REPORT ON GEOCHEMICAL ANALYSES OF PISTON CORED SAMPLES, OFFSHORE NOVA SCOTIA

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Sampling sites for piston-coring were carefully selected based on satellite and seismic data. Unfortunately, many of the sites predicted to have the highest chance of showing evidence of the seepage of thermogenic hydrocarbons could not be sampled because of equipment malfunction on the CCGS Hudson. This prevented sites in water depths greater than 2500 m from being sampled for most of the cruise. Samples were collected from twenty five sites with only one site (#6) from a water depth greater than 2500 metres.

Three sites show evidence of gas when sampled (sites 5, 6 and 9) and these were the only three sites where C_2-C_4 gases were detected by head space gas analysis, although in low concentration compared to methane. Only very low concentrations of methane were present in samples from other sites. Samples with higher concentrations of hydrocarbon gases were selected for isotopic analysis, although only 6 samples from 5 core samples had sufficient hydrocarbons to get data from. As indicated on Figure 1, in samples which only contain methane, the methane has a biogenic origin. Samples from sites 6 and 9 which have the highest amount of C_2-C_4 gases (lowest dryness values) show isotopically the most evidence for their methane having a mixed biogenic-thermogenic origin ($\delta^{13}C$ -60.8 to -68.6‰). The sample from site 5 which contains a small amount of ethane besides methane has an intermediate methane $\delta^{13}C$ value of -84.6‰, possibly indicating a small contribution of thermogenic methane. Hence the gas data from sites 6 and 9, and possibly 5, are considered indicators of possible thermogenic hydrocarbon seeps at these locations.

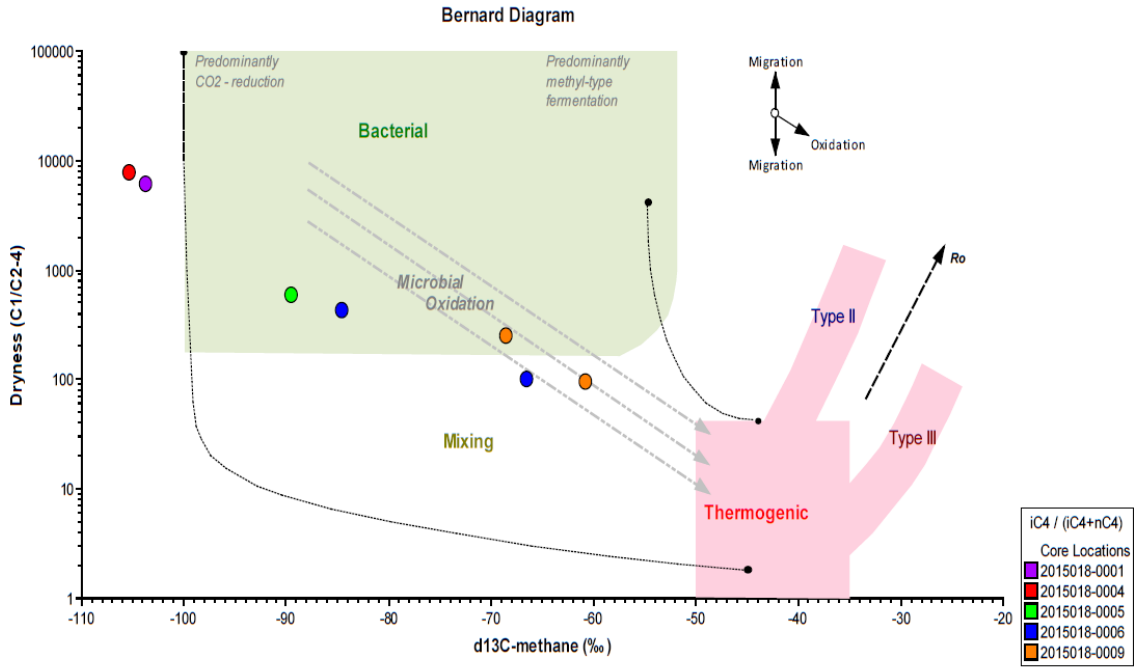


Figure 1. *Plot of Methane Carbon isotopic value versus gas dryness displaying the possible mixing of thermogenic and biogenic methane in samples from sites 6 and 9. Note in order to be able to plot the pure biogenic gas samples from sites 1 and 4 on this figure, they were given a very low ethane concentration of 1 mole%.*

The total extracts obtained after ultrasound extraction of the eighty six sediment samples were analysed by gas chromatography (GC). Almost all the GCs show abundant C_{23}-C_{33} n-alkanes with an odd carbon number preference indicating an origin from recent higher land plant material and not related to thermogenic seeps. A plot of nC_{17}/nC_{27} versus nC_{19}/nC_{29} GC-EOM peak areas is often used to indicate potential seeps with the assumption that samples with more mid-weight n-alkanes (nC_{17} and C_{19}) are more likely to have a thermogenic origin. However, this did not correlate with gassy cores and those showing possible indications of thermogenic gases. Eighteen samples, as well as the drilling grease, were selected for GC-MS analysis of their combined saturate and aromatic hydrocarbons based on the gas data and the proportion of mid-weight hydrocarbons. Almost all the samples gave very similar results of biomarker distributions dominated by low maturity biogenic compounds with small amounts of more thermally mature compounds with very similar characteristics. This suggests that the thermogenic hydrocarbons are an artifact rather than derived from petroleum seepage. The 2.00-2.06 m sample from core 9 shows a much higher abundance of petrogenic hydrocarbons with very different and more mature distributions compared to the other samples. This is evident from Figure 2 which shows the relative distributions of C_{27}-C_{29} regular steranes and shows that the core 9 sample has a much

lower relative abundance of C_{29} steranes than the other samples, as well as differing from the drilling grease sample (which also contains oleanane not found in the core 9 sample). It also shows other different biomarker characteristics including a much higher abundance of tricyclic terpanes, and a high abundance of rearranged steranes and hopanes compared to their unrearranged counterparts. This would appear to support the gas isotopes that site 9 may contain thermogenic hydrocarbons derived from petroleum seepage. A second sample from site 9 (2.97-3.02 m depth) does not show strong evidence for the presence of petrogenic hydrocarbons although there are some indications that they may be there in small amounts (e.g. Fig. 2). This may be evidence that the hydrocarbons in the 2.00-2.06 m sample are an artifact but may reflect the sandier nature of the 2.00-2.06 m sample. Biomarker distributions for samples from core 6, which also shows isotopic evidence for possible thermogenic gases, do not indicate a petrogenic contribution.

If the hydrocarbons in the core 9 2.00-2.06 m sample are truly representative of a petroleum seepage, then their sterane carbon number abundance of 50:21:29 for the C_{27}-C_{29} steranes, the very low abundance of C_{30} 4-desmethylsteranes, and high abundance of rearranged steranes could suggest a source rock dominated by algal organic matter deposited in a non-marine clastic environment, possibly lacustrine. It should be emphasize that this is very much a tentative conclusion at this time.

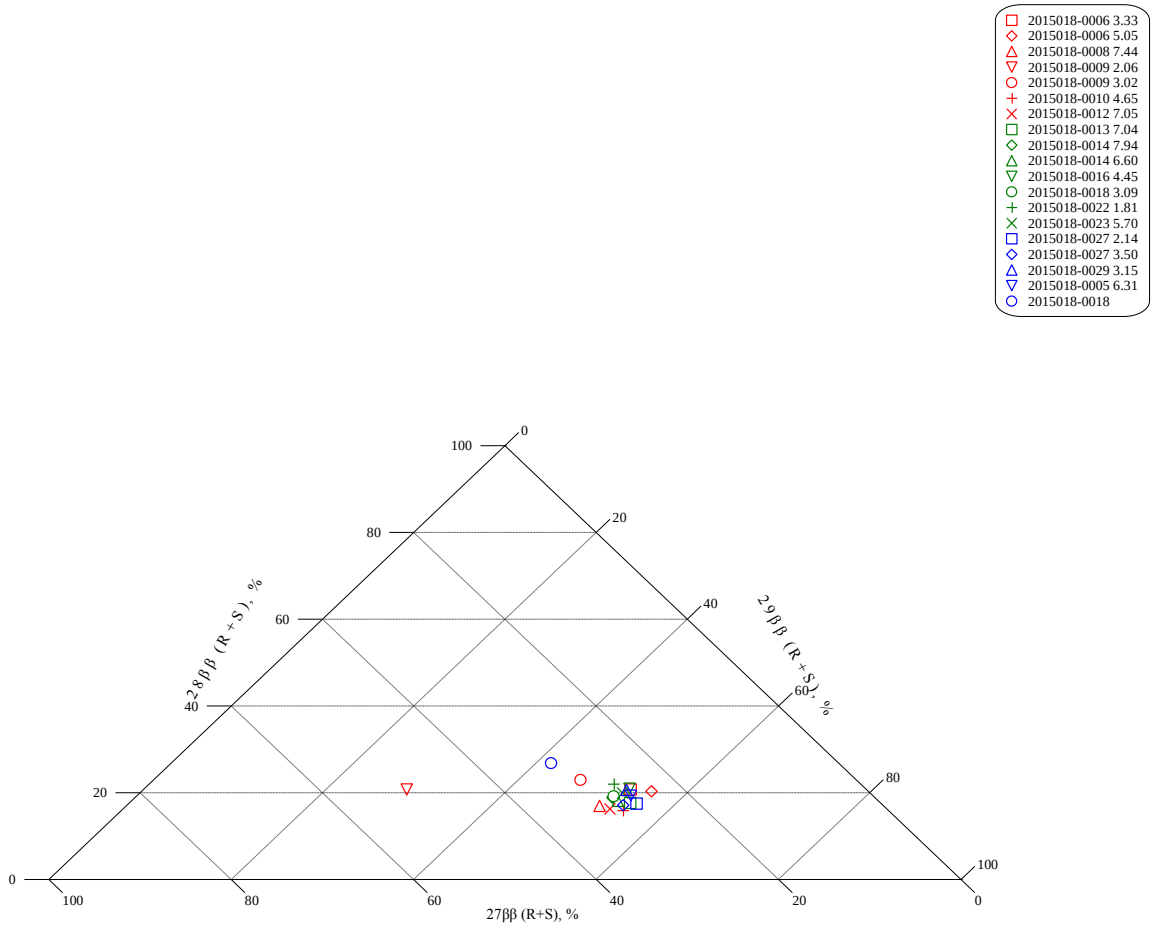
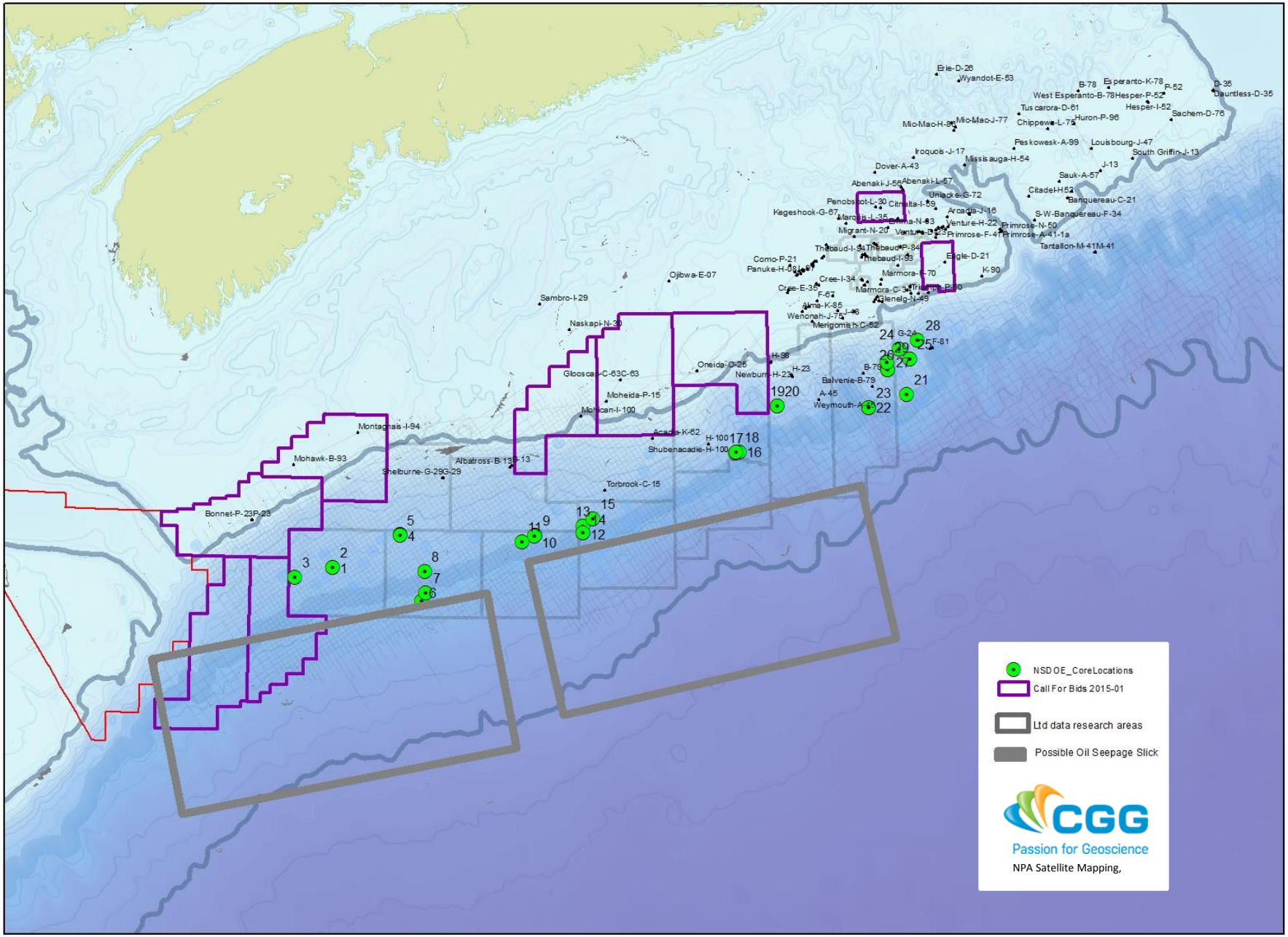


Figure 2. *Relative abundance of C_{27}-C_{29} αββ steranes in samples analyzed by GC-MS. Note the 2015018-0018 sample is drilling grease.*

Observed surface slicks were sampled using a Gore Sorber from the deck of the CCGS Hudson at three locations, with duplicate samples taken at one location. Slick samples went to Amplified Geochemical Imaging in Delaware for quantification of n-alkanes and isoprenoids by gas chromatography (GC) and biomarker identification by gas chromatography-mass spectrometry (GC-MS). The concentration of hydrocarbons in the four samples was too low to represent a surface hydrocarbon seep. The height of the CCGS Hudson above the slick, combined with the wind and wave conditions of the sea and the inability to launch a smaller vessel under these conditions were responsible for reduced control in slick sampling, and therefore, the low hydrocarbon concentration in the analysed samples.

In summary, based on present geochemical data there seems to be good evidence for petrogenic hydrocarbons at Site 9 and possibly at Site 6.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Wyandot-E-53
B-78
Esperanto-K-78
P-52
D-35
West Esperanto-B-78
Hesper-P-52
Dauntless-D-35
Hesper-I-52
Tuscarora-D-61
Sachem-D-76
Huron-P-96
Chippewa-L-75
Mic-Mac-H-86
Mic-Mac-J-77
Louisbourg-J-47
Iroquois-J-17
South Griffin-J-13
Mississauga-H-54
J-13
Dover-A-43
Sauk-A-57
Abenaki-J-56
Abenaki-L-57
Citadel-H-52
Uniacke-G-72
Banquereau-C-21
Penobscot-L-30
Kegeshook-G-67
Marquis-I-35
Arcadia-J-16
S-W-Banquereau-F-34
Migrant-N-20
Venture-H-22
Primrose-N-50
Primrose-F-41
Primrose-A-41-1a
Tantallon-M-41
Thebaud-I-94
Thebaud-P-84
Como-P-21
Panuke-H-08
Eagle-D-21
K-90
Ojibwa-E-07
Cree-I-34
Cree-E-38
Marmora-C-34
F-67
Alma-K-85
Wenonah-J-75
Merigomish-C-52
Sambro-I-29
Naskapi-N-30
Oneida-O-25
Newburn-H-23
Glooscap-C-63
Moheida-P-15
Mohican-I-100
Montagnais-I-94
Mohawk-B-93
Albatross-B-13
Shelburne-G-29
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Bonnet-P-23
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