

Preliminary Geochemical Interpretation of Preserved Shallow Cores, Labrador Basin Complex, Labrador Sea, Canada

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Summary

Amplified Geochemical Imaging technology (Anderson, 2006) was utilized to geochemically sample shallow sea bottom cores for the presence of hydrocarbons at nanogram (10^{-9}) levels. To date, this

technology has been tested and successfully used on fresh core material (Abrams and Dahdah, 2011), but it had not been attempted on archived material.

To that end, an extensive archive of ocean seabed core samples exist for the east coast of Canada collected over a period from 1965 to present. The cores are stored at the Geological Survey of Canada at the Bedford Institute of Oceanography in Dartmouth, Nova Scotia.

170 cores were selected by Nalcor Energy Oil and Gas as a pilot program to perform geochemical sampling from select areas off the coast of Newfoundland and Labrador. The objective was to determine if there are indications of petroleum hydrocarbons on any of the cores.

The cores selected for study were selected from sealed and refrigerated material collected over the last 11 years on the assumption that these were the most likely cores to retain significant geochemical signature. Results from this pilot study are encouraging, prompting Nalcor Energy Oil and Gas to expand the study into other areas, and investigate the use of older core material.

Introduction

The Labrador Sea, located in the northern region of offshore Newfoundland and Labrador, Canada, is one of the largest under-explored areas along the eastern Canadian Margin. Numerous vintage 2D seismic surveys have been acquired over the past 50 years, and 29 wells have been drilled on the Labrador Shelf from the 1970's through the 1980's. Since that time there has been a hiatus of exploration in the region, until the summers of 2011 and 2012, when 40 000 line kilometers of new, long offset 2D seismic data were acquired by TGS-NOPEC over the shelf, slope and deep water of the Labrador Sea.

As a complement to the seismic data acquired, various other studies have been undertaken and used in pre-drill exploration of this area. One such study is the Shallow Core sampling project.

To that end, consideration was given to extracting new information from an extensive archive of ocean seabed core samples that exists for all areas of the east coast of Canada. These cores have been collected over the last 50 years and are stored at the Geological Survey of Canada-Atlantic at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia.

This study used 83 Labrador Sea area cores as part of a broader pilot study of 170 cores selected by Nalcor Energy Oil and Gas. These cores were all collected in the last 11 years for regional surficial geology and geohazard studies and are stored in sealed plastic sleeves under refrigerated conditions (4°C) at GSC-Atlantic.

The aim of this study was to test a geochemical sampling technique with the objective of determining if there are useful indications of petroleum hydrocarbons within any of the archived cores. Using the Amplified Geochemical Imaging technology from W. L. Gore & Associates, hydrocarbon signatures in the nanogram range have been identified. When plotted spatially, these signatures correlate with seeps, identified from satellite observations and hydrocarbon chimneys, seen on the recent 2D seismic acquired in the Labrador Sea.

Theory and/or Method

The primary purpose of the evaluation was to assess whether properly stored core material had sufficient amounts of organic compounds to be instructive for the indication of petroleum hydrocarbons. Additionally, as a secondary objective, it would be helpful if these data would reveal any statistical significance to the distribution of these organic compounds, should there appear to be sufficient amounts.

Each core was sub-sampled and a small amount (approximately 60 cc) of the core material placed in a clean jar with sensitive adsorbents (Gore Modules), which would acquire a sample of the volatile and semi-volatile organic compounds over the course of a 20-day exposure. All sampler analyses are

accompanied by instrument calibration samples for all compounds on the analytical list of this method (Table 1). In addition, several classes of quality control blank samples are included for analysis with the field samplers of this project. As an aggregate, quality control and instrument calibration samples constitute about 40% of the samplers analyzed for this survey.

Table 1: Analytical Compound List by Compound Class

Typical Petroleum Constituents			
<i>Carbon number in ()</i>			
Normal Alkane: 17 compounds Ethane (2) Propane (3) Butane (4) Pentane (5) Hexane (6) Heptane (7) Octane (8) Nonane (9) Decane (10) Undecane (11) Dodecane (12) Tridecane (13) Tetradecane (14) Pentadecane (15) Hexadecane (16) Heptadecane (17) Octadecane (18)	Iso-alkane: 11 2-Methylbutane (5) 2-Methylpentane (6) 3-Methylpentane (6) 2,4-Dimethylpentane (7) 2-Methylhexane (7) 3-Methylhexane (7) 2,5-Dimethylhexane (8) 3-Methylheptane (8) 2,6-Dimethylheptane (9) Pristane (19) Phytane (20)	Cyclic Alkane: 15 Cyclopentane (5) Methylcyclopentane (6) Cyclohexane (6) cis-1,3-Dimethylcyclopentane (7) trans-1,3-Dimethylcyclopentane (7) trans-1,2-Dimethylcyclopentane (7) Methylcyclohexane (7) Cycloheptane (7) cis-1,3/1,4-Dimethylcyclohexane (8) cis-1,2-Dimethylcyclohexane (8) trans-1,3/1,4-Dimethylcyclohexane (8) trans-1,2-Dimethylcyclohexane (8) Ethylcyclohexane (8) Cyclooctane (8) Propylcyclohexane (9)	Aromatic and PAH: 17 Benzene (6) Toluene (7) Ethylbenzene (8) m,p-Xylenes (8) o-Xylene (8) Propylbenzene (9) 1-Ethyl-2/3-methylbenzene (9) 1,3,5-Trimethylbenzene (9) 1-Ethyl-4-methylbenzene (9) 1,2,4-Trimethylbenzene (9) Indane (9) Indene (9) Butylbenzene (10) 1,2,4,5-Tetramethylbenzene (10) Naphthalene (10) 2-Methylnaphthalene (11) Acenaphthylene (12)
Byproduct and Alteration Compounds			
<i>Included in this method to provide a comprehensive inventory of the geochemical system in the surface soil zone</i>			
Alkene: 10 Ethene (2) Propene (3) 1-Butene (4) 1-Pentene (5) 1-Hexene (6) 1-Heptene (7) 1-Octene (8) 1-Nonene (9) 1-Decene (10) 1-Undecene (11)	Alteration/Byproduct: 3 Octanal (8) Nonanal (9) Decanal (10)	Biogenic: 4 alpha-Pinene beta-Pinene Camphor Caryophyllene	Nitrogen/Sulfur/Oxygen Compounds: 9 Furan 2-Methylfuran Carbon Disulfide Benzofuran Benzothiazole Carbon Dioxide Carbonyl Sulfide Dimethylsulfide Dimethyldisulfide

All geochemical samplers were analyzed after the exposure period to the seabed material. Analysis was accomplished using gas chromatography – mass spectrometry (GC/MS), for a range of hydrocarbon compounds from ethane (C2) to octadecane (C18), but also including pristane (C19) and phytane (C20).

Several methods of data processing were used to evaluate the geochemical information provided by these samples.

- A linear discriminant analysis was used to qualify the data with regard to gross geochemical response in order to determine if the samples exposed to the sediment core material have acquired a unique signature.
- A summation of several classes of compounds was charted and used to identify those samples that contain an abundance of normal alkanes relative to the other samples. This exercise also shows the differences in mass response from QA/QC samples as compared to the core samples.
- A Hierarchical Cluster Analysis (HCA) was performed on the qualified samples and four primary groups of samples were identified, which categorize the samples according to their geochemical composition.
- The samples were divided into three primary groups (assigned by geographic regions), and an HCA evaluation was performed on each area to try and assess which samples have the greatest probability of expressing a petroleum accumulation.

Examples

The samples from the Labrador area were isolated from the overall pilot study and processed via HCA in order to evaluate the geochemical compositional differences among the samples in this area.

Figure 1 shows the HCA dendrogram output for the Labrador samples. The samples that appear to be most prospective for hydrocarbon accumulations have been color-coded red, and non-prospective samples grey.

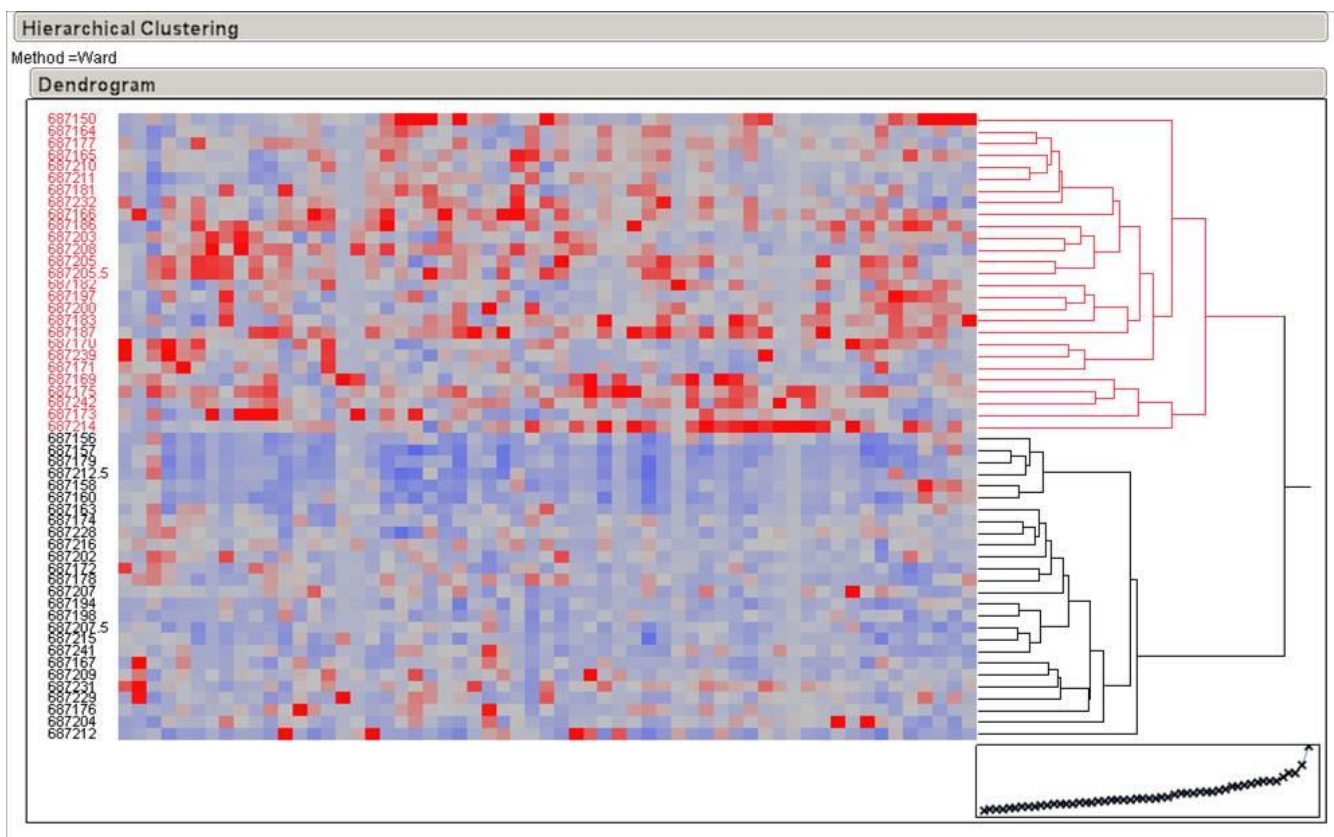


Figure 1: HCA Dendrogram of the samples from the Labrador area

Figure 2 illustrates the geographical distribution of this same sample set, using the same colour scheme.

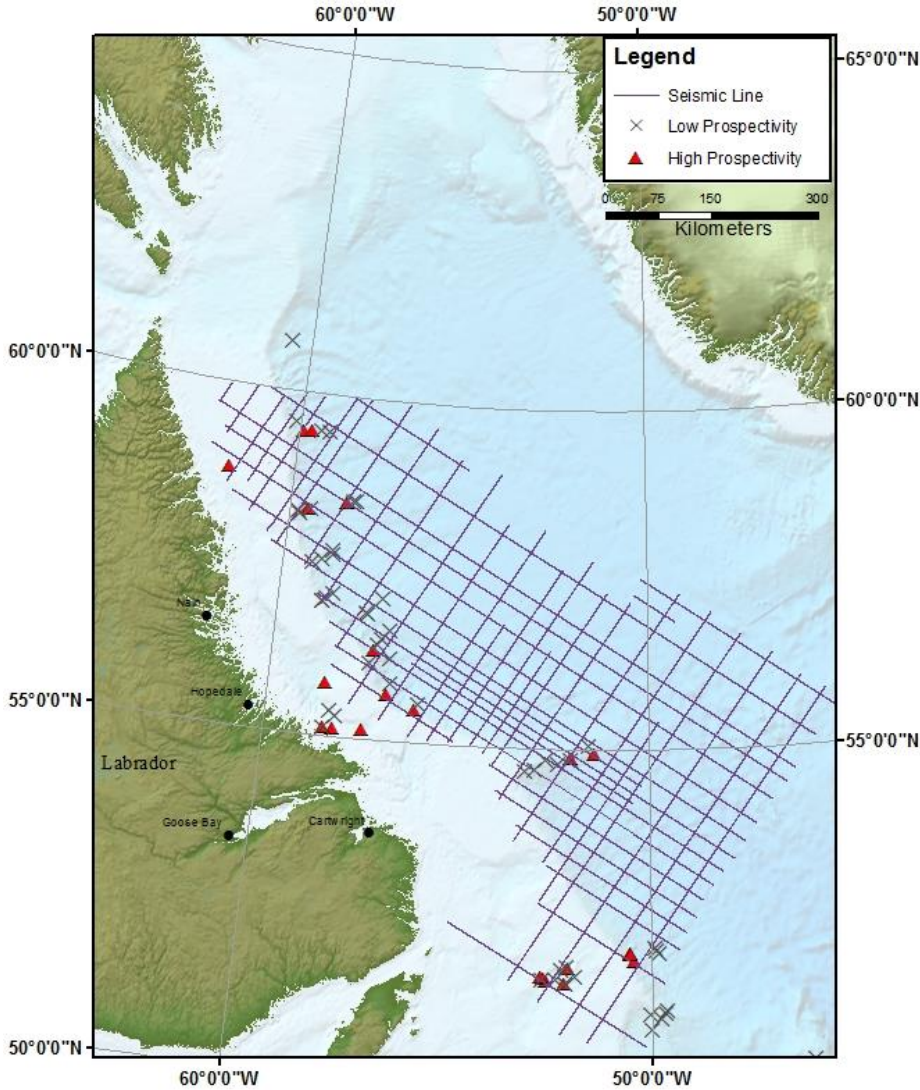


Figure 2: Spatial distribution of samples as color coded from the HCA Evaluation, in Figure 1 (Prospective: red triangle; Non-prospective: grey X)

While care must be taken with the interpretation and use of any single data set, the cores that suggest possible hydrocarbon accumulations do show positive correlations with recently acquired seismic and satellite seep data in the Labrador Sea area.

Comparison of geochemical results with host sediment type shows that most samples are from muds ultimately derived from crystalline basement in Labrador. Carbonate-rich intervals derived from Paleozoic rocks of Hudson Strait and Bay do not have systematically different geochemistry. This suggests that the geochemical signature is not detrital, but results from upward seepage of hydrocarbons.

Conclusions

This study has shown that the preserved core samples exposed to hydrocarbon microseepage have acquired and retained a unique signature, which is not a function of any manufacturing or analytical artifact, and which is derived from the sample exposure to the core material. This answers the primary objective of this evaluation whereby it appears that properly stored core material can yield a meaningful organic signature, even after 11 years of storage. These encouraging results have led to planning of a larger and more comprehensive follow on study, covering larger areas, and testing older core material, as well as integration with seismic and seep data to highlight petroleum potential over the shelf, slope and deep water, offshore Labrador.

Acknowledgements

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References

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