

## **Isotopically Determined Mannville Group Gas Families**

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Large amounts of natural gas with variable isotopic compositions are produced from the Lower Cretaceous Mannville Group in the WCSB. Our database of carbon isotope analyses of production gas, collected as part of an environmental remediation project, contains 233 gas samples from the Mannville Group. Our goal is to understand the origin, geographic distribution, and degree and mechanism of alteration of Mannville Group gas by examining gas carbon isotope ratios and molecular abundances.

Based on their rhenium-osmium isotope dating of hydrocarbons in the giant oil sands deposits of Alberta, Canada, Selby and Creaser (2005) suggested that the Mannville Group tar sand and heavy oil was emplaced in one event 112 +/- 5.3 Ma, having migrated eastwards from the deeper Paleozoic shales in the center of the basin. This timing is almost contemporaneous with deposition of the unlithified to poorly lithified Mannville Group sands, silts, shales and coals.

Our study initially assumes that the majority of Mannville Group gas was generated and migrated with the oil that now occurs as the present-day tar sand and heavy oil deposits. By examining the chemical compositions and carbon isotope values of Mannville gases from our database, we observed six isotopically different families of gases that have had different alteration histories and production potentials (Table 1 and Figure 1).

The least altered F1 Mannville gases have not migrated significantly and are located only in the center of the basin. They are isotopically and chemically most representative of the starting thermogenic gas before migration. F6 gases also did not migrate significantly. They are located in a band slightly northeast of F1 gases and have methane isotope values that are the same or only slightly lower than F1 gases. However, ethane and propane clearly show that these gases are biodegraded. Anomalously high  $\delta^{13}$ C values for CO<sub>2</sub> suggest an additional process has altered the gas, either bacterial fermentation or dissolution of high  $\delta^{13}$ C carbonate cements.

F2 gases migrated farther eastwards and mixed with pre-existing, shallow, biological methane as suggested by Creany and Allan, 1992. The proportion of isotopically lighter methane is greater towards the southeast. F2 gases are not biodegraded to any significant degree.

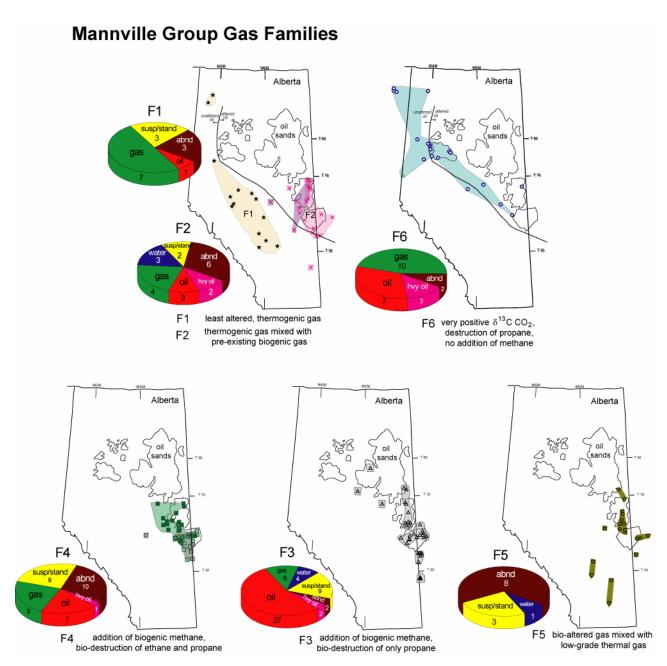
F3 and F4 gases migrated to the margins of the basin, F3 more so than F4. Both families of gases mixed with biological methane and are biodegraded. However, F3 gases suffered only biodestruction of propane, whereas F4 gases have also lost ethane. On average, F4 gases are deeper than F3 gases, suggesting that there may be a unique depth window where biological communities destroy ethane.

F5 gases occur within the Mannville Group sediments but are not typical of Mannville Group gases. Their  $\delta^{13}$ C values are anomalously low. These gases probably represent zones where the original Mannville gas was lost or never accumulated, and the small amount of gas present now is new gas, generated in place at ambient conditions. Note that all wells from our database which have F5 gas are commercial failures.

In summary, natural differences in gas families are the result of variations in (1) the extent of gas migration; (2) the degree of mixing with pre-existing biological gas; and (3) the actual biocommunities that act on the gas. In some areas not discussed in this presentation, thermally enhanced recovery has caused *in situ* generation of new gas with very low  $\delta^{13}$ C methane. Interestingly, F1 gases encompass mostly gas wells, F3 gases are associated with oil production, and F5 are commercial failures.

 Table 1. Mannville Group Gas Families

Gas Family	Family Characteristics	δ <sup>13</sup> C Methane (per mil)	δ <sup>13</sup> C Ethane (per mil)	δ <sup>13</sup> C Propane (per mil)	δ <sup>13</sup> C Carbon Dioxide (per mil)
1	least altered, oil-associated, thermogenic gas	-48 to -43	-34 to -28	-32 to -26	-19 to -3
2	oil-associated, thermogenic gas mixed with pre-existing biogenic gas	low δ <sup>13</sup> C <sub>1</sub> -70 to -55	-35 to -29	-33 to -26	-29 to +8
		high $\delta^{13}$ C <sub>1</sub> -54 to -51	-35 to -29	-29 to -26	-4,+5
3	addition of biogenic methane, bio-destruction of propane, not ethane	-73 to -55	-34 to -28.5	-25 to -5	-46 to +7
4	addition of biogenic methane, bio-destruction of both ethane and propane	low δ <sup>13</sup> C <sub>1</sub> -71 to -55	-28.5 to -21	-28 to -10	-27 to +6
		high δ <sup>13</sup> C <sub>1</sub> -54 to -48	-28.5 to -18	-30 to -11	-7 to +7
5	bio-altered gas mixed with incipient thermal gas	-68 to -50	-46 to -35	-35 to -19	-21 to +3
6	unusual gas, very positive δ <sup>13</sup> C CO <sub>2</sub> , no new methane, but destruction of propane, not ethane	-54 to -44.5	-33 to -25.5	-28 to -9	+9 to +20



**Figure 1.** Maps of Alberta showing the geographic distribution of the Mannville gas families based on our database. The major tar sand and heavy oil areas are also outlined. The curve separating regions of unaltered from altered oil is from the WCSB Atlas (Chpt. 19). Mannville Group gas was generated in the center of the basin (southwest-central Alberta) and migrated in a northeasterly direction. Note that F1 and F6 are located in separate areas, whereas F2, F3, F4, and F5 have significant geographic overlap. F3 is generally slightly to the east of F4. Pie diagrams for each gas family summarize the present-day well status for gas samples from ourdatabase. Note that all F5 gases come from wells that have been unsuccessful producers. F3 gases are the most common gases associated with oil producing wells and F1 gases are often from with gas producing wells.

## References

Creaney, S. Allan, J., 1992. AAPG Memoir 55, p. 279-308.

Selby, D., Creaser, R.A., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science 72 May 2005, v. 308, n. 5726, p. 1293-1295.