

# Molecular and Isotopic Study of Bitumens from the Alberta Oil Sands

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## Summary

Molecular and isotopic analyses of oil samples from Athabasca, Peace River and Cold Lake oil sands reservoirs in Alberta, Canada, were conducted to evaluate the effect of biodegradation processes on the molecular and isotopic compositions of these oils. The results indicate that all studied samples are affected by biodegradation to different degrees. Based on the molecular composition, the levels of biodegradation range from at least PM5 to PM8 in Athabasca, PM5 to PM6 in Peace River and PM4 or lower at Cold Lake. Increasing levels of oil biodegradation from top to bottom of the oil columns was observed everywhere. Biodegradation does not cause observable systematic carbon, nitrogen or sulfur isotope changes vertically in whole bitumen columns; however, some <sup>32</sup>S-enriched oils found locally may reflect secondary sulphur incorporation related to local microbial activity. Major differences in the sulfur and nitrogen isotopic composition of oils across the province are suggested to be source rock related.

## Introduction

The Alberta oil sands are sands saturated with heavily to severely biodegraded oil, where Lower Cretaceous unconsolidated sandstone pools host more than 1.3 trillion barrels of heavy and extra heavy oil. Variations in composition and oil properties are common across the basin. Regional variations are caused by different maximum reservoir burial temperatures, mixtures of charged oils and some oil maturity variations (Adams et al., 2006; Larter et al., 2008). Locally, within a single reservoir, biodegradation level increases with reservoir position have been observed. Different gradients have been explained by proximity to the water leg, height of the water leg and the relation between fresh oil input and biodegradation rate (Larter et al., 2008); hence these oil sands constitute an interesting location for studying biodegradation processes.

Molecular analysis of oil is a powerful tool in determining biodegradation levels, which can be estimated in different ways. In this work, the biodegradation scale of Peters and Moldowan (PM) (Peters and Moldowan, 1993) is used for establishing the level of oil alteration based on the interpretation of molecular data. Stable isotope measurements are used for determining sources of C, N and S, and the occurrence of different processes in subsurface environments. Considering that biochemical reactions related with biosynthesis and biodegradation are often kinetically controlled, isotopic fractionation may potentially occur during biodegradation of oil. The extent of isotope fractionation may provide information about the biodegradation mechanisms. In addition, the isotopic composition of nitrogen may provide additional information about sources of nutrient input to the petroleum biosphere. The aim of this study is to evaluate molecular and isotopic variations in biodegraded bitumens from the Alberta oil sands.

## Methods

The sample set consisted of core samples and produced oils from the three major oil sand accumulations in Alberta: Athabasca, Peace River and Cold Lake. Prior to isotopic and molecular analyses, the bitumen was extracted from the oil sand samples using soxhlet extraction, with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). For molecular investigations, the total hydrocarbon fractions were isolated following de-asphalting of the bitumen and heavy oil samples. Quantitative GCMS analysis of the hydrocarbon fraction was performed on an Agilent 6890 N network gas chromatograph (GC) system, coupled to an Agilent 5975 XL MSD. Resin fractions were analysed for carbazoles quantification on an Agilent 6890 N network gas chromatograph

(GC) system, coupled to an Agilent 5972 inert MSD. The ratios of stable isotopes of carbon ( $^{13}\text{C}/^{12}\text{C}$ ) and organic nitrogen ( $^{15}\text{N}/^{14}\text{N}$ ) were measured with a Continuous Flow Isotope Ratio Mass Spectrometer (Thermo Finnigan-Delta Plus XL) coupled with an Elemental Analyzer (EA-CF-IRMS); Total sulfur was extracted via Parr bomb analysis and converted into  $\text{BaSO}_4$  and  $^{34}\text{S}/^{32}\text{S}$  ratios were determined by EA-CF-IRMS. Isotopic compositions are reported using the  $\delta$ -scale, in parts per thousands relative to V-PDB for carbon, air for nitrogen and V-CDT for sulfur with uncertainties ranging from  $\pm 0.15$  ‰ for C and N to  $\pm 0.5$  ‰ for S isotope analyses.

## Results and Discussion

All samples are affected by biodegradation to different degrees. The samples from Athabasca and Peace River lack n-alkanes and isoprenoid alkanes, retaining only the unresolved complex mixture (UCM), corresponding to the more bioreistant highly branched isoprenoids and other highly branched and cyclic alkanes (Peters et al. 2005). These results indicate biodegradation levels of at least PM5. On the other hand, some isoprenoid alkanes such as pristane and phytane, as well as some of the high molecular weight n-alkanes are preserved in the studied Cold Lake samples, indicating biodegradation levels of PM4 or lower (figure 1).

The progressive removal of polynuclear aromatic hydrocarbons (PAHs) with increasing biodegradation level seems to be the best indicator of the degree of alteration at severe alteration levels. The resistance of these compounds to biodegradation has been documented with increasing aromatic hydrocarbon ring number and the number of alkyl substituents (Fisher et al. 1998). This selective biodegradation is observed in alkynaphthalene and alkylphenanthrene compounds in Athabasca and Peace River bitumens. The Athabasca bitumen appears to be generally more altered than Peace River's with, for instance, naphthalene, methyl, ethyl and dimethyl naphthalenes compounds almost completely removed.

In a single reservoir column it is generally observed that naphthalene, dimethylnaphthalenes (DMN), trimethylnaphthalenes (TMN) and tetramethylnaphthalenes (TeMN) are progressively removed toward the bottom of the oil column, which is in agreement with the mechanisms of biodegradation, occurring mainly at oil-water contacts (Larter et al., 2003). Fluid viscosity behavior varies with biodegradation levels (figure 2) with viscosity increasing significantly from top to bottom in the oil leg of the investigated wells. Steranes and hopanes are affected in the most biodegraded samples at the bottom of the oil columns, where biodegradation levels reach at least level PM6 in Peace River and up to PM8 in some Athabasca columns. Monoaromatic and triaromatic steroid hydrocarbons do not seem to be affected.

Selected samples were analysed for  $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}$  and  $\delta^{15}\text{N}$  in bulk bitumen.  $\delta^{13}\text{C}$  values in Athabasca and Peace River obtained from bulk bitumen are in the range  $-31.0$ ‰ to  $-29.0$ ‰, and  $\delta^{15}\text{N}$  values range between  $0.3$ ‰ and  $2.9$ ‰.  $\delta^{34}\text{S}$  values determined for bitumens in the three oil sands reservoir samples, Athabasca, Peace River and Cold Lake, ranges between  $-0.1$ ‰ and  $6.3$ ‰. Carbon isotopic compositions of whole bitumen show no significant variation with biodegradation levels down oil columns, usually.  $\delta^{15}\text{N}$  values in bulk bitumen also do not show any trend with biodegradation either, as may have been expected from the observed behaviour of carbazole, alkylcarbazoles and benzo[b]carbazoles studied in the polar fraction of the oils, which change both concentration and distribution with biodegradation levels. In general, the sulfur contents increase slightly with increasing biodegradation, while  $\delta^{34}\text{S}$  shifts are not significant. However, lower values of the sulphur isotopic composition at the bottom of two of the studied columns suggest that secondary incorporation of some  $^{32}\text{S}$ -enriched sulfur, possibly associated with microbial action might be occurring.

Figure 3 shows that Peace River bitumen and Athabasca bitumen differ by ~3‰ in  $\delta^{34}\text{S}$  and ~2‰ in  $\delta^{15}\text{N}$ . The lack of significant changes of the bulk isotopic composition of related oils with different degrees of biodegradation suggests that the observed isotopic variations are mostly source rock related and importantly this confirms that sulphur and nitrogen isotopic signatures can be used in very degraded oils as stable source signatures. Supporting this important conclusion, the sulfur isotopic composition and other biodegradation stable geochemical proxies of oil sand bitumens correlate strongly in a regional suite of samples representative of oils sourced from the main source rocks of the area (Exshaw, Gordondale and Duvernay) shown by Adams and Marcano et al (2009) and clearly differentiate the probable source contributors.

## Conclusions

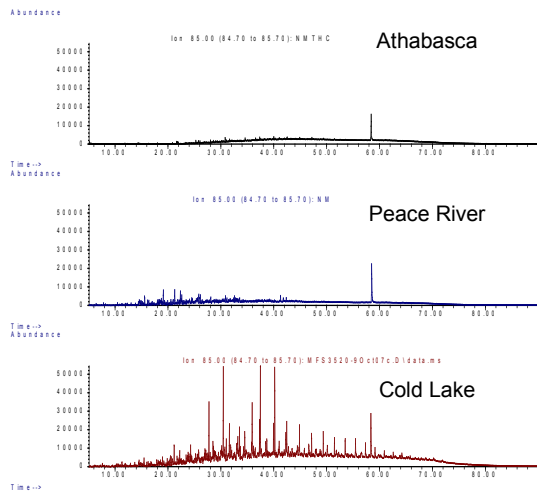
Based on the molecular composition of the studied bitumens, the levels of biodegradation range from at least PM5 to PM8 in Athabasca, PM5 to PM6 in Peace River and PM4 or lower in Cold Lake from the observed sample though we have seen higher levels of degradation elsewhere. Increasing biodegradation from top to bottom of oil columns was observed. The biodegradation sensitivity of each compound class in order of increasing resistance to degradation was observed to be naphthalene, methylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes > tetramethylnaphthalenes > pentamethylnaphthalenes, methylphenanthrenes, ethylphenanthrenes > dibenzothiophenes, carbazole, methylcarbazoles > dimethylcarbazoles > steranes > hopanes > aromatic steroid hydrocarbons, tricyclic terpanes, diasteranes; but many inconsistencies are locally seen. The results show that biodegradation does not cause observable systematic carbon, nitrogen or sulfur isotope changes in the whole bitumen; however, local variations in the sulfur isotopic composition, where  $^{32}\text{S}$ -enriched oils were found, may be related to microbial action. The work confirms that sulphur and nitrogen isotopic signatures can be used in very degraded oils as stable source signatures with major changes in the sulfur and nitrogen isotopic compositions of Albertan oils being largely source rock related.

## Acknowledgements

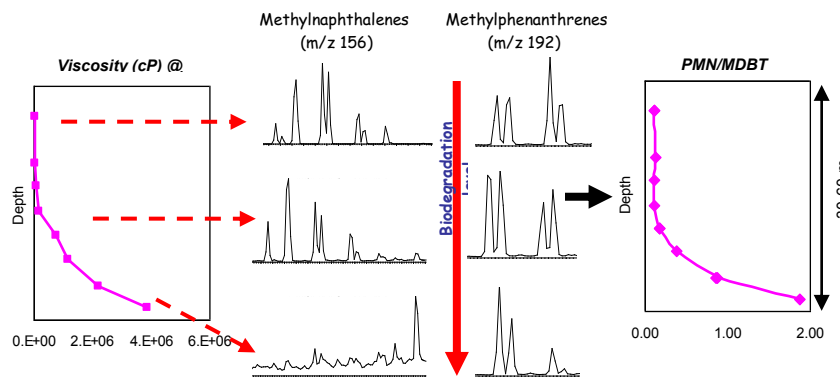
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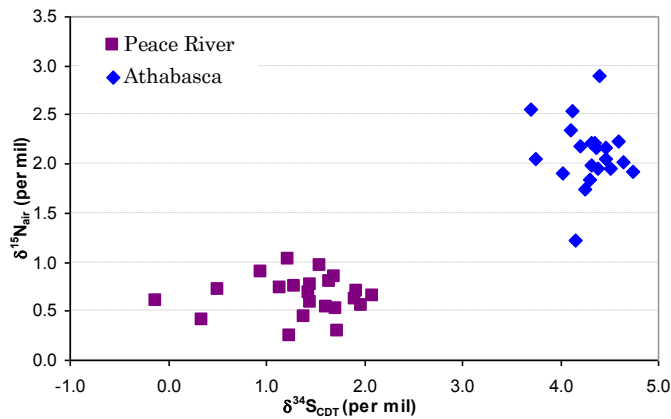
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**Figure 1:** Mass chromatograms of the ion  $m/z$  85 of the n-alkanes, depicting the complete removal of these compounds by biodegradation in Peace River and Athabasca oils and the preservation of some of these compounds in the Cold Lake oils. The peak near the end of the chromatogram is a standard.



**Figure 2:** Profile of viscosity, content of methyl naphthalenes ( $m/z$  156), methylphenanthrenes ( $m/z$  192) and the ratio pentamethyl naphthalenes / methyl dibenzothiophenes (PMN/MDBT) in one of the investigated columns in Peace River, depicting the increase in the values of oil viscosity and in the alteration of the molecular parameters toward the bottom of the column



**Figure 3:**  $\delta^{15}\text{N}$  vs.  $\delta^{34}\text{S}$  values showing two different groups that differentiate Peace River from Athabasca bitumens based on sulfur and nitrogen isotopic compositions