

Canadian oil sands; a window on the deep petroleum biosphere

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Covering an area over 100,000 km² the Canadian oil sands deposits are a vast testament to the consequences when the biosphere meets the geosphere. By integrating laboratory and field based studies of the microbiology, geochemistry and geology of the Canadian oil sands we have developed a more complete understanding of the processes that led to their formation and factors that may control in-reservoir petroleum biodegradation. Studies of methanogenic oil degradation in the laboratory suggest that in the initial stages of biodegradation when the bulk of the crude oil hydrocarbons, principally saturated hydrocarbons, are removed, oil degradation is driven by consortia of bacteria from the *Syntrophaceae* and methanogenic archaea. However field studies of the microbial communities currently predominant in the heavily biodegraded oil sands paint a very different picture with apparent predominance of known hydrocarbon degrading taxa conventionally considered to be aerobes. In addition, the communities in produced water samples contrast with communities detected in core samples and are dominated by *Epsilonproteobacteria* which are typically thought to play a role in sulfur cycling. The reasons for the contrasting views obtained using different approaches and sampling strategies will be explored and linked to geochemical patterns characteristic of heavy oil reservoirs.

Based on the occurrence of geochemical gradients in biodegraded petroleum reservoirs it was initially inferred that the petroleum reservoir microbiota should be most abundant and active at the base of the reservoir where oil saturated rock transitions to water saturated rock [1]. This theory appears to hold up to empirical scrutiny and we have shown that bacterial 16S rRNA gene abundance is around 2 orders of magnitude greater in these oil water transition zones. We will discuss our most recent findings integrating geochemical and metagenomic results to gain further insights into the potential role of the microbiota currently dominant in oil sands reservoirs and the implications for the petroleum deep biosphere and other hydrocarbon-impacted anoxic environments.

[1] Head I.M., Jones D.M. and Larter S.R. (2003). Biological activity in the deep subsurface and the origin of heavy oil. *Nature* 426, 344-352.

Orbitrap high resolution mass spectrometry characterization of Athabasca oil sands acids in environmental samples

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Type The Athabasca oils sands region of Alberta, Canada is one of world's largest bitumen reserves with a proven 170 billion barrels of crude oil. Approximately 3 barrels of river water are used during the alkaline/hot water extraction process of the mined oil sand for every barrel of oil produced. During the extraction process, acidic bitumen components (including naphthenic acids) are solubilized in the water. This oil sands process water (OSPW) is stored in tailings ponds in accordance with a zero discharge policy. There is a growing need for development of analytical methods that can distinguish between compounds found within industrially derived OSPW from those derived from natural weathering of oil sands deposits. This is a difficult challenge as possible leakage beyond tailings ponds containments will likely be in the form of a mixture of water soluble organic acids that are similar to those leaching naturally to aquatic environments. An overview is given on the progress of analytical developments and the current state of mass spectrometry analysis of environmental samples. The potential for Orbitrap high resolution mass spectrometry and accurate mass measurements for chemical fingerprinting of oil sands acids from tailing ponds, interceptor wells, groundwater and reference river surface waters is evaluated. Particular emphasis is given to (i) new developments which recognize that the oil sands acid fraction contains more components than the traditional structures of naphthenic acids; and (ii) the influence of extraction procedures on what is being measured. Significant differences in high resolution mass spectrometry results were observed for the same sample set that are attributed to the extraction procedure and/or extraction solvent of choice.