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Evolution of Groundwater Hydrochemistry, North Athabasca Oil Sands Region

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Groundwater compositions are publicly available for Devonian through Holocene sediments rocks in the North Athabasca Oil Sands (NAOS) region. The Athabasca River forms a significant regional hydrogeological divide. West of the River flow is up-dip whereas to the east flow is westward towards the River from recharge regions along the Devonian subcrop edge and downwards through Quaternary cover.

Groundwater hydrochemistry varies systematically from Recent to Devonian age rocks. Groundwater compositions in surficial and near-surface Quaternary aquifers recharged directly from surface are characteristically enriched in calcium, magnesium and bicarbonate and transition to sodium, calcium and sulphate dominated compositions where oxidation of Clearwater shale has occurred. The salinity of groundwater in surficial and Quaternary aquifers is low and stands in contrast to the compositions of groundwaters in Cretaceous rocks, particularly the basal water sand aquifer of the Lower McMurray Formation. Within the McMurray Formation salinities increase to several thousand milligrams per litre total dissolved solids (TDS) and water compositions are typically calcium-sodium-bicarbonate to sodium-calcium-bicarbonate-chloride and sodium-chloride-bicarbonate types. The basal water sands aquifer lies directly on Devonian rocks of the Waterways Formation and its composition reflects contributions from lateral flow within Cretaceous rocks and vertical flow out of the Devonian.

Three distinct water types are recognized in Devonian aquifer systems and these can be directly linked to the mineralogy of the aquifer systems. Characteristics of these water types are as follows:

- **Type 1** Devonian groundwaters occur within the Waterways Formation and have contributed to elevating the groundwater salinities in the Cretaceous basal water sands aquifer. Type 1 groundwaters are defined as belonging to the Na-HCO_3 hydrochemical facies and reflect interaction with carbonate minerals calcite and dolomite, and contain variable amounts of chloride and low sulphate concentrations.
- **Type 2** Devonian groundwaters have higher salinities than Type 1, but are typically less than about 12,000 mg/L TDS. These groundwaters belong to the Na-SO_4 hydrochemical facies and are typically found within the Keg River ramp and reef where they indicate interaction with carbonate and sulphate minerals calcite, dolomite and gypsum. They generally contain low concentrations of chloride and bicarbonate, the latter reflecting equilibration with calcite/dolomite.
- **Type 3** Devonian groundwaters are the most recognizable Devonian groundwater type and are characterized by compositions within Na-Cl hydrochemical facies. Type 3 Na-Cl groundwaters occur in Prairie Evaporite Formation aquifers and in discharge areas proximal to the Athabasca River. Type 3

Devonian groundwaters have a large range in salinities, from less than 10,000 mg/L to as high as 350,000 mg/L, but characteristically show molar Na/Cl ratios near 1 indicating that halite dissolution is the dominant control on solute chemistry, even at high dilution. Type 3 groundwaters indicate halite dissolution; no residual evaporite brines are recognized east of the Athabasca River.

Although it would seem possible that mixtures of all three Devonian groundwater types should occur, publicly available data show that Type 1-3 and Type 2-3 intermediate groundwater compositions are dominant with few instances of Type 1-2 mixtures and few if any ternary mixtures of all Devonian water types. It is suggested that the intermediate water types are more reflective of the flow path mineralogy rather than large scale mixing of different flow systems, except in regional discharge areas.

The distribution and composition of groundwater types in the NAOS region east of the Athabasca River reflects the groundwater flow regimes and mineralogy of Devonian through Recent sediments. The trends are similar to the evolution of groundwaters in other areas such as the Michigan Basin in southern Ontario where near-surface bicarbonate-dominated compositions give way with depth to sulphate-dominated groundwaters of intermediate salinity and eventually to chloride-dominated brines indicative of interaction with halite in deep evaporate formations. The flow system east of the Athabasca River is fundamentally different than the system west of the river and in deeper regions of the Alberta Basin where there has been no or little influx of meteorically derived fluids. This condition has persisted for tens of millions of years and may be the fundamental control on the localization of highly biodegraded and water-washed bitumens of the Athabasca Oil Sands region.