential, mbsf – metres below seafloor. Acoustic turbidity (AT) depth refers to gas front depth range relative to the seabed surface as described in Section 4.3 and as presented of Fig. 7. AT depth is given as a range, representative of the area covering ± 10 m radius from the sample or replicate location. 'No data' indicates that sample location was outside of the acoustic footprint of the sub-bottom profiler. Water column samples are described depending on whether they were collected from outside or inside of the pockmark field (PF) as constrained by sub-bottom data presented on Fig. 7.

Site	Grain size (μm)							Gravel	Sand	Silt/clay
	> 2000	> 1000	> 500	> 250	> 125	> 63	< 63			
17	14.9	13	10.4	8.9	8.9	11.2	32.7	14.9	52.4	32.7
18	7.4	9.9	9.7	8.1	9.2	17.1	38.6	7.4	54	38.6
41	19.2	10.2	10.2	9.4	9	15.6	26.4	19.2	54.4	26.4
19	6.3	12.3	14.1	11.7	10.8	12.5	32.3	6.3	61.4	32.3
20	12.3	9.8	8.7	7.9	6.9	15.7	36	12.3	49	36
21	15.1	10.9	9.1	7.6	9.3	14	33.8	15.1	50.9	33.8
22	6	12.1	12.4	11	10.8	13.6	34.1	6	59.9	34.1
39	5.3	6.9	39	5.1	6.9	12.1	24.7	5.3	70	24.7
16	2.2	5.5	5.8	4.7	14.3	31.1	36.4	2.2	61.4	36.4
40	15.4	12.8	9.7	8.4	9.3	11.6	32.8	15.4	51.8	32.8

The electrode was routinely checked for sulphide poisoning and tested for reproducibility between measurement series with saturated quinhydrone pH buffer solutions (pH=4.0 and 7.0, with expected $\Delta E_{\text{H}}=172 \pm 4$ mV). Sediment cores (10 cm^3) for interstitial gas analyses were collected with cut-off syringes and transferred to head-space vials and processed similarly to water samples. Pore waters for sulphate and chloride analysis were extracted by centrifugation and stored at 2–4 °C. Concentration of these ions was determined on-shore by ion chromatography according to standard methodology. Granulometric analysis was performed on dried sediment from each benthos station. Approximately 100 g of sediment was sieved through a series of Wentworth graded sieves (McMahon et al., 1996).

3.8. Benthos sampling

A Perspex core was taken from each sample for on-shore meiofaunal assemblage analysis, the remaining sample was sieved on a 1 mm mesh sieve and the retained macrofaunal assemblage was preserved in a 10% buffered formalin solution. All meiofaunal and macrofaunal assemblages were sorted under a microscope into four main groups: Polychaeta, Mollusca, Crustacea and Others which consisted of echinoderms, nematodes, nemertean, cnidarians and other phyla. The taxa were identified to a species level where possible.

Univariate and multivariate statistical analyses were carried out on the combined replicate station-by-station faunal data. The following diversity indices were calculated: Pielou's Evenness index (J), (Pielou, 1977) and Shannon–Wiener diversity index (H'), (Pielou, 1977). The PRIMER[®] programme (Clarke and Warwick, 2001) was used to carry out multivariate analyses. All species/abundance data were fourth root transformed and used to prepare a Bray–Curtis similarity matrix in PRIMER[®]. The fourth root transformation was used in order to down-weight the importance of the highly abundant species and to allow the mid-range and rarer species to play a part in the similarity calculation. The Bray–Curtis similarity matrix was subjected to a non-metric multi-dimensional scaling (MDS) algorithm and cluster analysis (Kruskal and Wish, 1978).

3.9. Sediment profile imaging

Sediment profile images were taken in five replicates at the same locations as benthic samples with a Sediment Profile Imagery camera (SPI; AQUAFAC International Services Ltd., Ireland). SPI cameras permit in situ images of the undisturbed sediment

water interface to be obtained, which is impossible to obtain ex situ mainly due to sediment disruption and compaction during sampling with use of conventional apparatus (Sommerfield and Clarke, 1997). SPI cameras mounted on a frame are slowly lowered on to the seabed to minimise sediment disruption and then a hydraulic or gravity based system is triggered from the vessel to insert the prism into the seabed.

4. Results and discussion

4.1. Water column and seabed sediments bulk parameters

Thermo and haloclines were well defined with an average depth of 11 m. Average water temperature just below the thermocline was 10.6 °C and 9.6 °C at near bottom. Dunmanus Bay is fed by only a few streams and a relatively small river (River Durrus). It therefore experiences little freshwater influence and has marine water column characteristics close to that of the open sea. The salinity (in PSU) reaches average open ocean values and generally follows the thermocline fronts with surface water reaching a salinity of 34.92 and increasing to 35.05 below the pycnocline and 35.08 in near bottom waters. The influence of weak coastal upwelling was observed in the water column but, as in the Bantry Bay, the strongest upwelling is believed to be observed in the mouth of the bays rather than their interior (Elliott and Clarke, 1991). Dunmanus Bay experiences semi-diurnal tidal cycles but overall tidal activity is low as the bay is out of the main tidal flow.

Chlorophyll *a* (Chl *a*) concentrations were similar at all stations and varied between 2.33–3.33 $\mu\text{g/l}$. A Chl *a* maximum was present at an average depth of 17 m. The concentration of phytoplankton started to increase just below the pycnocline, with the lower boundary located around 30 m. A slight decline in concentrations ($R^2=0.41$, $n=9$) can be observed across the W to E transect, suggesting increased plankton activity towards land, possibly due to nutrient runoff into the bay. There is no plankton data published for Dunmanus Bay, but these observations are consistent with those from a previously reported study of neighbouring Bantry Bay (Gribble et al., 2007).

Surface sediments at all stations are similar across all Wentworth size classes, comprising mainly fine to coarse sands with a small percentage of gravel and with a significant, but not dominant, silt/clay component (Table 2). The percentage of gravel varied from 2.2% to 19.2% and more gravel was found in those stations located in the vicinity of rock outcrops suggesting an erosional

Table 2

Particle size distribution of surface sediments in the Dunmanus Bay pockmark field measured at the biological stations. Sands are the dominant substrate type with significant proportions of silts and clays, and occasional gravel. Control station is marked with an underline.

Station	Species	Individuals	Evenness	Diversity
<u>16</u>	77	908	0.58	3.66
17	46	632	0.57	3.14
18	39	1462	0.37	1.96
19	43	1878	0.37	2.01
20	34	382	0.61	3.09
21	23	568	0.35	1.60
22	43	786	0.36	1.94
39	35	929	0.42	2.17
40	32	741	0.40	2.02
41	41	579	0.60	3.19

origin, rather than alluvial transportation. Sands are fairly evenly distributed between the five sand size classes (grand mean 11.3%, $n=50$) with the finer grain size fractions being slightly more

abundant (11.2–31.1%). Silt and clay comprised approximately a third (mean 32.8%, $n=10$) of the total weight of the sediment.

Overall, variability in water column and sediment characteristics in the study area was low and we conclude that Dunmanus Bay pockmark field is a relatively homogenous habitat. The uncertainties arising from variability in plankton distribution and abundance, water column structure are negligible and thus, do not affect the benthic community structure (Clarke and Green, 1988). Although particle size distribution is fairly similar in all stations, some minor effects on the benthos distribution were observed. These are discussed in more detail in Section 4.6.

4.2. Pockmark morphology and distribution

Dunmanus Bay pockmark field contains 121 pockmark features. Many of them ($n=50$) have a composite morphology with at least one or more of the side walls shared with other pockmarks and having significantly lower slope. In most cases however, individual pockmark units can be distinguished and almost all ($n=114$) of the features are sub-circular. The largest composite pockmark

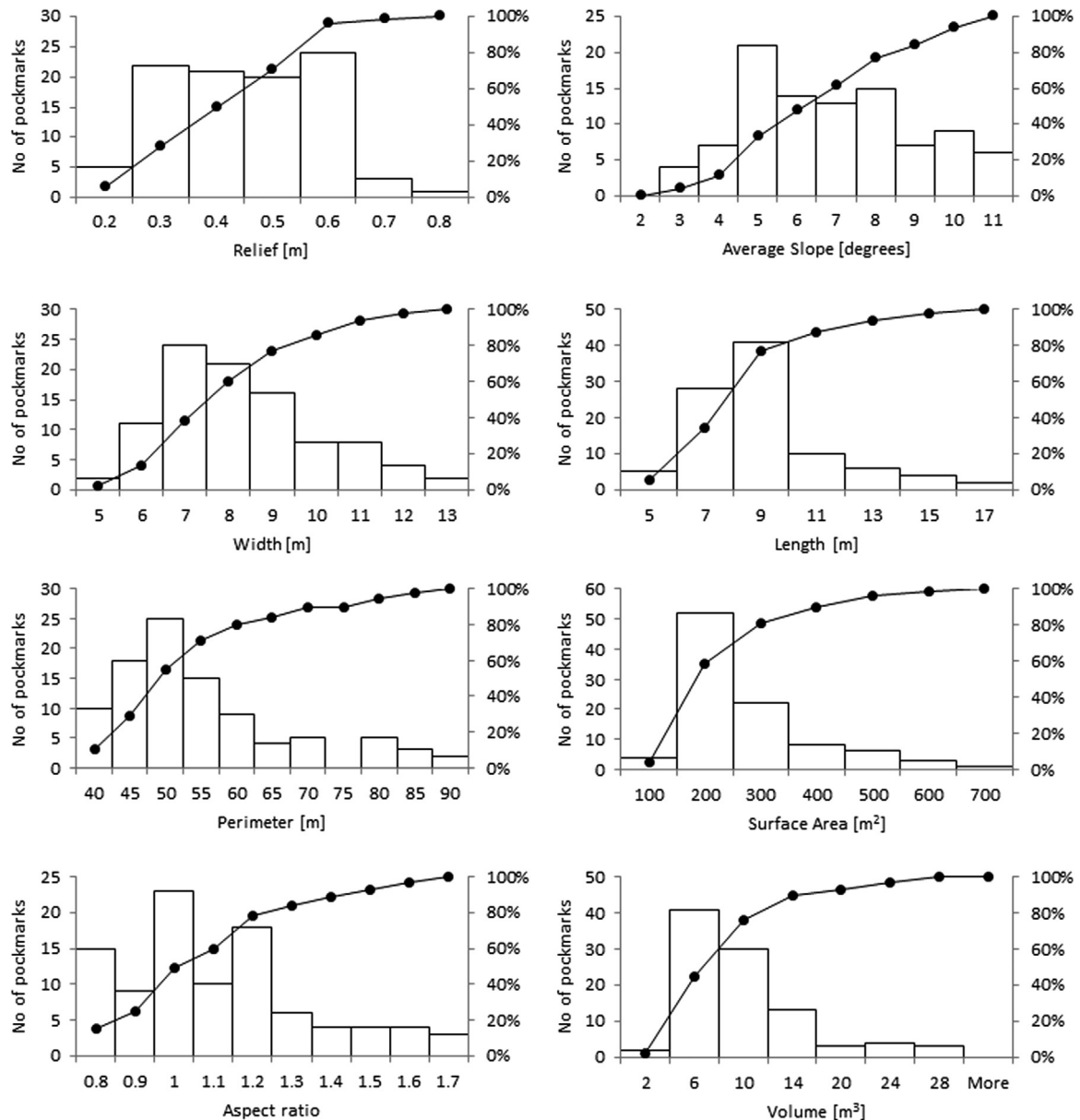


Fig. 2. Histograms and cumulative frequency curves depicting basic morphological characteristics of Dunmanus Bay pockmarks (DOUBLE COLUMN).

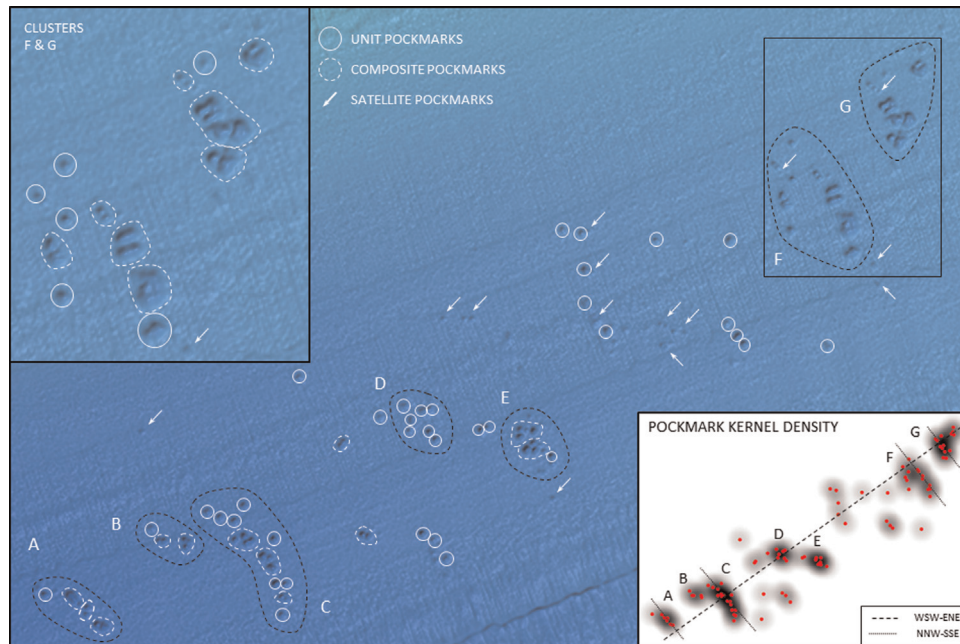


Fig. 3. MBES shaded relief bathymetry of the Dunmanus Bay pockmark field illustrating distribution of pockmarks and their morphology. Magnified region (top left insert), marked with black frame, shows major pockmark clusters F and G and their complex morphology. Kernel density map (bottom right insert) shows primary and secondary alignment of the field and the features respectively and illustrates the natural groupings of pockmarks into seven major clusters (DOUBLE COLUMN).

comprises 5 subunits and reaches 15 m in its widest point. However, the majority of these features are very small in comparison to other pockmarks reported in the literature (Judd and Hovland, 2007). The width and length of the pockmark units range between 5.0 and 14.0 m and between 4.5 and 17.0 m respectively, averaging 8.1 m and 8.5 m respectively (Fig. 2). These are also very shallow features with the vertical relief ranging from 0.2 to 0.7 m and an average of 0.4 ± 0.1 m. There is also a group ($n=25$) of very small (1–3 m) and very shallow (< 0.2 m) satellite pockmarks scattered across the field (Fig. 3). Part of these features ($n=11$) occur in the vicinity of larger craters and might be related to the most recent fluid discharges as suggested by Hovland et al. (2010), but most of them are isolated ($n=14$) and likely are remnants of small scale events possibly induced by subtle triggering mechanisms such as tidal pumping (Hovland et al., 2012). The perimeter of the Dunmanus Bay pockmarks areas vary between 34.6 and 88.9 m with an average of 52.3 ± 12.5 m. Most of these descriptors are negatively skewed towards lower values with the exception of a vertical relief which appears to be unimodal in distribution. Standard deviation of width and length (1.9 and 2.5 m respectively) implies more variability in the equatorial diameter which is most likely related to tidal and currents effects. These characteristics suggest that fluid release events occur frequently and on a small scale. Fine grained sediment seal thickness is probably the main controlling factor of pockmark sizes in Dunmanus Bay as observed in other, similar settings (e.g. Andrews et al., 2010). Thin, unconsolidated sediment layer and to smaller extent, low hydrostatic pressure, effectively lowers the overburden pressure threshold and thus favour frequent and low-magnitude venting events which in turn result in formation of small, clustered craters rather than large, isolated ones.

The average pockmark surface area is 225.0 m^2 and ranges from 94.3 to 612.3 m^2 . The surface area standard deviation is quite high (115.6 m^2) and implies a broad, but strongly negatively skewed, distribution of pockmark sizes. The cumulative surface area of pockmark scarred seabed is $21,595 \text{ m}^2$ which represents 5.4% of the study area delineated by the acoustic data. This is in keeping with the findings of other authors, where the percentage of

scarred seabed is typically reported as ranging from 1% to 10% of the total area (i.e. Dandapath et al., 2010, Gontz, 2002 and Hovland et al. 1984). However, in settings where favourable conditions occur, pockmark density might be much higher and represent as much as 24% of the seabed as reported by Andrews et al. (2010). The volume of pockmarks (calculated as half-spheroids) ranges from 1.3 to 27.1 m^3 with an average of 8.0 m^3 and represents a total of 767.5 m^3 sediment displaced during their formation. This equates to an approximate volume of $19 \times 10^2 \text{ m}^3 \text{ km}^{-1}$ of affected seabed and indicates rather small scale events in comparison to sites where more vigorous venting takes place and where large volumes of sediment are displaced, for example in the Nile Deep Sea Fan region where approximately $11,300 \text{ m}^3 \text{ km}^{-1}$ has been excavated (Moss et al., 2012). However, in settings with slow, diffuse fluid migration, such as the northern Californian margin, the amount of sediments moved can be considerably lower and reach volumes of $314 \text{ m}^3 \text{ km}^{-1}$ (Yun et al., 1999). This might suggest that the Dunmanus Bay field, despite its modest size, is or has been experiencing low to moderate fluid flux through the seabed.

The majority of Dunmanus Bay pockmarks have aspect ratios typical for circular features ($L/W=1.0\text{--}1.5$, 44%); only a few can be classified as elliptical ($L/W=1.5\text{--}2.5$, 7%). There are a considerable number of pockmarks within the group with a circular characteristic which are differently orientated to the majority ($L/W=0.8\text{--}0.9$, 25%). This suggests that seabed physical characteristics are the primary controlling factor for the shape of these pockmarks rather than the cumulative effects of tidal and current actions. The cross-sections of pockmarks varied between 'V'-shaped and 'U'-shaped profiles, with the latter being naturally more common among the larger features. The sidewall slopes vary from 0.7° in some composite features to 12.8° in some isolated craters. The average slope is 6.4° but the standard deviations of equatorial and polar sidewall slopes ranging from 2.2 to 2.6° imply some variability across the feature population (Fig. 2).

The Dunmanus Bay pockmark field shows clear WSW–ENE orientation and appears to be limited by two rock outcrops to the WSW and ENE. Individual pockmarks however, show a tendency

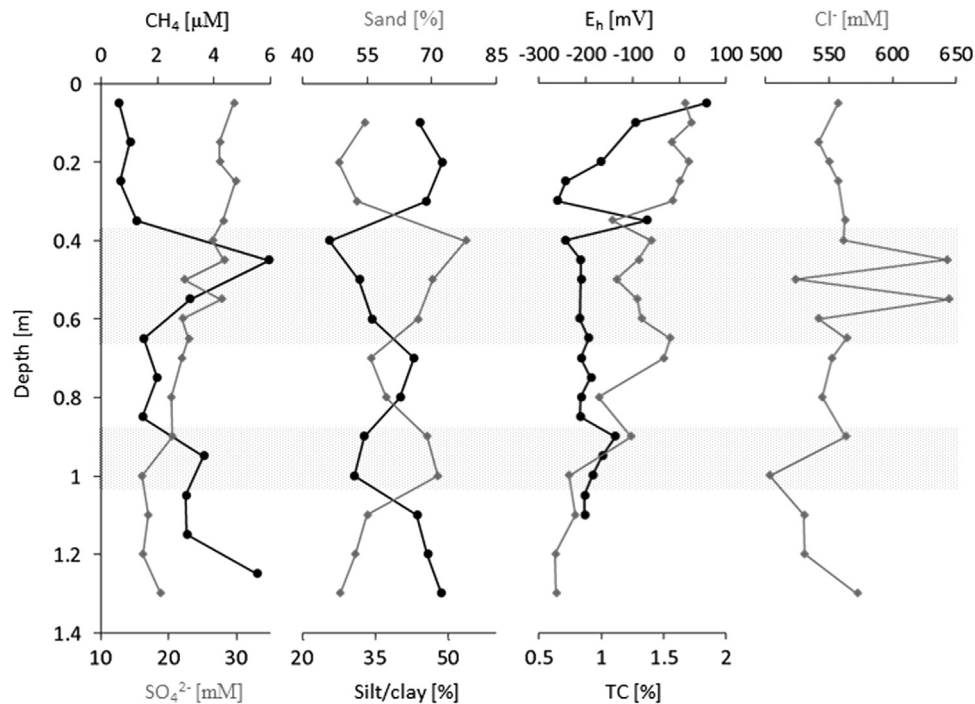


Fig. 4. Depth profiles of bulk sediment parameters: particle size (% of sand % of silt and clay), total carbon (TC); and pore water parameters: methane, sulphate and chloride concentrations and redox potential (E_h) from sediment core 3. The grey background indicates sand-enriched layers with higher concentration of methane (DOUBLE COLUMN).

to occur in clusters that appear to have a NNW–SSE orientation, which is particularly visible when considering only the major groupings. Kernel density analysis identified seven such clusters showing a varying degree of grouping (Fig. 3). The majority of pockmarks occur in these parallel clusters and only 24 individual units are observed outside of these pockmark groupings. The exact reason for the field orientation remains unclear as sub bottom data shows that the superficial sediments are predominately homogenous in structure and deep seismic data is not available. Pilcher and Argent (2007) demonstrated that on a larger, scale pockmarks can follow fault lines and form organised structures. It is therefore possible that the orientation of the field is related to the proximal Dunmanus Fault that is axially correlated with the field (Fig. 1). However, the orientation of individual clusters, due to their small size, is more likely related to shallow stratigraphy rather than deep structural features. Shallow sediment core analysis identified permeable, sand enriched strata, which could act as sub-surface conduits and channel the fluid to the surface as well as horizontally distribute it on a local scale (Fig. 4). The density of pockmark features suggest that these conduits are most likely reused and formation of new features should be expected in the vicinity of pre-existing clusters.

4.3. Pockmark formation

Pockmarks are features associated with fluid expulsion through the sediment. The fluid involved in the formation of most marine pockmarks is hydrocarbon gas, especially when associated with areas not adjacent to a landmass and therefore devoid of any aquifer influence (Judd and Hovland, 2007). Nevertheless, exceptions to this have been reported. In areas of the Florida Escarpment, part of the Florida Platform, freshwater seepages occur at depths exceeding 3000 m (Paull et al., 1984). Another example is Blake Ridge, located ca. 200 km offshore at 500 m depth (see Taniguchi et al., 2002 for review). However, in general, for estuarine, lacustrine and coastal settings, groundwater escape is a probable

mechanism for pockmark formation. Pockmarks formed by this mechanism have been widely reported (e.g. Christodoulou et al., 2003; Khandriche and Werner, 1995). Since the Dunmanus Bay pockmarks are located just 650 m away from the landmass, freshwater expulsion is a potential formation mechanism for these features.

There was no evidence of salinity changes similar to those reported by Christodoulou et al. (2003) and others that would imply active flow of freshwater into the water column in Dunmanus Bay. The salinity in the lowermost 10 m of the water column shows a gradually increasing trend downwards at all stations, with an average value of 35.07 at the seabed. However, due to weather conditions, the CTD carousel had to be kept approximately 5 m above the seabed to compensate for the swell induced rocking of the vessel and to protect the instrument from contacting the seabed. This limitation was significant as the salinity decrease reported by Christodoulou et al. (2003) was observed only in the 3 m above the seabed while the water column above was not affected. It is therefore possible that moderate freshwater flow exists but was not detected as a result of survey conditions and instrument limitations. Detailed video surveying of these pockmarks with a fly-by camera during a recent research cruise (2011 CE11_017) did not reveal any visible freshwater flow (Shane O'Reilly, personal communication, May 20, 2011). However, this finding does not preclude the possibility of freshwater expulsion which can occur episodically. The west coast of Ireland historically experiences high levels of precipitation and so does Dunmanus Bay. The 30-year average of annual rainfall means (Walsh, 2012) is varying between 1400 and 1600 mm/year in this area and is above the national average (1230 mm/year). Moreover, vegetation is limited, often in the form of regulated farmland, and higher plants are virtually absent, thus water absorption is limited. Additionally, permeable rocks such as sandstone and limestone are the dominant rock types in the area (Naylor, 1975). According to Burnett et al. (2003) the above, along with groundwater abstraction and topography, are the main factors controlling the likelihood of a

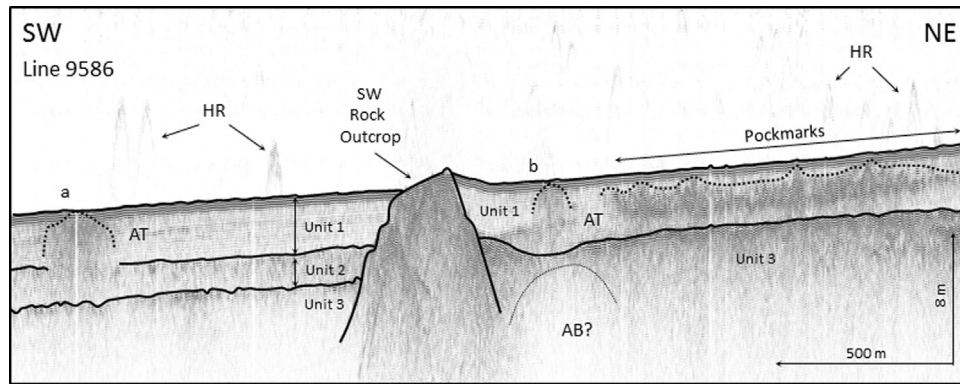


Fig. 5. Sub-bottom 3.5 kHz pinger profile showing cross section of the pockmark field and an area outwith the field and illustrating the shallow stratigraphy and gas-related acoustic signatures in this setting. Below the pockmark scarred seabed, a horizontally extended area of acoustic turbidity (AT) is clearly visible. Ambiguous hyperbolic reflectors (HR) are observed throughout the area and do not appear to be confined to areas marked with AT. The lefthand AT signal highlighted as 'a' is a clear indicator that gas signatures are also present outwith the pockmark region. AT signal highlighted as 'b' represent very shallow accumulations of gas over a virgin seabed. This area may become a location of crater formation in the near future. Below this signature we observe faster signal dissipation in comparison to surrounding seabed which might be attributed to weak, gas related acoustic blanking (AB) (DOUBLE COLUMN).

groundwater discharge in a coastal setting. Given the above, it might be expected that, episodically, particularly after heavy rainfall, the amount of freshwater in unconfined aquifers would increase producing a pressure gradient that could result in pore fluid displacement and/or freshwater expulsion. Additionally, Wilson and Rocha (2012) identified water temperature anomalies, typically associated with submarine ground water discharge, just 1 km SW from the studied pockmark field. This hypothesis is not, however, supported by the pore fluid data from the collected sediment core, though profiles show some interesting features (Fig. 4). The concentrations of chloride throughout the core show typical seawater values with no evidence of pore water freshening which would be expected if ground water was migrating through the seabed. Similarly, a reduction of sulphate is observed without any evidence of freshwater dilution. The sulphate profiles show an initial decrease and then at approx. 1.5 mbsf the trend is reversed, possibly by re-oxidation of sulphate. A sharp decrease would be expected in the case of intrusion and for a diffusive/advective scenario, a linear or concave profile would be expected (Hensen et al., 2003). Therefore, we find no evidence of pore water freshening of either the water column or the sediment and conclude that freshwater expulsion is not a likely mechanism for the formation of Dunmanus Bay pockmarks.

Since freshwater is unlikely to be involved in the formation of these features hydrocarbon gas may be responsible. The acoustic data contains multiple signals that are commonly interpreted as associated with shallow gas and gas venting into the water column (Fig. 5). Numerous and extensive areas of acoustic turbidity (AT) as well as hyperbolic reflectors (HR) in the water column in the vicinity of the AT are clearly visible. AT is a strong indicator of shallow gas accumulation and is frequently reported in similar settings where seeps and pockmarks are observed (e.g. Ferrin et al., 2003). The AT appears to extend over a relatively wide area and is confined to the uppermost sedimentary unit which contains permeable sandy bodies. Moreover, acoustic blanking (AB) typically observed below the gas front is virtually absent in this setting. An important feature of these seismic profiles is the lack of AB signals directly below the prominent AT area which are frequently observed in upward migration scenarios (e.g. Szpak et al., 2012). Only one faint amplitude decrease was observed below one of the pockmarks that could be ascribed to AB, however, signal starvation is equally possible for this feature (Fig. 5). Therefore, an alternative, lateral migration scenario is more plausible in this setting. Assuming that gas is continuously being vented from a deeper source, namely bedrock fault, signals such as AB or AT

connecting with the bedrock are to be expected. Such signals are not observed in this setting. However, this is only true for a continuous gas supply scenario. Periodic gas migration caused by successive cycles of seal failure-renewal is a viable hypothesis, particularly, given the vicinity of Gortavallig and Dunmanus Faults. AT signatures are observed also outside of the pockmark field and throughout the Dunmanus Bay but there are no surface gas expulsion features accompanying them. The prominent AT observed in the sub bottom profile located SW of the rock outcropping extends to the surface of the seabed and yet there are no pockmarks in this location (Fig. 5). This phenomenon can be attributed to changes in sediment type, as reflected in the coarser particle size distribution (Monteys et al., 2010). Pockmarks are generally formed in the fine-grained substrates since only these can provide the specific conditions needed for fluid over-pressurisation and subsequent forceful escape through the seabed upon seal failure. In Dunmanus Bay, medium to coarse sands dominate, including the south-western region shown in the sub-bottom profile (Fig. 5) included, and thus optimal conditions for pockmark formation are not abundant in this setting (Monteys et al., 2010).

The hyperbolic acoustic signals in the water column (HR) are ambiguous as fish swim bladders can produce similar features, though shape and migration patterns can help distinguish between them. Fish shoals, according to Judd et al. (1997), are more diffuse and horizontally extended, whereas, seeping gas will have more columnar, vertically extended characteristics. The shape of hyperbolic reflectors observed in the sub-bottom data (Fig. 5) is both horizontally and vertically extended and thus difficult to interpret. However, the MBES data also contains very narrow and vertical signals that are most likely caused by ascending bubbles (Fig. 6). As bubble diameter is directly related to its acoustic resonance frequency (Minnaert resonance) and selective visualisation of bubbles in data sets collected by instruments using different operational frequencies is not uncommon. Low frequency instruments, such as pinger, favour penetration rather than resolution unlike higher frequency instruments such as MBES which have narrow beam widths and are thus more suited for detection of gas plumes (Devaud et al., 2008). These signals do not appear to be artefacts since they occur in many locations (not all of such signatures are shown in Fig. 6) and more significantly the same vertical signals are observed in adjacent survey lines from the same seabed area. We therefore propose, given the acoustic data and the lack of evidence for water freshening from groundwater discharge, a venting mechanism based on successive cycles of seal failure-renewal as the probable formation mechanism for these pockmarks.

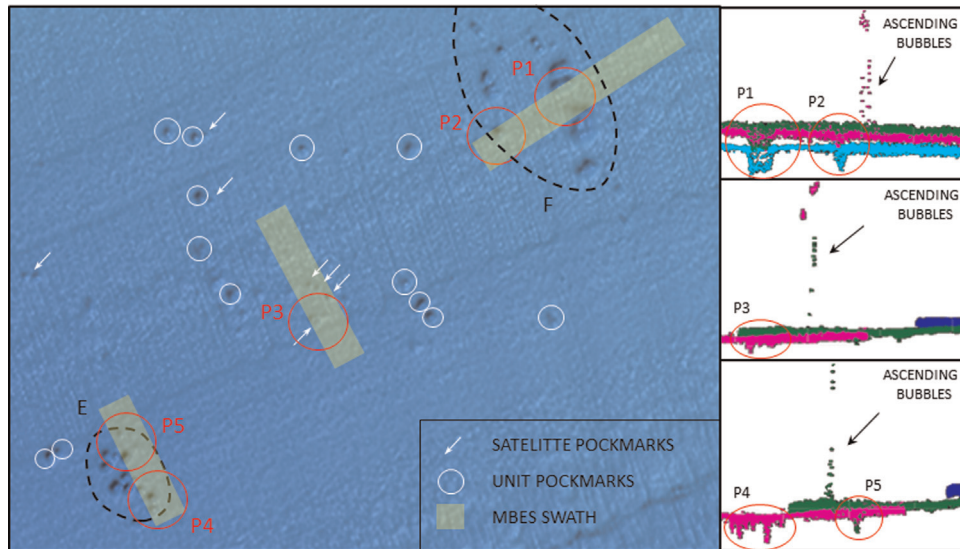


Fig. 6. MBES shaded relief bathymetry illustrating pockmark clusters D to F and individual MBES lines (right panel) with signals ascribed to ascending bubbles in the vicinity of the encircled pockmark features. Shaded areas represent MBES swaths for reference (DOUBLE COLUMN).

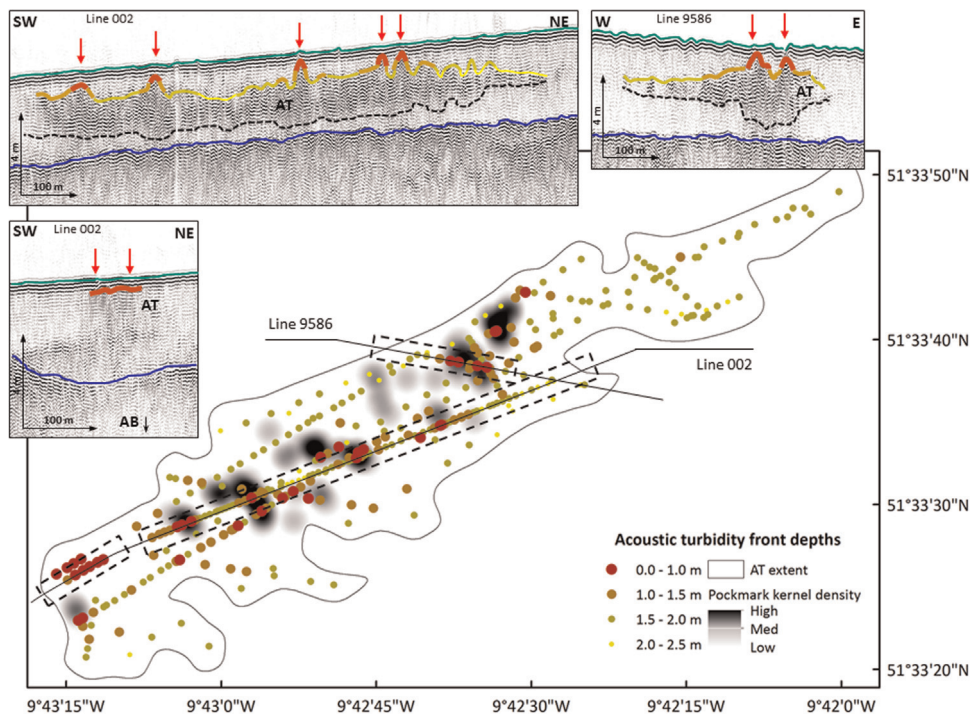


Fig. 7. Map of gas front depths derived from multiple 3.5 kHz sub-bottom (pinger) profiles illustrating correlation between these depths and the pockmark density depicted by kernel density heat map. The extension of the acoustic turbidity (AT) extent in the whole region is marked with a black outline. The acoustic front depths to seabed are size and colour coded and correlate with size and colour coded delineation of these fronts in two individual sub-bottom profiles (Line 002 and 9586) shown in panels above. The areas corresponding to these sub-bottom profiles are marked with dashed black lines (DOUBLE COLUMN).

Hovland et al. (2010) suggests that small, satellite features accompanying larger pockmarks may be indicators of the most recent fluid escape events. The MBES data presented here (Fig. 6) only partially supports this hypothesis. Although, we observe gas bubbles in the areas where pockmark density was low and the majority of features are very small, we also observed flares in the vicinity of larger pockmarks. Moreover, after examining more sub-bottom profiles, we see that AT fronts are correlated with both pockmark density and gas front depths (Fig. 7). It is clear from this data that the shallower the gas front, the greater the number of pockmarks on the surface. This implies that, contrary to the Hovland hypothesis, the most active fluid systems are not located in

the vicinity of smaller features in this setting. The moderate positive correlation ($R^2=0.41$, $n=435$) between the thickness of the gas front and its depth from the sediment water interface suggests the existence of pathways through which the gas is channelled through the seabed. It has been reported that AT front depth might show seasonal variability caused primarily by seasonal temperature fluctuations of bottom waters (Hagen and Vogt, 1999). In Dunmanus Bay however, such fluctuation will be minimal as these waters are well stratified throughout the year and seasonal temperature variability is on the order of $\pm 5^\circ\text{C}$ (O'Sullivan et al., 2014) as derived from Regional Ocean Modelling System (ROMS).

4.4. Estimation of methane in the subsurface and flux rates

The surface area of the gas charged sediments derived from extension of the AT observed in the sub bottom data sets (Fig. 5 and 7) covers an area of only 0.4 km². The thickness of the gas charged sediments estimated from sub-bottom data varies from 0.2 to 5.7 m with an average of 1.9 m (± 1.0 m, $n=435$). Thus, the total volume of gas charged sediments amounts to ca 754×10^3 m³, a relatively small figure compared with others reported from shallow settings (Hovland and Judd, 1992). In line with the evidence presented above, we propose that the shallow gas accumulations are primarily distributed within sand enriched and, thus, more permeable strata. Therefore, the highest recorded concentration of methane (96 ppb) within the sediment core is used for calculation of total methane trapped in the subsurface giving a conservative estimate of 0.72×10^6 g of methane present in the sub surface of the Dunmanus Bay pockmark field. For a more accurate distribution, more sediment samples should be analysed to: (i) verify the concentration of methane in acoustically distinguishable units, (ii) verify the composition of strata with prominent AT signatures, and (iii) to consider variability in the gas front thickness to represent more accurately the volume of the affected seabed.

Hovland and Judd (1992) reviewed many shallow gas accumulations globally and proposed three methane average flux estimates based on the physical evidence of ebullition: (i) 26 g CH₄ m⁻² year⁻¹ for settings with visible ebullition, (ii) 13 g CH₄ m⁻² year⁻¹ for settings with intermittent ebullition, and (iii) 6 g CH₄ m⁻² year⁻¹ for settings with no visible ebullition. Based on the evidence presented here, we suggest that Dunmanus Bay can be classified between scenarios (i) and (ii) yielding methane fluxes ranging between 2.4×10^6 g CH₄ m⁻² year⁻¹ and 5.2×10^6 g CH₄ m⁻² year⁻¹. Global annual methane flux from shallow settings to the water column (defined as areas < 250 m isobaths) is estimated at 1456×10^{12} g CH₄. Dunmanus Bay, by comparison, contributes only between 1.6×10^{-6} and $3.6 \times 10^{-6}\%$. We conclude, therefore, that Dunmanus Bay pockmarks are not an important source of methane on a wider scale.

4.5. Pockmark activity

Detection of active venting is rarely reported in the literature. However, climate change driven warming of the world's oceans may increase the discovery of active seepages in the near future (Skarke et al., 2014). According to current pockmark formation models (e.g. Cathles et al., 2010, Judd and Hovland, 2007), periodic gas expulsion, particularly after initial violent pockmark formation, is typical for most pockmarks and they are considered settings where moderate fluid migration is dominant. Nevertheless, active venting has been reported. Kelley et al. (1994) reported active venting in post-glacial sediments in Belfast Bay, US. Newman et al. (2008) demonstrated methane concentrations reaching 100 nM in pockmarks along the US mid-Atlantic shelf break. Christodoulou et al. (2003) reported both freshwater and gas related active pockmarks systems in the Patras and Corinth gulfs, Greece. In both of these studies the METS sensor (Garcia and Masson, 2004) was used to measure methane concentrations in the water column above and in the vicinity of pockmarks. We have employed the same instrument in Dunmanus Bay and observed that bottom (ca. 5 m above seabed) methane concentrations along the W to E transect (Fig. 1) ranged from 5.1 to 14.2 nM with an average of 9.5 nM. Slightly higher values were consistently recorded in the western part of the pockmark field, however, overall variability of the data is low and the highest concentrations only slightly exceed typical marine water methane values (Holmes et al., 2000). Although acoustic evidence of gas bubbles in the

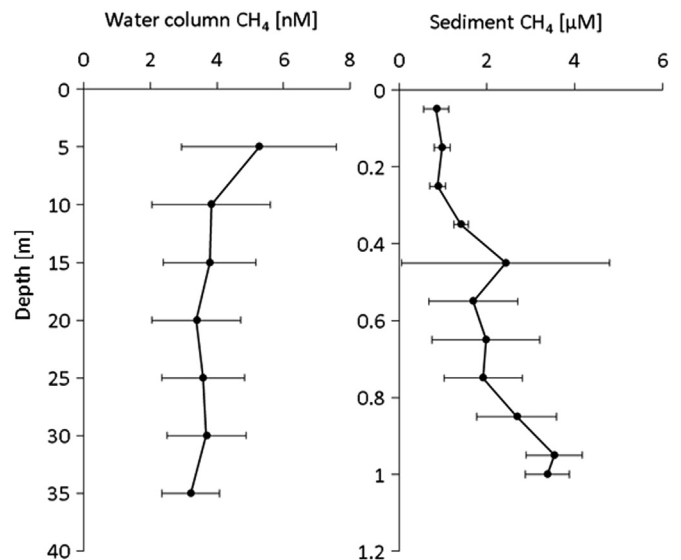


Fig. 8. Average concentration profiles of methane in the water column (casts 3, 8, 14 and 15) and sediment cores (cores 3, 4, 9 and 10). Error bars represent standard deviations between individual profiles. Note that largest variations in sediment cores are observed at the same depths as the sand-enriched layers (refer Fig. 4) (SINGLE COLUMN).

water column was acquired, the methane concentrations in the water column were not significantly elevated. Discrete samples collected across the water column show similar concentrations which ranged from 2.2 to 7.7 nM resulting in very similar concentration profiles (Fig. 8).

Although methane concentrations in the water column were low, despite acoustic evidence of seepage, this is not uncommon in other areas where shallow gas accumulation is observed along with evidence of vigorous venting. Dando et al. (1991) reported methane concentrations from a large active pockmark in the North Sea with only two of six stations exceeding 25 nM. For half of these, methane was below 15 nM. They found higher concentrations exceeding 50 nM only in areas where an echo sounder showed strong signals from gas bubbles in the water column. It is therefore possible that the gas dissipated into the water column and/or the magnitude of the seepage was so low that it was not captured during sampling. This suggests discreet and periodic seepage rather than continuous and that a more targeted approach, with use of instrumentation that can cover a large area and is quick to deploy, would be more appropriate. The bottom water methane concentrations recorded by the METS sensor were slightly higher than those from the head-space analysis but overall they are in good agreement. A gradual decrease in concentrations along the W–E transect was observed ($R^2=0.73$). The highest CH₄ concentrations (14.2, 12.2 and 13.3 nM,) were recorded for the first three stations (03, 01 and 02 respectively) followed by a drop to very low values ranging from 5.1 to 6.6 nM (stations 32 and 13, respectively).

The concentration of methane in the sediment cores (Figs. 4 and 8) shows a general increasing trend with depth. The values range from < 1.0 to 6 µM in the deeper sections. Higher hydrocarbons C₂₊ (mostly C₂) were present in trace amounts. Therefore, the gas can be considered dry and the lack of higher homologues implies microbial origin (Faber and Stahl, 1984; Floodgate and Judd, 1992). In a normal setting where shallow gas is absent, methane generation is only possible after sulphate has been depleted and methane is not present in the sediment above the sulphate depletion depth (Hensen et al., 2003). The sulphate is far from depleted yet methane presence was detected through the entire sediment core. This suggests that the methane is migrating

upward from the AT area observed in the sub-bottom profile (Fig. 5). The in situ generation of methane in the uppermost sediments is a possible contributor to the overall methane pool accumulated in these sediments; however, based on pore water and sediment composition, it is likely to be limited. The optimal conditions in the sediment for methanogens to thrive are: (i) a lack of oxygen, since all known methanogens are strict anaerobes, (ii) sufficient amounts of biologically available organic carbon, typically more than 0.5% (w/w), and (iii) sulphate depletion for competitively centred metabolisms. Nevertheless, methanogens are known to effectively utilise the availability of non-competitive substrates such as methanol and methylamines and thus produce methane even in the outlined geochemical setting (King et al., 1983). The redox potential measurements suggest that conditions in the sediment are indeed anoxic (Fig. 4), though the sediment was not fully reduced (black). This is an interesting finding given that a low redox potential (< 150 mV) marking the beginning of the anoxic zone is usually, however not always, coupled with depletion of sulphate which we did not observe. Nevertheless, given that sulphate is not depleted, the microbial generation of methane is probably limited.

Dunmanus Bay pockmarks are clearly features created by gas expulsion. The acoustic data confirms the presence of shallow, lateral gas accumulation and bubbles in the water column. However, the water column sampling did not provide sufficient evidence that these bubbles are methane gas. Judging from the pockmark size and the acoustic signals in the subsurface, gas venting may be moderate in nature. The pockmarks are relatively small and they are accompanied by scattered, small satellite features which appear to be remnants of past activity rather than the result of recent and active local seepage as suggested by Hovland et al. (2010). Methane concentrations in the water column measured on discrete samples (Figs. 4 and 8) and by the METS sensor show no evidence of the drastically elevated methane concentrations typically observed in sites where vigorous venting takes place.

4.6. Pockmarks and benthic communities

The variety and abundance of marine life associated with seepages can be remarkable across all trophic levels. Dynamic, energetic venting systems are known to support unique ecosystems (see Kiel, 2010 for a review). There is evidence that pockmarks on a smaller scale can support local communities, however, the debate continues (Judd and Hovland, 2007). To examine if local communities from Dunmanus Bay are affected by these features a benthic survey was conducted over the pockmark area (Fig. 1).

Benthic infauna from 10 grab sampling stations within Dunmanus Bay yielded 8865 individuals, which were identified to 122 species across 12 phyla (Station 16 – control; Stations 17 to 41 – experimental). The majority of these species were polychaete worms (57 species), with crustaceans (25), molluscs (13) and echinoderms (8) also well represented. Between stations, the number of individuals recorded from each station always exceeded 382, with a maximum of 1878 individuals, but abundance is not correlated to the number of species (Pearson correlation $r=0.179$, $p=0.62$). See Table 3 for summary of diversity indices.

Four species dominate the assemblages at most stations – the echinoderms *Leptopentacta elongata* (Cucumariidae, Duben and Koren) and *Amphiura filiformis* (Amphiuridae, Muller) and the polychaetes *Diplocirrus glaucus* (Terebellida, Malmgren) and *Scaelibregma inflatum* (Annelida, Rathke) – accounting for 5–17% of the species at each station and 75–92% of the individuals. *A. filiformis* and *D. glaucus* are correlated together (Pearson $r=0.721$, $p=0.019$), both preferring higher silt-clay locations (NS), as were *L. elongata* and *S. inflatum* ($r=0.571$, $p=0.085$). Although non-significant

Table 3

Diversity indices calculated for each biological station in the Dunmanus Bay. Individuals are total counts from five replicates.

ID	Lat	Long	Type	Analysis	Depth [m]	AT depth [mbsf]
39	51.5603	-9.7099	Day grab	PSA, Benthos	42.2	0.0–2.0
22	51.5605	-9.7105	Day grab	PSA, Benthos	42.3	0.0–2.0
21	51.5603	-9.7114	Day grab	PSA, Benthos	42.4	1.5–2.0
20	51.5587	-9.7137	Day grab	PSA, Benthos	43.1	0.0–2.0
19	51.5587	-9.7146	Day grab	PSA, Benthos	43.3	0.0–2.5
18	51.5582	-9.7170	Day grab	PSA, Benthos	43.7	1.5–2.0
17	51.5575	-9.7169	Day grab	PSA, Benthos	43.9	1.0–1.5
16	51.5574	-9.7104	Day grab	PSA, Benthos	42.7	Control
40	51.5613	-9.7096	Day grab	PSA, Benthos	42.1	0.0–2.5
41	51.5576	-9.7157	Day grab	PSA, Benthos	43.7	0.0–2.0
21	51.5604	-9.7119	SPI	SPI analysis	42.5	1.5–2.5
16	51.5576	-9.7100	SPI	SPI analysis	42.6	Control
39	51.5600	-9.7098	SPI	SPI analysis	42.3	1.5–2.5
22	51.5606	-9.7100	SPI	SPI analysis	42.9	0.0–1.0
40	51.5609	-9.7100	SPI	SPI analysis	42.4	1.0–2.0
17	51.5574	-9.7170	SPI	SPI analysis	44.0	1.0–1.5
18	51.5587	-9.7170	SPI	SPI analysis	43.6	1.0–2.0
41	51.5579	-9.7149	SPI	SPI analysis	43.6	No data
19	51.5587	-9.7138	SPI	SPI analysis	43.2	1.5–2.0
20	51.5590	-9.7135	SPI	SPI analysis	43.2	0.0–2.0
3	51.5604	-9.7111	Gravity core	PSA, TC, PW, R, DM	42.5	1.5–2.0
4	51.5605	-9.7097	Gravity core	R, DM	43.0	0.0–1.5
9	51.5581	-9.7163	Gravity core	R, DM	43.8	1.0–1.5
10	51.5585	-9.7145	Gravity core	R, DM	43.4	1.0–1.5
1	51.5570	-9.7167	Carousel WS	CTD, METS	43.9	Inside PF
2	51.5593	-9.7157	Carousel WS	CTD, METS	43.3	Inside PF
3	51.5593	-9.7187	Carousel WS	CTD, METS, DM	43.5	Outside PF
8	51.5593	-9.7138	Carousel WS	CTD, METS, DM	43.1	Inside PF
11	51.5593	-9.7085	Carousel WS	CTD, METS	42.2	Outside PF
12	51.5594	-9.7078	Carousel WS	CTD, METS	42.0	Outside PF
14	51.5593	-9.7115	Carousel WS	CTD, METS, DM	42.7	Inside PF
15	51.5593	-9.7152	Carousel WS	CTD, METS, DM	43.2	Inside PF
31	51.5594	-9.7103	Carousel WS	CTD, METS	42.4	Inside PF
32	51.5593	-9.7070	Carousel WS	CTD, METS	41.8	Outside PF
4	51.5602	-9.7118	Box core	PSA, R	42.6	No data
1	51.5590	-9.7129	Box core	PSA, R	43.7	0.0–1.0
3	51.5596	-9.7123	Box core	PSA, R	42.8	1.5–2.0
15	51.5602	-9.7097	Box core	PSA, R	42.2	1.0–1.5
33	51.5609	-9.7094	Box core	PSA, R	42.2	1.0–1.5
28	51.5613	-9.7093	Box core	PSA, R	42.5	0.0–1.0
32	51.5615	-9.7090	Box core	PSA, R	41.8	2.0–2.5
11	51.5614	-9.7095	Box core	PSA, R	42.0	2.0–2.5
6	51.5611	-9.7105	Box core	PSA, R	42.0	2.0–2.5

trends, the data suggests we should expect strong correlations had a greater number of stations had been sampled. All four species are predominantly deposit feeders utilising the sediment surface to obtain prey, rather than burrowing through it.

Cluster analysis was performed to find the similarity between stations. A multi-dimensional scaling (MDS) plot (Fig. 9) show a low stress ($\sigma=0.05$) value indicating a very good reproduction of the information contained in the distance matrix. Most experimental stations are 50–60% similar in terms of the species composition at these stations, with those spatially closer to each other

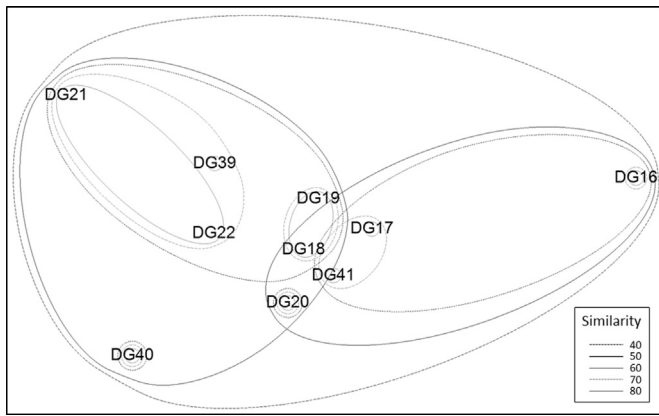


Fig. 9. MDS plot illustrating the degree of similarity between benthic communities in the Dunmanus Bay pockmark field. The reference station (16) is grouped outside of the other stations and shows moderate similarity with the more southerly stations. Stress is $\sigma=0.05$ (ONE and HALF COLUMN).

sharing more species, while the control station only shares a 40% similarity with all the experimental sites and 50–60% with the southern stations. Removing the four dominant species reduced the similarity to 47–71% between experimental stations and 38% to the control, but did not change the overall patterns significantly.

Communities of polychaetes and echinoderms have previously been observed in a North Sea pockmark (Dando et al., 1991), though the species composition differs in that there are few *Amphiura* sp. This composition is not specific to pockmarked regions; Oslo fjord, for example, is also dominated by polychaetes and bivalve molluscs (Webb et al., 2009a), but this is more representative of the regional biota than pockmark. The polychaete and echinoderm mix of infauna in Dunmanus Bay is similar to Killary Harbour, also in the west of Ireland, (Keegan and Mercer, 1986), particularly with regard to the *Amphiura* brittle star community, though *A. filiformis* dominates *A. chiajei* in Dunmanus Bay. Depth stratification between the species is known with *A. filiformis* common above 70 m water depth (Buchanan, 1964). *Scalibregma inflatum* is also common in Killary Harbour, reaching high abundances where the organic carbon levels are greater than 8%. This high organic biomass might be expected from the north-eastern stations given that *S. inflatum* is abundant here, and that such silty, high biomass conditions also benefit the *Amphiura* community (Rosenberg, 2001), but the source of this sediment is unknown given the lack of significant freshwater inputs. Interestingly, despite observing an *Amphiura* sp. community in Dunmanus Bay, no *Echinocardium* were observed though this species occurs frequently with *A. filiformis* (Buchanan, 1964).

The control site has the smallest proportion of the four dominant species as well as lower coarse sediments ($1.6\text{--}3.8 \times$ less coarse material) and higher fine sediment content than any of the experimental sites. Coarser sediments within pockmark centres may be the result of venting (Webb et al., 2009b), if sufficient gas is available to disturb the sediment structure. Equally, bottom currents might be responsible for the accumulation of coarser particles inside of pockmarks, particularly in settings with sufficient input of coarse material such as Dunmanus Bay (Pau and Hammer, 2013). Bottom currents, intermittent scouring or trawling will reduce the diversity of species, which may then take time to recolonise a region (Wildish et al., 2008). The control site also has 27 species unique to this station (22% of the total count), including 12 polychaete species and five molluscs. Contrastingly 45 species, found elsewhere in the study, did not occur at the control site, though 36 of these species are represented by fewer than five individuals across the 9 sites and 28 of them on only one occasion, making their absence at station 16 likely a result of chance.

Sediment structure is likely to have dictated the species composition, as fine sediments tend to increase species diversity in benthic habitats (reviewed by Gray, 2002) and oxygen saturation can also dictate the community composition (Rosenberg, 2001). Mobile echinoderms (such as starfish, brittle stars and holothurians) appear to be common colonisers of pockmarked regions, but abundances within the pockmarks can be lower than surrounding regions (e.g. Wildish et al., 2008). Contrastingly, we observed higher abundances of these species within the pockmark area than in the control site, but this may be dictated by the limited amount of gaseous activity in Dunmanus Bay.

Profiles of the sediment water interface collected with the SPI camera show numerous burrows, mainly vertical but also lateral, voids, and in places infauna (Fig. 10). The images show a substrate of mainly very fine sand with a few patches of coarser sand. Progression of natural geochemical zonation is visible in most profiles in the form of discrete colour change delineating the extent of apparent redox potential discontinuity (aRPD). However, in most images the transition is not sharp (e.g. stations 16, 18, 20) and marked with characteristic dark streaks. This might be indicative of bioturbation and/or bioirrigation given the high count of actively burrowing species. Data from Rosenberg (2001) suggests that the discontinuity would be quite shallow in this area, due to the absence of larger burrowing species and a community dominated by polychaetes and *Amphiura* sp. Overall, the images are generally in good agreement with the redox potential profiles taken on undisturbed box and gravity cores (Fig. 11).

Oxygenated sediment (with typical values $> +200$ mV) is present only in the very top few cm of the sediment. This part of the seabed comprised of photodetrital debris and loose sands, often referred to as 'drift', followed by a fine sand substrate. This was expected as the penetration of oxygen in marine sediments does not usually exceed a few cm and in areas with high particulate matter input from the water column, it can be as low as a few mm or even absent (Cai and Sayles, 1996). The post-oxic zone (with typical values from -150 to $+200$ mV) ranges from a shallow 4 cm to more than 15 cm at most stations and, from the SPI profiles, it is clear that burrowing species greatly affect the homogeneity and extent of this zone. Fully anoxic conditions (typically < -200 mV) are not reached in most stations, which is in concordance with redox and pore water data discussed in previous paragraphs. The only station with fully reduced sediment is station 22, which was located on top of a major pockmark cluster (see Fig. 1, and cluster F in Fig. 3). The aRPD in this profile reaches the sediment water interface but the natural succession is inverted, possibly due to increased infauna activity. Nevertheless, the post-oxic zone in this profile is virtually absent which indicates high organic matter loading. It is this loading which is likely to have dictated the community composition, unsurprisingly as depressions such as pockmarks often act as sinks for detrital matter leading to intensification of diagenetic processes and the rapid consumption of electron donors. However, a sufficiently high flux of methane can also push the redox boundaries towards the sediment water interface (Borowski et al., 1996). Therefore, the effect of rising methane gas cannot be out ruled.

Pockmarked environments can create niches for species with chemosymbiotic adaptations. Dando et al. (1991) identified two chemosymbiotic species from a pockmark in the North Sea. One of these genera, the bivalve mollusc *Thyasira* sp., was found in low abundances at St 20 and 40. This genus, is known to predominantly utilise sulphur-oxidising bacteria for obtaining nutrition, therefore, its presence may indicate the presence of gas seeps at these locations (Dando et al., 1991, Webb et al., 2009a, Wildish et al., 2008). It must be noted, however, that this genus also occurs in organic-rich sediments (Dando et al., 1991) and may also explain its presence in Dunmanus Bay. Other species known to

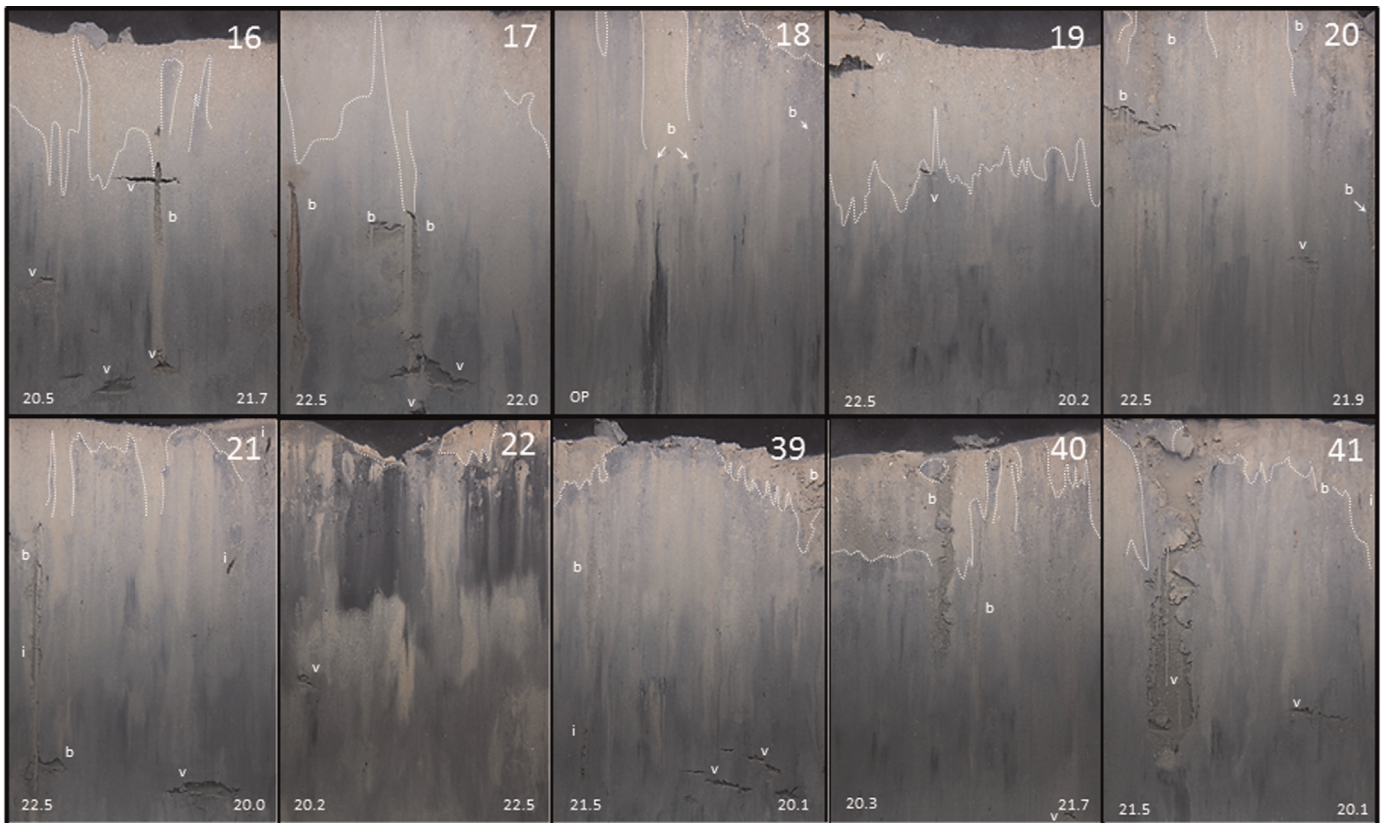


Fig. 10. SPI camera profiles showing the cross sections of the uppermost sedimentary substrate. White dotted lines delineate the apparent redox potential discontinuity (arPD), b – burrows, v – voids, i – infauna. Numbers in the left and right corners denote maximum and minimum penetration, OP – over penetration. For station locations see Fig. 1 (DOUBLE COLUMN).

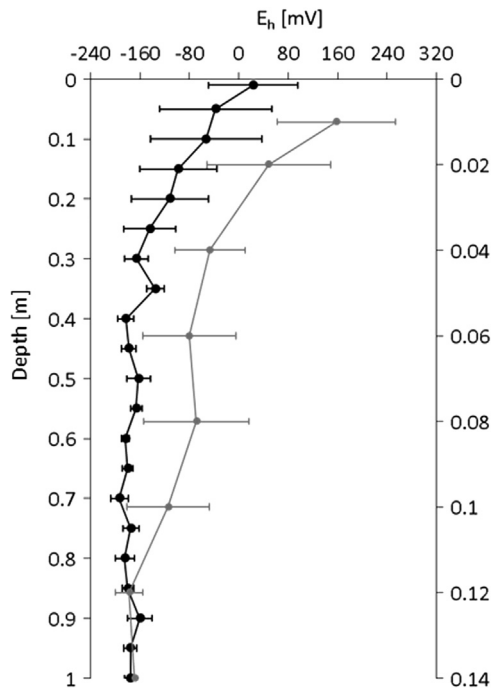


Fig. 11. Averaged redox profiles measured from box ($n=9$, grey line) and gravity cores ($n=4$, black line) collected throughout the Dunmanus Bay pockmark field and illustrating geochemical zonation of the shallow sediments in this setting. Error bars represent standard deviations in the individual profiles (SINGLE COLUMN).

utilise chemosynthetic bacteria or inhabiting reduced environments (e.g. Dando et al., 1991; Jensen et al., 1992; Kiel, 2010; Ritt et al., 2011, Schmaljohann et al., 1990) were not identified from Dunmanus Bay. The lack of species known to be abundant in methane venting settings suggests that the benthic communities observed here do not rely on the intermittent supply of hydrocarbon gas.

5. Conclusions

The survey of the Dunmanus Bay pockmarks revealed gas related features and that an active fluid system is present in the subsurface. The uppermost sedimentary unit in Dunmanus Bay pockmark field is comprised predominantly of fine-grained sediments occasionally mixed with gravel. Pockmark features are only present where silt, clays and fine sands are the dominant substrates though there is acoustic evidence of shallow gas accumulations outside of the field. The shallow gas accumulation is laterally extended and mostly located beneath the pockmark scarred seabed, though the migration pathways are not well defined. The accumulated gas is mainly methane with a very small component of higher homologues. The methane appears to be biogenic in origin but the relative contributions of in-situ versus deep sources were not discerned. The evidence suggests that pockmarks periodically vent accumulated gas in small scale events. The magnitude of the venting and the amount of accumulated methane in the sediments suggests that methane contribution to the water column from the Dunmanus Bay field is minimal and might have only regional implications. The benthic communities were dominated by four common species and overall show structures typical

for the sublittoral environment around Ireland. Organisms frequently encountered in areas with methane gas seepages were not common, indicating insufficient methane concentrations to alter the benthic communities in this setting.

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