Implications for Petroleum Systems on the deep water Scotian Slope, offshore Nova Scotia based on geochemical and microbiological analyses of piston core samples

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Summary
Geochemical and microbiological methods both indicate the probable presence of petroleum seepage from the subsurface on the deep water Scotian Slope, offshore Nova Scotia. This suggests the occurrence of one or more working petroleum systems in this very poorly explored area. Presently, the age and nature of the source rock for these hydrocarbons cannot be determined.

Introduction
In 2015 and 2016, the Nova Scotia Department of Energy, in collaboration with the Geological Survey of Canada, organized piston-coring cruises on the deep-water Scotian Slope, offshore Nova Scotia. The objective was to look for naturally occurring hydrocarbon seeps that could provide evidence of working petroleum systems in an area that has been little drilled. Hydrocarbon seeps can be detected by satellite imagery and seafloor surface cores. Satellite evidence is often subjective and hence is usually followed up with surface core sampling to provide stronger evidence of actual occurrence. Geochemical analysis of the core samples can differentiate biogenic and thermogenic hydrocarbons and, if the latter are present, potentially identify possible petroleum systems including the age and type of source rock. Microbiological evidence can supplement geochemical data and potentially detect evidence of seepage at locations where geochemical data is not conclusive.

Method
Recovered cores were up to 10 m long but generally significantly less was obtained. Cores were inspected for indications of obvious staining or odour and sandier horizons. A sample was collected immediately from each core near the base for headspace gas analysis. Multiple sediment samples were collected from each core for extraction, ranging from the deepest portion to within about a metre or so of the top of the core, for geochemical analysis, and additionally up to the top of the core for microbiological analysis. Replicate back-up samples were collected at each depth. Gas samples were analysed for their composition and a subset for their isotopic composition. Sediment samples were analysed for their Total Organic Carbon (TOC) content, extracted and the total extract (EOM) analysed by gas chromatography (GC). A subset of extracts was selected for more detailed analysis based on the appearance of their EOM GCs. These samples were analysed by Gas Chromatography – Mass Spectrometry (GC-MS). A few extracts were selected for diamondoid and isotopic analysis. Possible surface slick samples were obtained using an AGI ‘Gore Absorber’. The samples were analysed by AGI using thermal desorption gas chromatography – mass spectrometry (GC-MS). Details on the geochemical methodology and data can be found in Fowler and Webb (2015, 2016). Bacterial community compositions were determined on triplicate sediment samples from the top few centimetres of the cores, as well as in deeper samples down to 10 m depth. Community composition was determined through 16S rRNA gene amplicon libraries.
on an in-house Illumina MiSeq sequencer coupled to in-house bioinformatics using the MetaAmp sequence analysis platform (Dong et al., 2017).

Examples

During the 2016 cruise, gas hydrates were encountered for the first time on the Scotian Slope, at three separate sites. At two of these locations, the methane in the hydrate had a biogenic origin (Sites 48 and 49, Fig. 1). The composition and isotopes of the gases at the third site (site 41, Fig. 1) indicated a thermogenic oil associated gas based both on its composition (i.e. its wetness) and isotopes (e.g. $\delta^{13}C_1$ values between -42.2 and -49.0‰). Sediment samples from this site have Extractable Organic Matter Gas Chromatograms (EOM GCs) that show high amounts of lighter hydrocarbons over the nC$_{15}$-nC$_{20}$ alkane range including an unresolved complex mixture (UCM). Shallower samples show a larger UCM with n-alkanes in lower abundance relative to isoprenoids such as pristane and phytane, suggesting biodegradation is occurring in the shallow seabed. Samples from site 41 also show a higher relative abundance of thermally mature biomarkers compared to biologically inherited isomers which dominate in most samples. This sample also contains a higher concentration of diamondoids than other samples.

Site 41 appears to provide the best evidence to date for working petroleum system and oil-prone source rock on the deep water Scotian Slope. Unfortunately, the age and other details of the source rock cannot be determined at this time.

Piston coring at one of the two sites (site 49) with biogenic gas hydrates appeared to initiate a minor oil seep. This seep was sampled and of the slick samples collected showed the best evidence of being weathered petroleum. However, it shows very different biomarker characteristics to the sediments collected at the associated piston coring site and remains an enigma.

Indications of thermogenic gas and/or sediments with possible petrogenic hydrocarbons were observed at a number of other sites. Site 32 (Fig. 1) showed no evidence for thermogenic gas but had sediment extracts that were dominated by hydrocarbons with high abundances of C$_{15}$-C$_{20}$ n-alkanes and biomarkers with more mature characteristics than shown by other samples. A sample from this site had the second highest concentration of diamondoids after site 41. Site 32 appears to show evidence for an oil seep that is not associated with thermogenic gas. In contrast, a site from the south west of the area, site 4 (Fig. 1) had a headspace gas containing only methane with a $\delta^{13}C_1$ of -47‰ that implies it has a thermogenic origin. However, there was no evidence for petrogenic hydrocarbons in the sediment samples. Other sites show an enhanced abundance of lighter hydrocarbons like sites 41 and 32, but without supporting biomarker evidence for thermogenic hydrocarbons. It is possible that these could be hydrocarbons derived from a late mature source rock, or a source rock such as the Upper Jurassic on the Scotian Shelf that generates gas and condensate rather than black oil.

DNA sequencing revealed that sites that showed geochemical anomalies for the presence of hydrocarbons had higher relative abundances of sequences affiliated with the phylum Atribacteria. This was particularly true at site 41, mentioned above. Atribacteria is a poorly understood group that is only known from DNA sequencing surveys and not culture-based physiological studies. Atribacteria are common in deeper sediments, and were ubiquitous in the deeper (>1m) layers of the sediments sampled in this study. However, one particular sub-group of these Atribacteria was prevalent in the surface sediments at the sites with geochemical anomalies for hydrocarbons, suggesting that these bacteria (and its associated genomic marker sequences) can serve as biomarkers offering an additional line of evidence in petroleum seep prospecting on the Scotian Slope.

Conclusions

Overall, there is good evidence, both from geochemistry and microbiological methods, for a working petroleum system in the deep water Scotian Slope area of offshore Nova Scotia. A number of piston coring sites over a wide area (Fig. 1) show evidence for the presence of hydrocarbons that have migrated from the deep subsurface. This implies one or more source rocks with wide areal extent. The results from site 41 imply a source rock that can generate liquid hydrocarbons at least in this area. Results from other sites could suggest either a more mature source or one that generates mostly lighter...
hydrocarbons. The age and nature of the source rock(s) for the petrogenic hydrocarbons cannot be
determined.

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Figure 1 Map showing location of 2015 and 2016 piston coring sites offshore Nova Scotia, and indicating
which sites show evidence of possible oil and gas seepage. There is still a degree of uncertainty about
the occurrence of petroleum seepage at most sites. Only site 41 shows unequivocal evidence of
seepage.