Geophysical and geochemical survey of a large marine pockmark on the Malin Shelf, Ireland

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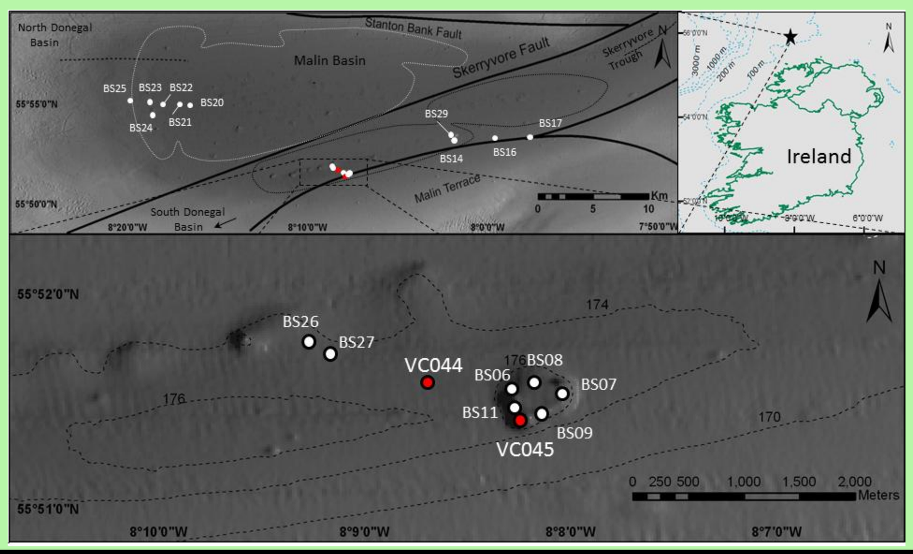
MALIN SHELF SETTING

The Malin Deep pockmark field lies on the Irish continental shelf, approximately 70 km offshore northwest Ireland (Fig. 1). The area lies in a complex structural setting, delimited to the North by the Stanton Banks Fault and to the south by the Malin Terrace. The Skerryvore Fault (SKF), a major normal fault, divides the study area into two different basins, the Donegal Basin and the West Malin Basin (Fig. 1). The Donegal Basin extends parallel to the north coast of Ireland into the area of the Malin Sea with an east-northeast trend. It consists of two different sub-basins. The North Donegal Basin, which is of Paleozoic age, lies to the northwest of the SKF. To the south lies the Donegal Basin, comprised of Permo-Triassic to Jurassic units. West of the SKF, the Malin Basin is dominated by three separate faulted synclines, the Skerrivore Trough, the Malin Trough and the half-graben formed from the western extension of the Colonsay Basin (see Fig. 3 for sub bottom).

Overall, the Malin Sea seafloor is characterized by complex seabed geology with a variety of sediment facies, including recent sand bedforms, gravel lags and coarser clasts ranging in size from pebbles to boulders. However, the basin floor around the pockmark field is characterized by a smooth and soft seabed composed of fine-grained marine sediments, ranging from fine sands to silts. The seabed in the study area contains more than 220 gas related pockmarks distributed in clusters primarily around the main structural lineaments. Large composite pockmarks are predominantly found in a micro-basin south of SKF (Fig. 1).



Hydrocarbons have been encountered in several of the northwest offshore basins, particularly as with thicker permotriassic sequences. Hydrocarbon prospects rely on the existence of carboniferous source rocks, however, Jurassic to Cretaceous source rocks have also been documented in the region. Palaeogene reactivation of fractures may have allowed the leakage of reservoired hydrocarbons to the upper subsurface.

Fig 1. MBES shaded relief bathymetry with sample site location (top panel) and index map with site location (top panel). Despite large scale of the map linear pockmark clusters are clearly visible in the Malin Deep micro basin south of SKF here marked a with black dotted line. Several minor unit pockmarks are visible in the Malin Deep area marked with a dotted light grey line. Detailed sampling site map (bottom panel) shows structural details of targeted composite pockmark.

EVIDENCE OF GAS

Pockmarks are considered surface expressions of seabed fluid expulsion. Although the exact formation mechanisms remain elusive, three types of formation fluids are thought to be responsible for formation of most pockmarks: groundwater springs, hydrocarbon gas and hydrothermal gas. Groundwater discharge was ruled out on the basis of structural constrains as well as pore water chloride concentrations. In the studied setting, chloride concentrations were typical for marine environments and have shown little variability down the cores (data not shown). There we also no significant differences between pockmark core and reference core with chloride concentrations being moderately positively correlated (R^2=0.46).

However, hydroacoustic surveys have revealed pockmark scarred seabed and a presence of shallow gas throughout the entire Malin Deep area. Most of the pockmarks in the Malin Deep area are sub-circular unit pockmarks scattered across the 23000 km^2. However in the micro-basin on the southern boundary of the Malin Deep (Fig. 1) there are several composite features created by repeating venting events. This might indicate that fluids underneath these features reach the seabed more frequently than in other places. Profiler data clearly illustrates a visible gas pocket underneath one of the composite pockmark which was extensively surveyed (Fig. 2).

Multiple gas enhanced reflectors (ER) are observed above the gas pocket just above the gas front characterized by visible acoustic turbidity (AT) followed by acoustic blanking (AB) due to a decrease in the backscatter of the acoustic signal (Fig. 2). These signals mark the impermeable boundary of this shallow gas accumulation. Just above the gas front more discrete, ERs are visible possibly indicating gradual upward migration of gas and accumulation in more gas permeable, coarser sediment layers such as sand lenses or gravel patches. Similar signals are present west of the pockmark where particle size and logging data from vibrocore VC044 confirmed the presence of sandy layers that coincide with the observed lateral ER (Fig 2). Directly underneath the pockmark (P) featureless, mixed sediment is visible, possibly a remnant of pockmark formation, contrary to clear lamination that is visible in sediments in the vicinity of this feature. Moreover, numerous occurrences of vertical acoustic blanking (AB) are present in the surrounding sediments. These signals are likely to be indicative of active fluid migration or fluid related sediment structure alteration, particularly with other evidence of fluid in the subsurface. However, acoustic signal effects such as signal starvation or amplitude blanking cannot be ruled out as AB formation is still poorly understood. Interestingly though, these signals are clearly more abundant above and in the vicinity of igneous intrusions (Dy) which are commonly associated with fluid migration pathways.

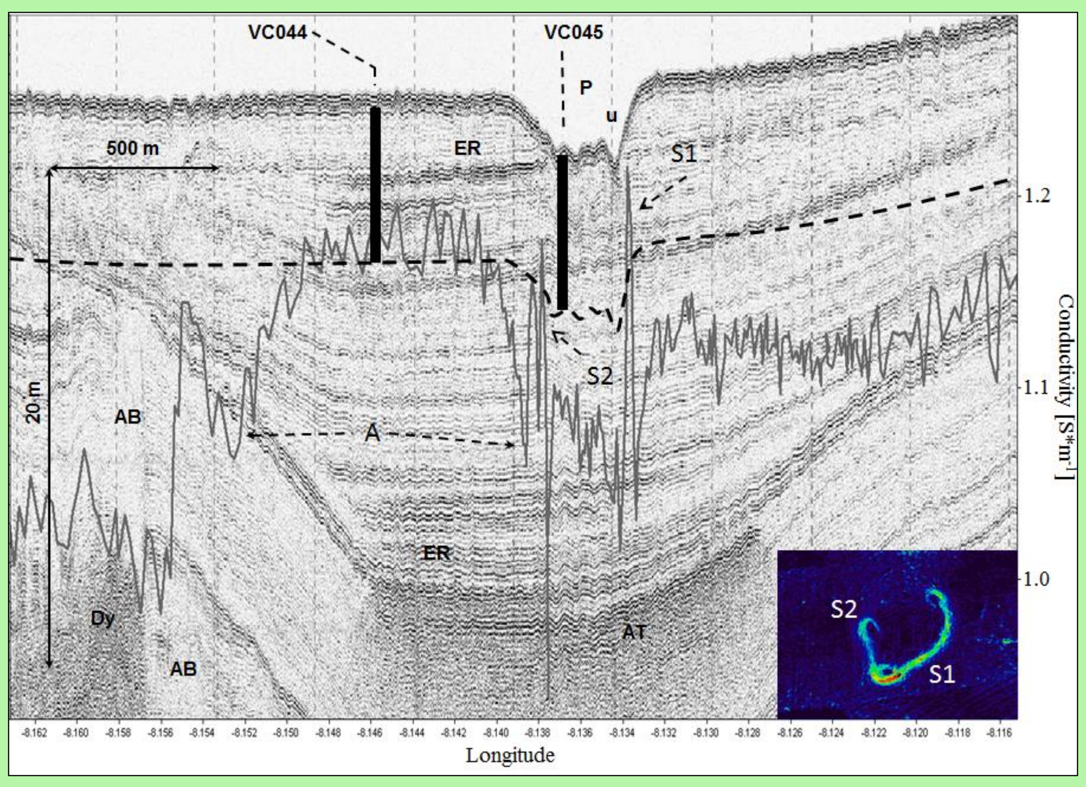
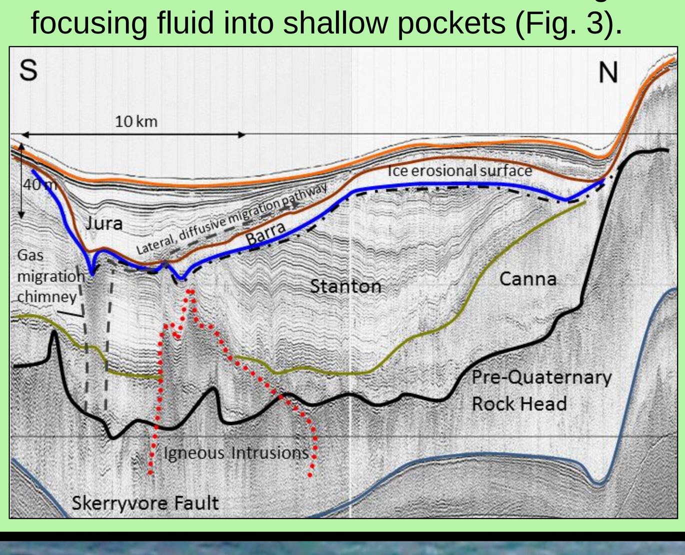


Fig 2. Sub-bottom pinger profile of the composite pockmark (P) in the Malin Deep microbasin with one of the pockmark units (u) visible. The pockmark is 750 m wide with three sub-circular units approximately 50 m wide and 8.5 m deep. Overlayed grey line shows conductivity measurements derived from towed EM system and the dashed black line denotes the depth range for the system. High conductivity values present in both sides of the pockmark (S1 and S2) are associated with disturbed sediment on the edges of the unit pockmarks. The largest conductivity anomaly (A) correlates accurately with the extent of the strong reflector in the sub bottom record associated to gas facies and cannot be explained by changes in sediment structure. Gas enhanced reflectors (ER), acoustic turbidity (AT) and numerous vertical acoustic blanking (AB) signals particularly in the vicinity of igneous body (Dy) are clearly visible. Vertical bold lines depict approximated locations of two 6 m long vibrocores collected at the site, length of the lines is to scale.

Additional evidence of gas is given by the marine electromagnetic survey crossing the pockmark region and imaging approximately the upper 6 m below seafloor. Conductivity measurements are significantly affected by shallow gas pockets and/or gas disturbed sediments (Fig. 2). The presence of gas and changes in sediment porosity is expected to modify the conductivity of the seafloor as gas within the sediment framework will act as an electrical insulator, potentially decreasing conductivity by several orders of magnitude. However, the degree to which the bulk conductivity will be modified by the gas phase depends on several parameters including the gas concentration and how it is distributed between grains. In general, the extent of the gas pocket, as recorded in the sub-bottom profiles, falls in an area of lowered and more irregular conductivity values (and is likely to be the dominant factor responsible for the conductivity minimum in this area indicating migration of gas to the seabed from the underlying gas reservoir).

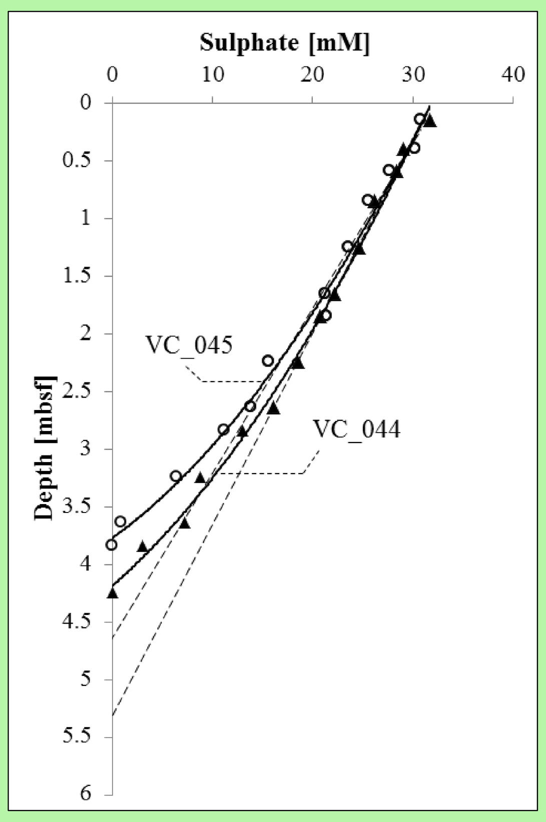
ORIGIN OF THE GAS AND ACTIVITY

The origin of this shallow gas remains unclear although structural features of this setting suggest a deep source. The pockmark spatial distribution is axially correlated with primary and secondary faults and folds. Fluid accumulation facies are present at the base of post glacial, fine-grained Jura formation with evidence of possible lateral migration toward the center of the basin. Historical sub-bottom data suggests that Paleogene igneous intrusions indeed act as natural obstacles for stratified diffusive fluid migration and might contribute to numerous gas accumulations by channeling and focusing fluid into shallow pockets (Fig. 3).



The Malin Deep is a setting with thick fine-grained sediment cover and quite high sedimentation rates ranging from 30 cm/ky to over 130 cm/ky in the last 5 ky. With sufficient flux of organic carbon to the seabed these sedimentological conditions would have favored shallow anoxia and intensive microbial methanogenesis. However, the organic carbon content of the Malin Deep surface sediments does not exceed 0.5% and therefore it appears that without a deep, rich in organic carbon source rocks microbial methanogenesis is likely to be a contributor rather than the dominant source of the Malin Deep gas.

Fig 3. Sub-bottom pinger profile with description of stratigraphy across the Malin Shelf, with acoustic signatures of deep gas migration through the facies associated with the Skerryvore Fault.



Intensive video surveying was also carried out to assess the activity and surface topography of the studied pockmark. We did not record any hard ground outcrops, bacterial mats, increased macrofauna accumulation or obvious seepage in any of the video lines despite several crossings of all of the pockmark sub-units. This is in agreement with the acoustic data and suggests that fluid activity is confined to the sub-surface sediments. Interestingly, pore water sulphate profiles from both cores show a slight concave up curvature (Fig. 4). Both profiles show a clear linear gradient to around 2.7 mbsf with the pockmark core showing a slightly higher rate of sulphate consumption than in the reference core. From around 3.2 mbsf new steeper gradient was observed in both cores indicating more rapid sulphate removal than expected in a stead state scenario. Similarly, the pockmark core gradient is higher than the one in the reference core. Rapid change in depositional conditions and/or upward methane flux, control the shape of the sulphate profiles in settings with a high methane flux derived from intensive methanogenesis as well as deeper. Malin Deep changes in sulphate profiles might indicate that methane from the shallow reservoir (Fig. 2) was migrating upwards and influencing microbial processes in the first few meters of the seafloor and the sulphate-methane transition zone (SMTZ) in particular. Additionally, the flux intensity varies between the pockmark and the reference core. Both profiles show evidence of an increased upward methane flux but in the reference core the flux is 25% lower than directly above the reservoir and results in a deeper SMTZ.

Fig 4. Sulphate concentration versus depth for the pockmark (VC045) and the reference (VC044) cores. Black curves are second order polynomial fits showing non-linear concentration change with depth indicating flux variation. The dashed line depict linear sulphate gradient observed in the first 3 mbsf and the predicted SMTZ depths should the sulphate depletion rate have stayed constant.

MICROBIAL ACTIVITY

Fig. 5 displays the 0-6 ppm region of the ^{1}H NMR spectra from different core depths inside and outside the pockmark. Microbial cells appear to be in abundance, as indicated by the very intense signal from peptidoglycan at 2.03 ppm (N-acetyl functional group) which is a major component in bacterial cell walls. It has been used to estimate bacterial concentrations and can be protected from microbial degradation after cell death by copolymerization reactions and transformation. However, this peak cannot be assigned with certainty from the ^{1}H NMR spectra alone. Alternatively, HMQC NMR spectroscopy provides ^{1}H-^{13}C bond correlations which help resolve overlapping signals from ^{1}H NMR data. Fig. 6 shows the HMQC NMR spectrum of an alkaline extract from inside the pockmark at 6 mbsf. The N-acetyl functional group from peptidoglycan is prominent in this and all HMQC NMR spectra from all depths inside and outside the pockmark.

To further emphasize the strong signature from microbial biomass, diffusion edited (DE) NMR was performed. In DE NMR experiments, small molecules are essentially gated from the final spectrum but signals from macromolecules and/or rigid domains (for example cellular structures) which display little translational diffusion are not gated and appear in the spectrum. The diffusion edited spectra of the four depths from both cores are shown in Fig 7. The presence of aliphatic chains and carbohydrates suggests that they exist in rigid domains or are macromolecular in structure. Peptidoglycan is macromolecular and its resonance peak is extremely strong in all spectra but particularly so outside the pockmark. The organic matter outside the pockmark is dominated by microbial biomass and there is less organic matter obvious from other sources. This is particularly evident when comparing the relative intensities of the peptidoglycan peaks to those in the aliphatic region of the spectra. The microbial signature is not as strong relative to other carbon such as carbohydrates and lipids in the first three depths inside the core. The organic matter from the outside core appears to be strongly associated with bacteria while much of the organic matter inside the core may come from other sources. While there are clear differences in the top three depths between the cores, the DE spectra for the lowest depth (6 m) are again similar. Further evidence of the dominance of microbial biomass is provided by the clear contribution from α-CH units (microbial peptides/proteins) and vertical elongation of the CH_3 band (protein side chains).

Sharp resonances in Fig 5 are consistent with small molecules which can be related to microbial activity in environmental samples. Metabolic activity of microbes is evident on the surface sediment of both cores and is consistent down the outside core profile apart from the deepest sample. However, signs of activity are only detectable on the surface of the inside core and not observed down core suggesting that the activity within the pockmark is considerably decreased. Signatures of microbial activity differ on the surface of both cores indicating that microbial communities may not be the same. Despite the lack of activity within the inside core, there are still strong peptidoglycan signals and an accumulation of aliphatic structures (e.g. lipids). In this case, the microbial signatures may be derived from the cell walls of non-living microbes that are degrading or dormant microbes that are less active than their counterparts from outside the pockmark. This is consistent with the diffusion editing data (Fig. 7), which show microbial signatures in abundance and organic matter from other sources (i.e. potential food sources) depleted outside the pockmark relative to inside. This suggests the microbes outside the pockmark are utilising the organic matter and thus are active, whereas the microbes inside the pockmark are less active as other sources of organic matter have accumulated.

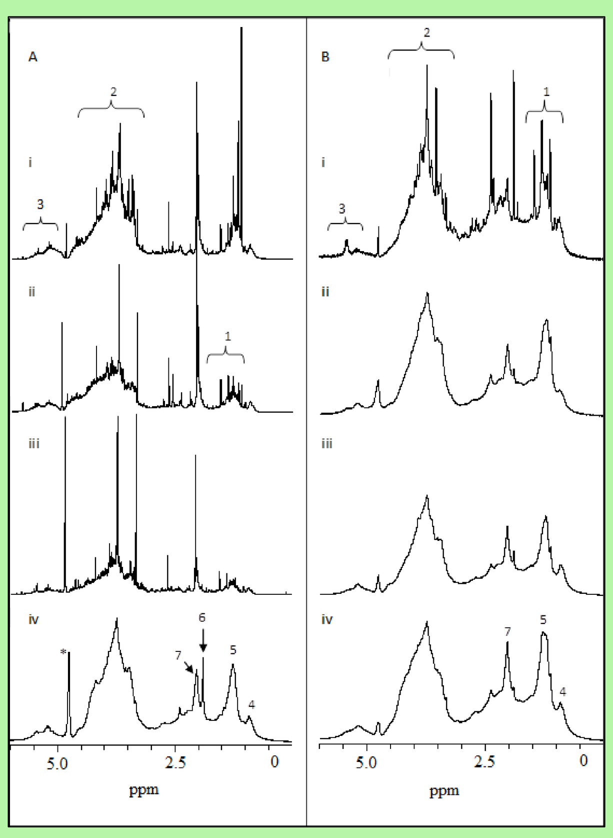


Fig 5. 1D ^{1}H NMR spectra (0-6 ppm) of sediment profiles from outside (A) and inside (B) the pockmark. (i) Surface, (ii) 2 mbsf, (iii) 4 mbsf and (iv) 6 mbsf. Designations 1-3 indicate general spectral regions: 1) aliphatics; 2) carbohydrates and amino acids (O-alkyl) and 3) aromatic carbon. Designations 4-7 indicate specific assignments: 4) aliphatic CH_3; 5) aliphatic methylene $(CH_2)_n$; 6) acetic acid; 7) peptidoglycan. *Residual water.

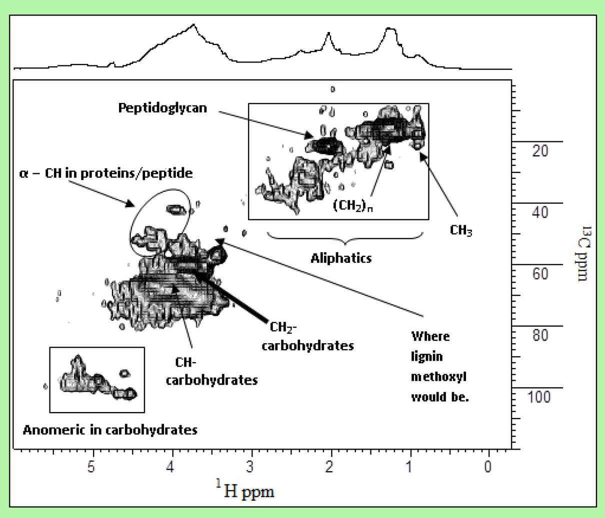


Fig 6. Zoom region of ^{1}H-^{13}C HMQC for sediment extract from inside the pockmark (6 mbsf). The lack of a strong resonance in the methoxyl region indicates that lignin is not a major component of the samples studied here.

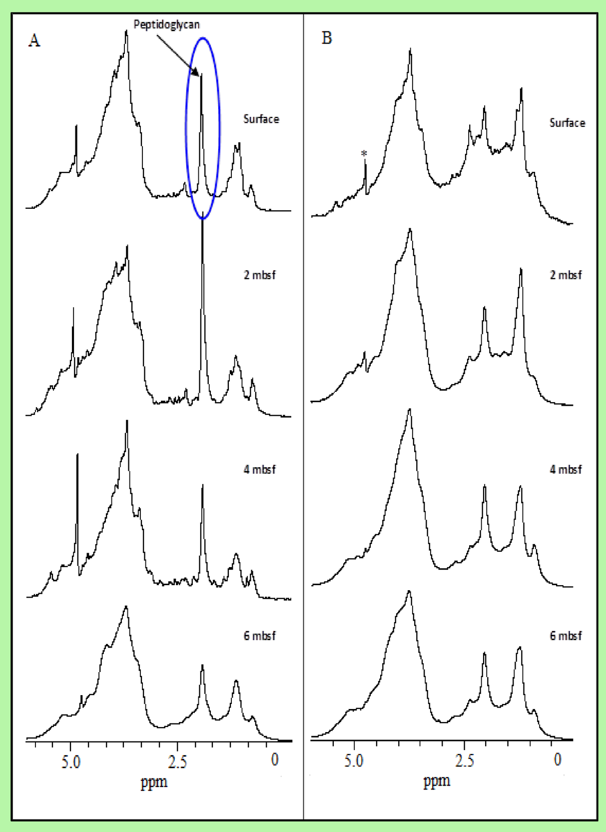


Fig 7. Diffusion Edited ^{1}H NMR of sediment cores from inside and outside the pockmark. Profound peptidoglycan signals are found in the reference core indicating increased microbial presence.

CONCLUSIONS

Gas related acoustic signatures were recorded in the sub-bottom profiles of a large composite pockmark on the Malin Shelf, Ireland. Sub-bottom profiles reveal a relatively large gas pocket approximately 20 meters underneath the pockmark feature, subtle fluid flow vertical signatures and indicators of lateral gas accumulation in the near-seabed subsurface. Despite an abundance of these subsurface gas related signals there was no evidence of seepage to the water column during data acquisition. However, an active fluid system is present and fluid is migrating within the sedimentary body.

Electrical conductivity profiles within the pockmark show anomalous lows attributed to the presence of gas. However, several sharp high conductivity peaks underneath the pockmark and its vicinity are present. One of these peaks can be correlated to high levels of peptidoglycan in the sediment facies. This relationship may be attributed to increased bacterial presence or presence of bacterial necromass.

Sulphate profiles from both sediment cores indicate a recent upward movement of gas. The methane flux is higher underneath the pockmark than in the reference site suggesting that the main migration pathway is partially active and connected to the main gas accumulation reservoir underneath. As a result the SMTZ of the reference core is slightly deeper than the pockmark core.

Microbial activity derived from peptidoglycan NMR signatures shows different levels of activity in gas charged and gas free sediments. The decreased microbial activity within the pockmark may be linked to less available methane within the first meters of sediment as suggested by the presence of reworked sediment. Outside however lateral gas bearing bodies can provide an additional carbon source for microbes and the observed high activity is likely facilitated by access to this source.

For detailed discussion of the results and references see: *Szpak et al, 2012*, G-Cubed 13 (1), DOI:10.1029/2011GC003787