

## **Aqueous geochemistry and stable isotope ratios as predictive risk management tools for assessing vertical hydraulic connectivity in the Athabasca Oil Sands Region**

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### **Summary**

Recent unexpected discharges of steam, brine, or bitumen to the surface of oil sands resource developments suggest a gap in understanding of the subsurface fluid flow system in the Athabasca Oil Sands Region (AOSR) and a need to identify where such discharges might occur. These surface discharge events have common spatial and geochemical characteristics that we will attempt to frame in a context of identifying and managing the risks associated with vertical movement of fluids during oil sands resource development by mining or steam-assisted gravity drainage (SAGD). Aqueous geochemistry and stable isotope ratios of McMurray Formation waters and dissolved sulfate can provide a leading indicator of upward groundwater flow from Devonian strata below the sub-Cretaceous unconformity. The highly localized nature of high-salinity fluids suggests that upward flow is occurring via karst conduits. Areas of upward groundwater flow across the sub-Cretaceous unconformity are spatially correlated with the partial dissolution edge of the Prairie Evaporite Formation and instances of unanticipated fluid discharge to ground surface. A risk assessment framework that incorporates the aqueous and stable isotope geochemistry of formation waters in the AOSR may help delineate vertical connectivity during the reservoir characterization process and decrease the probability of surface discharge incidents during oil sands development proximal to the Prairie evaporite partial dissolution edge.

### **Predicting Vertical Connectivity: an Industry-wide Challenge**

Several major unexpected incidents of steam, brine, or bitumen discharge have occurred in the AOSR during development of oil sands resources. These discharge events include steam blowouts into overburden, brine eruptions into tailings ponds, and bitumen discharges into surface waters. These incidents can have high economic costs that range from large-scale remediation efforts to abandonment of entire projects. A key objective of this work is developing a general predictive model to identify areas where karst features are active, and where vertical connectivity is most likely.

Each of the four known major incidents have occurred along the partial dissolution edge of the Prairie Evaporite Formation, and are plausibly facilitated by an active karst system. The extent of karst and associated overlying collapse breccias in the northeast Athabasca region was recently described and mapped (Broughton, 2013), confirming the widespread variability in the regional Devonian structural surface. LIDAR imaging has brought to light new evidence of active karst in the AOSR, and is consistent with other structural and geochemical observations in the region that suggest recent karst activity (Broughton, 2013). It is possible that karst processes have locally weakened the overburden, or provided conduits through which fluids may flow preferentially.

### **Athabasca Oil Sands Regional Groundwater System**

The regional groundwater system in the AOSR is complex, particularly in the bitumen-bearing McMurray formation. Recent research has proposed areas of upward formation water flow from Devonian aquifers into the McMurray Formation along the partial dissolution edge of the Prairie Evaporite Formation (Cowie et al., in review). Within this narrow geographic band trending from northwest to southeast across the AOSR, upward formation water flow occurs locally via karst conduits in the underlying Devonian units. The saline Devonian waters have distinct hydrogen and oxygen isotope ratios that reflect glacial origin of this water, and a chemical composition that reflect Devonian salts (Grasby and Chen, 2005; Gue, 2012). Groundwater flow into the McMurray Formation also occurs via gravity-driven topographic recharge (WorleyParsons, 2010). The presence of many Quaternary channels that down-cut into the McMurray Formation (Andriashek and Atkinson, 2007) has been suggested as an additional local influence providing a mechanism for locally increased groundwater flux into the McMurray Formation. These hydrogeological processes have resulted in highly variable salinity in McMurray Formation waters at a lease-area scale. Total dissolved solids (TDS) concentrations in McMurray Formation waters can range from 1 000 to 100 000 mg/L over lateral distance of tens of kilometres. The occurrence of upward groundwater flow can be identified using geochemical ion ratios and stable isotope measurements of McMurray Formation waters. Upward flow of highly saline waters requires mass removal from the underlying evaporite units, resulting in increasing void space underlying the McMurray Formation, and possible fractures or faulting. Therefore we propose that geochemical and stable isotope measurements of McMurray Formation waters can be used predictively to delineate areas with higher probability of active karst conduits, and thus, identify sites with greater risk to structural integrity in the subsurface.

## Sub-glacial Meltwater Hypothesis for Devonian Formation Waters

Formation waters in Devonian strata that underlie the McMurray Formation are unusual, if not unique, in that these waters have moderate to high salinity ( $30\,000 < \text{TDS} < 300\,000$  mg/L), and very low hydrogen and oxygen isotope ratios that are indicative of glacial recharge (Grasby and Chen, 2005; Gue, 2012). The proposed mechanism for generating this type of water is increased hydraulic head induced by continental ice sheets during the last glacial maximum that forced glacial meltwater deep into the Devonian units (Grasby and Chen, 2005). During glacial periods, low-salinity meltwater with low hydrogen and oxygen isotope ratios, under great pressure from the overlying ice volume, was injected into the basin from the subcrop edge in the northeast, reversing regional flow patterns that previously trended from southwest to northeast. These waters encountered the Prairie Evaporite Formation, resulting in the dissolution of salt, and translation of the evaporite dissolution edge toward the west. As the ice sheets retreated, the driving force for downward flow was removed, and the groundwater system responded to this new state of disequilibrium. The result of the removal of the continental ice sheet on the groundwater system was generally up-dip flow of Devonian formation waters toward the edge of the basin in the northeast. However, where karst conduits exist, saline waters flowed vertically into the McMurray Formation, acting as a pressure release valve for over-pressured Devonian aquifers. The dissolution of the Prairie Evaporite Formation during the Pleistocene resulted in removal of rock volume from the Devonian strata, however, the amount of Quaternary subsidence is presently unknown and likely highly variable.

## Geochemical and Stable Isotope Tools for Risk Assessment

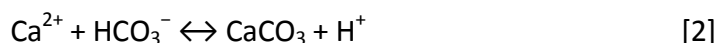
TDS concentrations can provide some indication about the location of vertical groundwater flow from the Devonian formation water systems into the McMurray Formation. Ion-specific analysis may provide important information about the source and timing of these inputs, and thus, the relative risk of modern upward saline formation water flow into a mine or in-situ reservoir. Formation waters from the Devonian aquifers are primarily Na-Cl type due to halite dissolution, however these waters also contain dissolved calcium and sulfate ions due to anhydrite dissolution (Hackbarth and Nastasa, 1979). Water derived from modern recharge does not contain concentrated Ca and  $\text{SO}_4$ , therefore the distinct geochemistry of upward-flowing formation waters from Devonian strata can be characteristically identified.

## Microbial Alteration of Formation Waters

Under modern oil sands reservoir conditions, sulfate is highly reactive with organic carbon in the presence of an active microbial community. Therefore when water from Devonian aquifers infiltrates into the McMurray Formation, bacterial sulfate reduction (BSR) alters the composition of reservoir fluids by removal of sulfate, biodegradation of hydrocarbons, generation of alkalinity and formation of  $\text{H}_2\text{S}$  via Equation 1:



Increased reservoir alkalinity due to BSR may also drive the precipitation of secondary calcium carbonate that is commonly observed in the oil-water transition zone of oil sands reservoirs via Equation 2:



The precipitation of calcium carbonate is an equilibrium reaction that is dependent on the pH and concentration of bicarbonate and calcium ions. Calcium is elevated in Devonian formation waters due to anhydrite dissolution, and pH is increased via BSR (Eq. 1), thus driving Equation 2 to the right, resulting in

CaCO<sub>3</sub> precipitation. The two geochemical processes (Eqs. 1 & 2) remove calcium and sulfate from McMurray Formation waters on relatively short time scales, potentially constraining the timing of vertical flow for recently intruded Devonian waters. Therefore, if McMurray Formation reservoir water contains abundant sulfate and calcium ions, it is likely that the sulfate-rich water is a recent phenomenon, and therefore carries a higher risk of vertical flow in this area.

Stable isotope geochemistry may provide additional insight into the occurrence of vertical groundwater flow. Sulfate in Devonian formation waters has a characteristic sulfur isotopic fingerprint that is indicative of anhydrites. Furthermore, bacterial sulfate reduction preferentially partitions the light stable isotopes of sulfur (<sup>32</sup>S) into the reaction product H<sub>2</sub>S, increasing the δ<sup>34</sup>S value of residual sulfate. Measurement of the sulfur isotope ratios and subsequent Rayleigh isotope fractionation modeling may provide further insights into 1) the source, amount, and timing of initial sulfate that infiltrated into the reservoir (and by extension, the mass of Devonian formation water infiltrating the reservoir may be calculated), 2) the amount of sulfate consumed by bacterial sulfate reduction since injection and 3) the timing of saline water infiltration into the McMurray Formation.

## Conclusions

Geochemistry and stable isotope ratios of formation water and its dissolved constituents provides a new risk-assessment tool for development of oil sands resources along the karst-impacted Prairie Evaporite dissolution edge where upward vertical flow of Devonian formation water into the McMurray groundwater system can have substantial negative economic and environmental impacts. The simultaneous presence of karst features (sinkholes), and McMurray Formation water with abundant dissolved calcium and sulfate should serve as a cautionary indicator of the potential for unexpected vertical flow paths, both above and below the McMurray Formation.

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