

## Sulfur and Nitrogen Compounds Reveal Oil Sands Source

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### Summary

The relative contributions of the various putative source rocks to the Alberta oil sands have been debated for decades. This regional study of produced oils of north-central Alberta characterizes Lower Cretaceous tar sands oil quality and identifies charge mixing using bulk oil sulfur content,  $\delta^{34}\text{S}$  and  $\delta^{15}\text{N}$  values, as well as biodegradation ultra-resistant source fingerprinting using FTICRMS of high molecular weight fractions. Molecular concentrations, metals and S contents and isotopic signatures clearly show that the westernmost Peace River oil sands bitumen is mostly derived from Gordondale Fm. source rocks whereas eastern Peace River bitumens closely resemble biodegraded Exshaw oil as do the Athabasca and Cold Lake deposits. Analysis of this wide spectrum of components clearly differentiates mixed source oils.

### Introduction

Over 3 trillion barrels of heavy oil and bitumen of highly variable levels of biodegradation are widely distributed across Alberta in Lower Cretaceous and carbonate reservoirs of Western Canada, yet the contributing source rock(s) remain(s) controversial despite many years of study (e.g., Deroo et al., 1977; Mossop, 1980; Brooks et al., 1988; Allan and Creaney, 1991; Riediger, 1994; Riediger et al. 2000; Adams et al., 2006; Higley et al., 2009; Mehay et al., 2009). Most authors agree that mature conventional oils migrated long distances into Peace River, Athabasca, Cold Lake, and Lloydminster area reservoirs, where they were altered by biodegradation to varying degrees. Previous biomarker studies have shown that these oils are genetically related with a common source and similar maturities (e.g., Deroo et al., 1977; Brooks et al., 1988; Allen & Creaney, 1991) despite some biomarker biodegradation locally.

Oil quality and producibility is strongly dependent on source rock type, maturity and degree of oil alteration. Predicting local and regional fluid property variations generated by the interplay of charge and extensive biodegradation is of major economic significance. While the biodegradation process and how it impacts oil properties locally is understood (Larter et al., 2008), the greatest uncertainty is charge oil composition and timing. Establishing the proportion and composition of the oil charge from each source rock by fingerprinting single-source, unaltered Alberta oils is preferred over basin modeling which is notoriously approximate. Classical petroleum geochemical approaches are, however, hampered by the severe biodegradation of these oils. This type of source charge allocation (SCA) or de-mixing of multi-sourced oils would greatly inform biodegradation predictions and targeting oil viscosity sweet spots.

The wide range of oil charge scenarios described in the literature from classical biomarker oil-source rock correlation studies are related to the impact of variable biodegradation levels as well as the variable maturity and native concentration of biomarkers in each of the oils from key Alberta source rocks. Compounds or proxies not as susceptible to biodegradation include those containing metals (Ni and V), heteroatoms, S and N stable isotope ratios and other refractory organic compounds (i.e., high molecular weight multi-heteroatom (HMWMH) components) best suited to molecular source typing of severely degraded oils and application of SCA. Recent advances in analytical instrumentation (FTICRMS; Rodgers et al., 2005) now allows for detailed imaging of the HMWMH compounds in the polar fraction of oils to unlock the "black box" of super-biodegraded oils. Here, a regional study of oils in the Peace River area investigates the source of the Peace River bitumen and the regional oil geochemistry of western Lower Cretaceous fields in comparison to the other oil sands bitumens.

## Methods

To establish possible precursor oil compositions and develop oil-source rock and oil-oil correlations, single source, non- or lightly biodegraded produced oils well correlated to source rocks in the Duvernay, Exshaw, Doig, and Montney formations, as well as the Jurassic Gordondale Member (e.g., Riediger et al., 1994; Snowdon et al., 1998; Fowler et al., 2001; Manzano-Kareah, 2001) were compared to oils produced and mechanically extracted from the Athabasca, Cold Lake and Peace River oil sands and fields to the west (Figure 1). Oils were analyzed for chemical composition by GCMS, sulphur content,  $\delta^{34}\text{S}$  (‰ CDT) and  $\delta^{13}\text{C}$  (‰ PDB). A subset of the oils was also analyzed for stable N (‰ air) isotopes by Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS). Quantitative molecular composition of the solid phase extracted total hydrocarbon fraction was analyzed on an Agilent 5890 Series II gas chromatograph (GC) coupled to an Agilent 5973 Mass Selective Detector (MSD). Sulphur content was measured on produced oils using a LECO SC-444DR sulphur and carbon analyzer on a 0.35 to 1 g sample. For  $\delta^{34}\text{S}$  analyses on total sulphur, the oil-S was converted to  $\text{BaSO}_4$  by Parr Bomb combustion and  $\text{BaCl}_2$  addition, and then analyzed by CF-IRMS.

## Examples

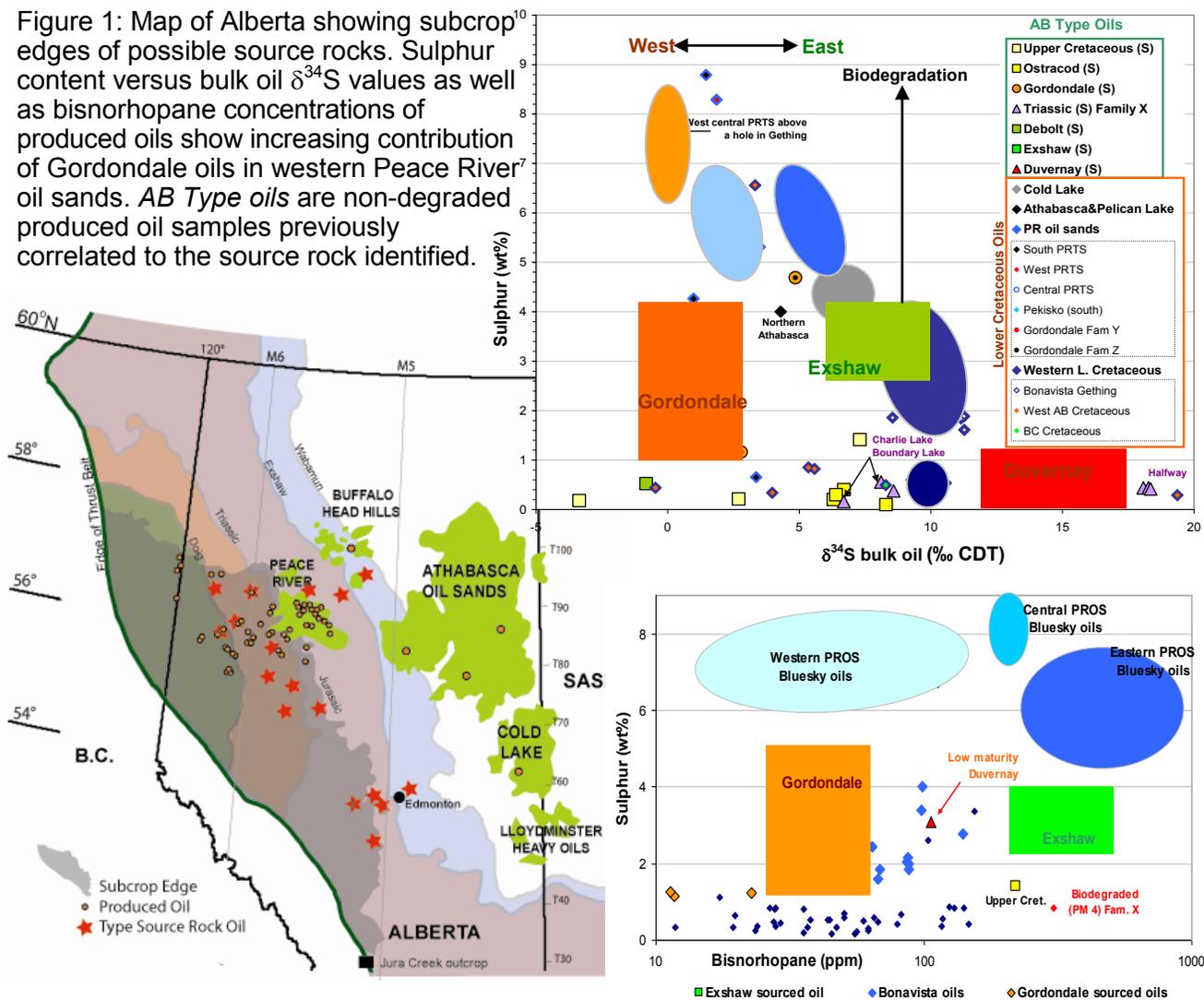
Regionally, oil biodegradation levels increase from west to east and north across Alberta and API gravity increases from 6° in the eastern Athabasca oil sands to 38°API in the Gething Formation pools west of the Peace River oil sands (PROS; Adams et al., 2006). Biodegradation removes light end hydrocarbons from oil and concentrates resistant components, such that approximately 50% of the charged PROS oils and over 60% of the Athabasca oil have been removed. Thus enrichment of the bitumen in S, metals and HMWMH by a factor of at least two means that the original non-degraded oil had S contents of 2-5 wt% at PROS and 1.2-1.7 wt% in Athabasca. The high sulphur content of the Exshaw and Gordondale derived oils contrasts with the other potential Duvernay, Upper Cretaceous and Triassic sourced oil containing less than 1 wt% S, which thus cannot have been the precursors of the 4 to 10 wt% S oils found in the oil sands. Similarly, the PROS bitumen has very high Ni (40 - 90 mg/kg) and V (80 - 250 mg/kg) concentrations and the V/Ni ratios of the western (3.2) and eastern (2.7) PROS bitumen are very close to those of the Gordondale and Exshaw, which also have compatible metal concentrations. In contrast, the Triassic, Devonian and Upper Cretaceous sourced oils have much higher or lower V/Ni ratios and much lower Ni and V concentrations.

In these oils, the most effective metric for discerning source rock contributions may be the  $\delta^{34}\text{S}$  (Mehay et al., 2009) and  $\delta^{15}\text{N}$  values. Bulk oil  $\delta^{34}\text{S}$  from a suite of reservoirs west of and in the PROS area vary widely from -12 to 20‰, with Duvernay oil having 3 to 8 ‰ higher  $\delta^{34}\text{S}$  values than Exshaw oil, which in turn has 5‰ higher  $\delta^{34}\text{S}$  values than those of Gordondale oils (Figure 1). The Athabasca bitumen  $\delta^{34}\text{S}$  is most similar to Exshaw oil and consistently more  $^{34}\text{S}$  enriched than the PROS bitumen.  $\delta^{15}\text{N}$  values also differ by ~2 ‰ between PROS and Athabasca bitumen, with nitrogen isotope ratio variations over a narrower range of 0.3 to 2.9‰ (Figure 2). The observed isotopic variations are considered to be related to source rock and maturity because biodegradation level does not significantly impact  $\delta^{34}\text{S}$  and  $\delta^{15}\text{N}$  values (Marcano et al., 2010). Different source signatures for PROS and Athabasca bitumen is further supported by relative abundances and double bond equivalent (DBE) distributions of resistant NS- and NS<sub>2</sub>-bearing HMWMH compounds and within their DBE9 and DBE 12 domains as well (Oldenburg et al., 2010).

Near the PROS, only the Gordondale Member and Exshaw Formation sourced oils have S contents > 1.5 wt% and  $\delta^{34}\text{S}$  values similar to those of PROS bitumen (-1 to 4‰). Duvernay sourced oils have substantially more  $^{34}\text{S}$  enriched isotope ratios (12-18‰). Although the Upper Cretaceous and some of the Triassic oils have comparable  $\delta^{34}\text{S}$  values to Exshaw oils their distinctive biomarker signatures and low S contents preclude them as significant contributors. Cold Lake and southern Athabasca  $\delta^{34}\text{S}$  values are most similar to Exshaw oils whereas S

content increases and  $\delta^{34}\text{S}$  values become more  $^{34}\text{S}$  depleted from east to west towards the Gordondale subcrop. Very similar mixing trends from east to west are evident in bisnorhopane (a key component of the Exshaw sourced oil) concentrations (assuming a factor of two increase due to biodegradation) with end member values of 350 to 400 ppm in Exshaw oils and only 10 to 60 ppm in Gordondale oils. These data suggest that the PROS bitumen may be a mixture of oils eastward migrating from the Gordondale and oils migrating upwards from the Exshaw source rock. High sulfur Gordondale charge oil to the PROS explains the anomalously high S contents of the PROS oils (4 wt% in the east to 10 wt% in the west) compared to lower S (3 - 4 wt%) but more degraded Athabasca bitumen. This is inconsistent with findings of Riediger et al. (1994), but similar to reduced charge estimates from recent 3D basin models (Higley et al. 2009).

Figure 1: Map of Alberta showing subcrop edges of possible source rocks. Sulphur content versus bulk oil  $\delta^{34}\text{S}$  values as well as bisnorhopane concentrations of produced oils show increasing contribution of Gordondale oils in western Peace River oil sands. AB Type oils are non-degraded produced oil samples previously correlated to the source rock identified.



Some Gordondale oils may have spilled into northern Athabasca but the southern Athabasca and Cold Lake accumulations seem to be mostly sourced by Exshaw oil. Biomarker signatures cannot rule out the Duvernay Formation as a source of the oil sands, but bulk carbon isotopes from oil sourced from the Duvernay and Debolt formations are much more  $^{13}\text{C}$  enriched ( $\sim -29\text{‰}$ ) than Gordondale and Exshaw sourced oils and oil sands bitumen ( $-30$  to  $-31\text{‰}$ ) making significant charge contribution from the Duvernay Formation unlikely with this extensive biodegradation.

### Conclusions

Bulk stable S, C and N isotopic compositions and biomarker concentrations indicate variable contributions from predominately the Exshaw Fm. and Lower Jurassic Gordondale Member,

with some possible contribution from Duvernay oils to the south. Ni, V and S contents and isotopic signals of the oil sands also support charge mixing across the PROS with more S-rich low biomarker Gordondale charge dominating in western PROS and Exshaw charged oils found further west and in the underlying Pekisko reservoirs. Double bond equivalent (DBE) distributions of two key domains of variably resistant HMWMH compounds (NS; NS<sub>2</sub> heteroatom contents) also indicate different source signatures for the two largest oil sands deposits.

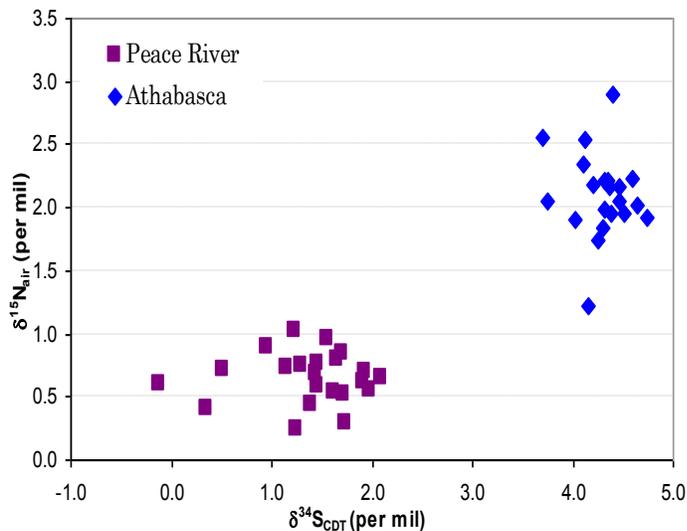


Figure 2:  $\delta^{15}\text{N}_{\text{ir}}$  and  $\delta^{34}\text{S}$  values clearly differentiate Peace River from Athabasca bitumen (after Marcano et al., 2010).

## Acknowledgements

This study was made possible by oil contributions by many producers and by the financial support of PRG and AGG research groups (NSERC, AIF, PRG). The authors acknowledge the assistance of the Petroleum Reservoir Group laboratory staff and the Isotope Science Laboratory staff at the University of Calgary.

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