***Series Title:* The Isotopic Characterization of Natural Gas and Water in Paleozoic Bedrock Formations in Southwestern Ontario**

Volume IV. The Isotopic Characterization of Natural Gas in Natural Gas Reservoirs in Southwestern Ontario – Abandoned Works Program

FINAL REPORT

January 30, 2018

This document arises from a contract and collaboration between the University of Western Ontario and the (Ontario) Ministry of Natural Resources and Forestry (Petroleum Operations) (Terry Carter, Lee Fortner), as supported by the Abandoned Works Program.

Prepared by

Mitchell Skuce, MSc, The University of Western Ontario
Fred J Longstaffe, Principal Investigator, The University of Western Ontario
Terry Carter, Consulting Geologist, London, Ontario, Canada

And reporting to

Lee Fortner, Chief Geologist, Petroleum Operations, Ministry of Natural Resources and Forestry

Special acknowledgements to:

- Joanne Potter, London, Ontario, for helping to collect, and for analyzing the new samples reported here, and assisting materially with analyses reported by Farisha Mohd Zaffa (2010)
- Farisha Mohd Zaffa, who analyzed and described 10 additional samples included here
- Neil Banerjee and Claudia Cochrane, supervisors of the Farisha Mohd Zaffa's BSc thesis
- Robert Cochrane who helped materially in the collection of samples reported by Farisha Mohd Zaffa
- Elizabeth Sutherland who prepared the sample location maps contained in Appendix A.

Suggested Citation

Parts of this publication may be quoted if credit is given. It is recommended that reference to this report be made in the following form:

Skuce, M., Longstaffe, F.J. and Carter, T.R, 2017. The isotopic characterization of natural gas in natural gas reservoirs in southwestern Ontario. Oil, Gas and Salt Resources Library, Open File Data Release 2017-3.

Executive Summary

In 2011, the Ministry of Natural Resources and Forestry (MNRF) initiated a project to acquire isotopic fingerprints of the natural gas and water in the Paleozoic bedrock of southern Ontario. The results of the isotopic geochemistry for the natural gases are included in this report. Isotopic fingerprinting of water is documented in Skuce (2014a), Skuce et al. (2015a,b), and several precursor unpublished reports (Skuce et al., 2014a-c; Skuce, 2014b).

The MNRF will use the study results to identify the probable geological sources of natural gases leaking from orphan wells in southwestern Ontario, and thus to assist plugging efforts by the Abandoned Works Program (AWP). This tool is based on significant isotopic differences among gases in the various natural reservoirs in the region. The existence of such differences has been identified by several previous authors (Barker & Pollock, 1984; Sherwood-Lollar et al., 1994; Mohd Zaffa, 2010) and followed up most recently by Potter and Longstaffe (2011). The characterization of these differences is significantly furthered by the results of this study.

This project builds on the existing data by adding further geochemical analyses from a new, extensive suite of natural gas samples from the major Cambrian through Silurian natural gas reservoirs in the region. The isotopic compositions of these gases, along with highlights of their most distinguishing features, provide ‘fingerprints’ that, combined with geological knowledge of the region, will help AWP geoscientists make the best possible interpretations regarding the sources of leaking gases at orphan wells.

Introduction

This project was undertaken in partnership between the MNRF and the University of Western Ontario (UWO) in order to develop a tool to help identify the sources of gases and waters leaking from abandoned oil and gas wells, using the isotopic geochemistry of the leaking fluids. Hundreds and perhaps thousands of orphan wells exist throughout southwestern Ontario, commonly with corroded or non-existent casings. It is the mandate of the MNRF’s Abandoned Works Program (AWP) to identify and plug these wells on a priority basis. In many cases, records for these wells are unavailable and the original completion depth is unknown, or obstructions within the well bore make reaching the bottom impossible or impractical. For such cases, a geochemical guide utilizing the isotopic and geochemical fingerprints of leaking fluids to identify the geological source could be used to establish required minimum depths for plugging.

A geochemical tool for identifying the source of leaking formation water has been developed (Skuce, 2014a; Skuce et al., 2015a,b) and has already been used successfully for plugging of a well with artesian flow of sulphur water (T012111). The present study has established a similar geochemical guide using the isotopic compositions of natural gases sampled from gas wells with reliable documentation on well completion depths and producing formations. This report outlines the specifics of this natural gas fingerprinting project, presents the results of the isotopic differences between gases from different geological strata, and details their use for identifying the sources of unknown samples.

Scope of Project

During this project, 75 natural gas samples were collected and analyzed for a range of isotopic and chemical parameters in order to achieve the best possible characterization for each major gas-bearing bedrock unit in southwestern Ontario. Stable carbon and hydrogen isotopes ($\delta^{13}C$ and $\delta^{2}H$) were measured for methane (CH_4), and where possible, ethane (C_2H_6), propane (C_3H_8) and butane ($n\text{-}C_4H_{10}$ and $i\text{-}C_4H_{10}$). The concentrations of these gases were also determined for most samples. Data for 10 sites previously reported by Mohd Zaffa (2010) have also been added to the database generated during the present project. That work, as in the present study, reported the exact well locations sampled, which makes possible the best possible characterization of the units. The study area considered in this project encompasses the peninsula of southwestern Ontario, extending from Essex County to the south, through to the Bruce Peninsula in the north and the Niagara Peninsula region to the east (Fig.1).

Geological Context and Oil and Gas Plays

Southern Ontario is underlain by a relatively undeformed succession of marine sedimentary rocks of Paleozoic age up to 1400 metres thick, overlying a Precambrian basement complex of crystalline metamorphic and igneous rocks (Figs. 1 & 2). The Paleozoic strata dip at very low angles toward the Chatham Sag along the strike of the Algonquin and Findlay arches, and into the Michigan and Appalachian basins to the west and southeast, respectively.

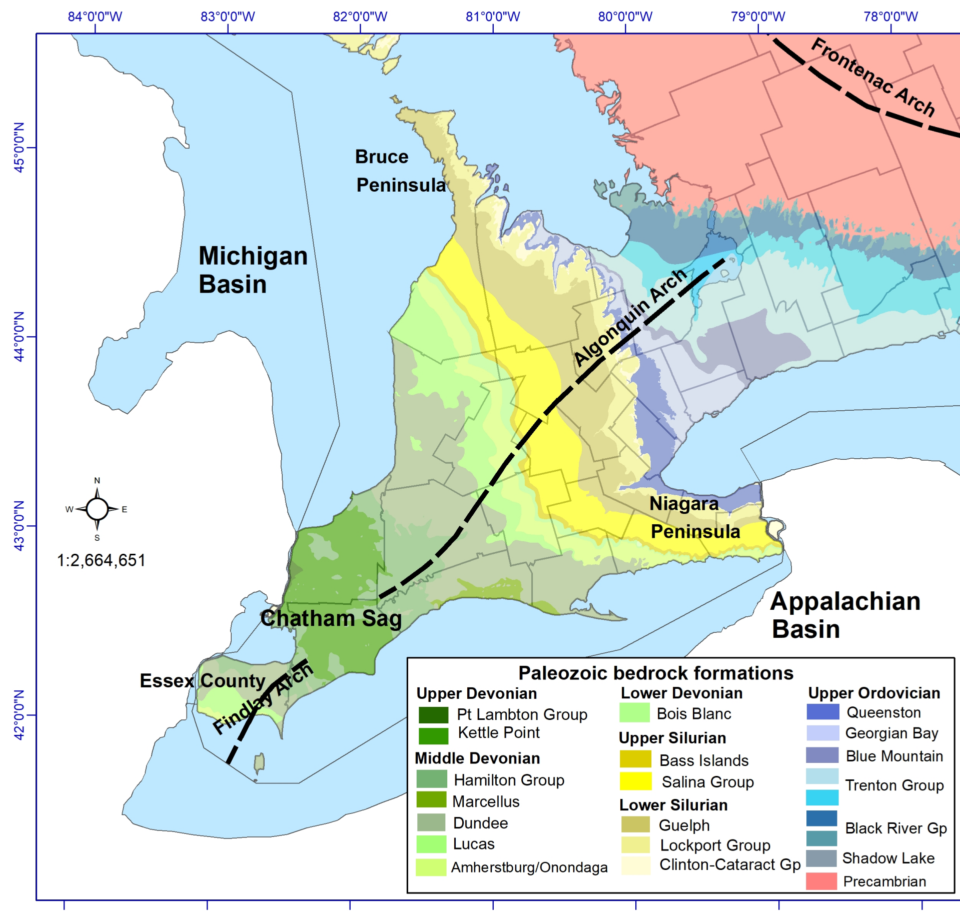


Figure 1. Bedrock geology and regional structural features of southwestern Ontario. Adapted from Armstrong and Dodge (2007).

Commercial discoveries of conventional reservoirs of oil and gas occur at several stratigraphic intervals and comprise 5 principal plays: CAM – structural and stratigraphic traps in Cambrian sandstones and sandy dolomites; ORD – hydrothermal dolomite reservoirs in Upper Ordovician limestones of the Trenton Group and Black River Group; CLI – stratigraphic traps in Lower Silurian sandstones and associated carbonates, including the Irondequoit, Reynales, Thorold, Grimsby and Whirlpool formations; SAL – reefs and structural traps in Lower Silurian Lockport Group carbonates and associated carbonates of the Salina A-1 Carbonate and Salina A-2 Carbonate; and DEV – structural traps in Devonian fractured, dolomitized carbonates and sandstones, including the Dundee and Lucas formations and the Columbus Member of the Lucas Formation (Lazorek and Carter, 2008; Carter et al., 2016). Samples were obtained for this study from all the major gas-bearing strata.

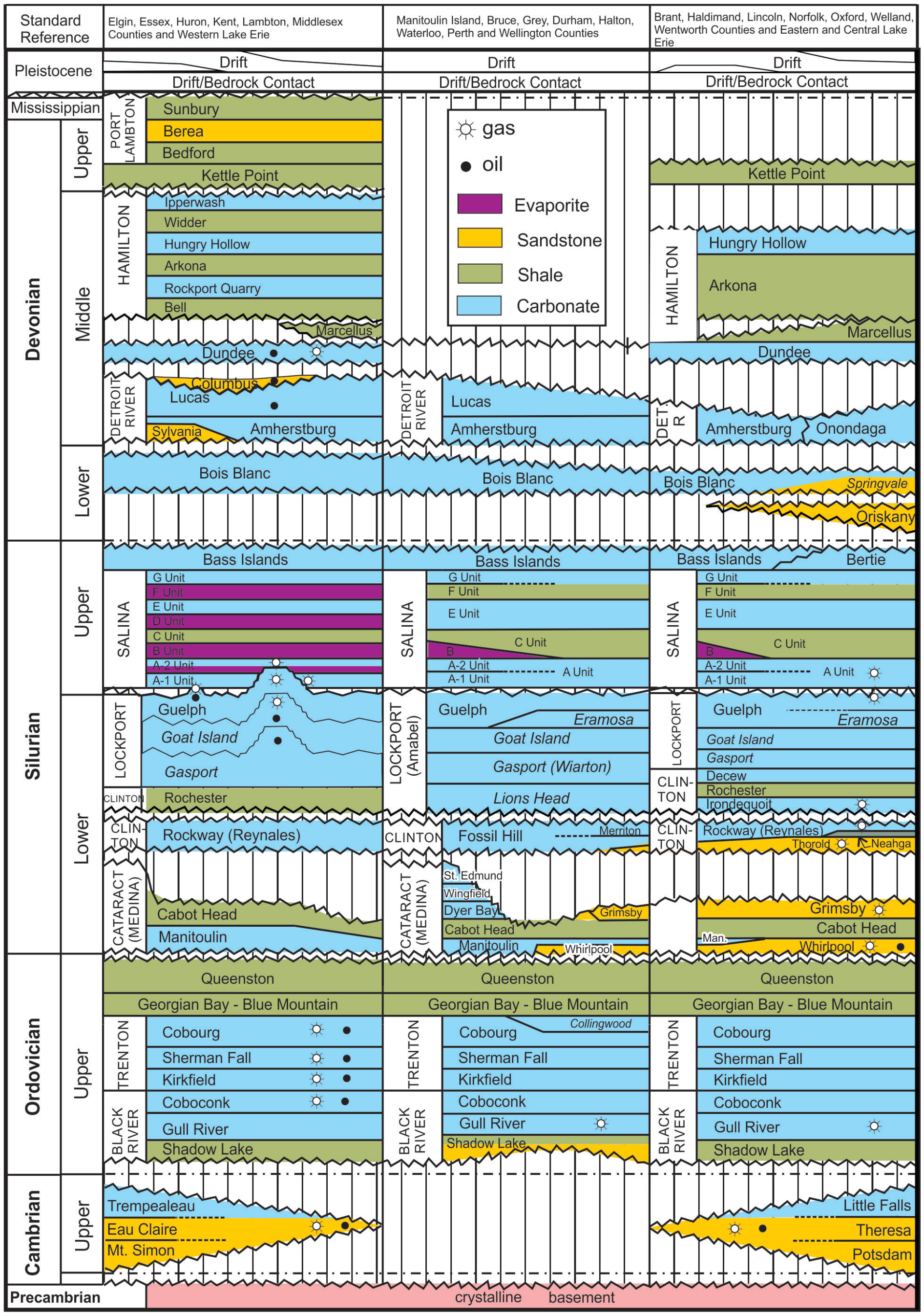


Figure 2. Paleozoic bedrock stratigraphy of southern Ontario showing principal oil and gas producing intervals. Modified from Armstrong and Carter (2010).

Sampling and Methodology

Gas samples were collected from active well heads using clean, evacuated 0.5 L stainless steel outage sampling tubes fitted with Swagelok® valves and appropriate connectors. The sampling tubes were flushed for 5-15 min to ensure full equilibration with the reservoir gases. Gas pressure at the wellhead was also noted to ensure safe handling of the sample during and following its collection. Once in the laboratory, representative and equilibrated aliquots of the gas sample were transferred to an evacuated Exetainer®, which was then attached to the Agilent 6890 Gas Chromatography - Combustion – Thermo Scientific Delta^{Plus} Isotope Ratio Mass Spectrometer (GC-C-IRMS) system for carbon- and hydrogen-isotope analysis. Following cryogenic cleaning to remove extraneous H_2O, the gases were then condensed on a 13 nm molecular sieve. Gases were then released from the sieve by heating, and swept using He through a Poraplot Q GC capillary column at 30°C (with subsequent ramping to 120°C for C-isotopes, when required). The eluting gases were then passed through (i) a CuNiPt combustion reactor (set at 940°C), which served to convert any hydrocarbon species to CO_2 for carbon-isotope analysis, and (ii) through a hollow ceramic pyrolysis reactor (set at 1420°C), to crack hydrocarbons, thus producing H_2 for hydrogen-isotope analysis. Reported results typically reflect the average of three (range 2-5) analyses per sample for each of the carbon and hydrogen isotope compositions of each gas phase measured.

The stable isotope results are expressed in the standard δ-notation relative to VPDB for carbon and VSMOW for hydrogen. Values for carbon-isotope internal standards for carbon dioxide, methane, ethane and propane were established against NBS 19-calibrated NIST natural gas standards RM8559 (formerly NGS1) and RM8560 (formerly NGS2), based on average values first reported by Hut (1987) and revised and collated by NIST (2007). The values measured for $\delta^{13}C_{CO2}$ (–44.3±0.5 ‰, SD, n=72), $\delta^{13}C_{CH4}$ (–43.5±0.5 ‰, SD, n=70), $\delta^{13}C_{C2H6}$ (–30.9±0.4 ‰, SD, n=71) and $\delta^{13}C_{C3H8}$ (–25.0±0.3 ‰, SD, n=64) compare well with the accepted values of –44.3, –44.0, –30.8, and –25.0 ‰, respectively (Potter et al., 2013). For samples, individual analyses were typically reproducible to ±0.2 ‰ (SD) for methane, ethane and propane, ±0.8 ‰ (SD) for n-butane, and ±0.7 ‰ for i-butane (methyl propane). Reproducibility for carbon dioxide samples was poorer, ±1.7 ‰ (SD).

Sample hydrogen-isotope compositions were established using two internal standards (EI-7, ethane; EIL-8, methane) originally provided by the University of Waterloo and NIST natural gas standard RM8560 methane (formerly NGS2), all of which had been calibrated to the VSMOW-SLAP scale. Values of EIL-7 δ^2H_{C2H6} (–324±3 ‰, SD, n=65), EIL-8 δ^2H_{CH4} (–65±3 ‰, SD, n=61) and RM8560 δ^2H_{CH4} (–173±6 ‰, SD, n=32) compare well with accepted values of–325±3 ‰ for EIL-7 (Environmental Isotope Laboratory, University of Waterloo, as reported in Potter and Longstaffe, 2007), –65 ±3 ‰ for EIL-8 (Environmental Isotope Laboratory, University of Waterloo, as reported in Potter and Longstaffe, 2007), and –174±3 ‰ for RM8560 (Potter and Siemann, 2004; originally –172.5±3 ‰ in Hut, 1987). For samples, individual analyses were typically reproducible to ±2 ‰ (SD) for both methane and ethane.

The $C_1/(C_2+ C_3)$ gas ratios were calculated from peak area responses recorded by the IRMS using NIST natural gas standards RM8559 (formerly NGS1) and RM8560 (formally NGS2). The following Accepted volume % values were used, following NIST (2007):

	Methane	Ethane	Propane
RM8559	81.238	2.832	0.387
RM8560	52.775	2.650	1.290

Results and Discussion

This section presents the geochemical results obtained in this study (alongside those of Mohd-Zaffa, 2010), on a formation-by-formation basis. Sample locations are illustrated in Appendix A, Map 1; additional sample location information is summarized in Appendix A, Table A1.

Overall, the natural gases in Southwestern Ontario show a wide range in isotopic compositions, often overlapping considerably with other formations (Figs. 3 & 4). Some of this variation is driven by regional differences within formations, which must be taken into account when attempting to trace the source(s) of unknown gas samples. However, each formation has certain distinctive characteristics that help set it apart from the others. These characteristics are presented in the following subsections. The gases are predominantly of thermogenic origin, although some of the Silurian units (Guelph, Salina A-1) show significant contributions of bacterial methane.

In terms of the natural gas concentrations (normalized to 100%), methane ranges from 77.1–94.9% across all formations; ethane varies from 3.9–13.0% and propane, 1.1-9.9%. The gas wetness ratio, $C_1/(C_2+C_3)$, varies from 3.4–18.6%. Apart from the Thorold and Grimsby Formations, there is generally quite a high degree of variability and overlap between the compositions of the various formations, and little correlation between the gas concentrations and isotope compositions (Fig. 5).

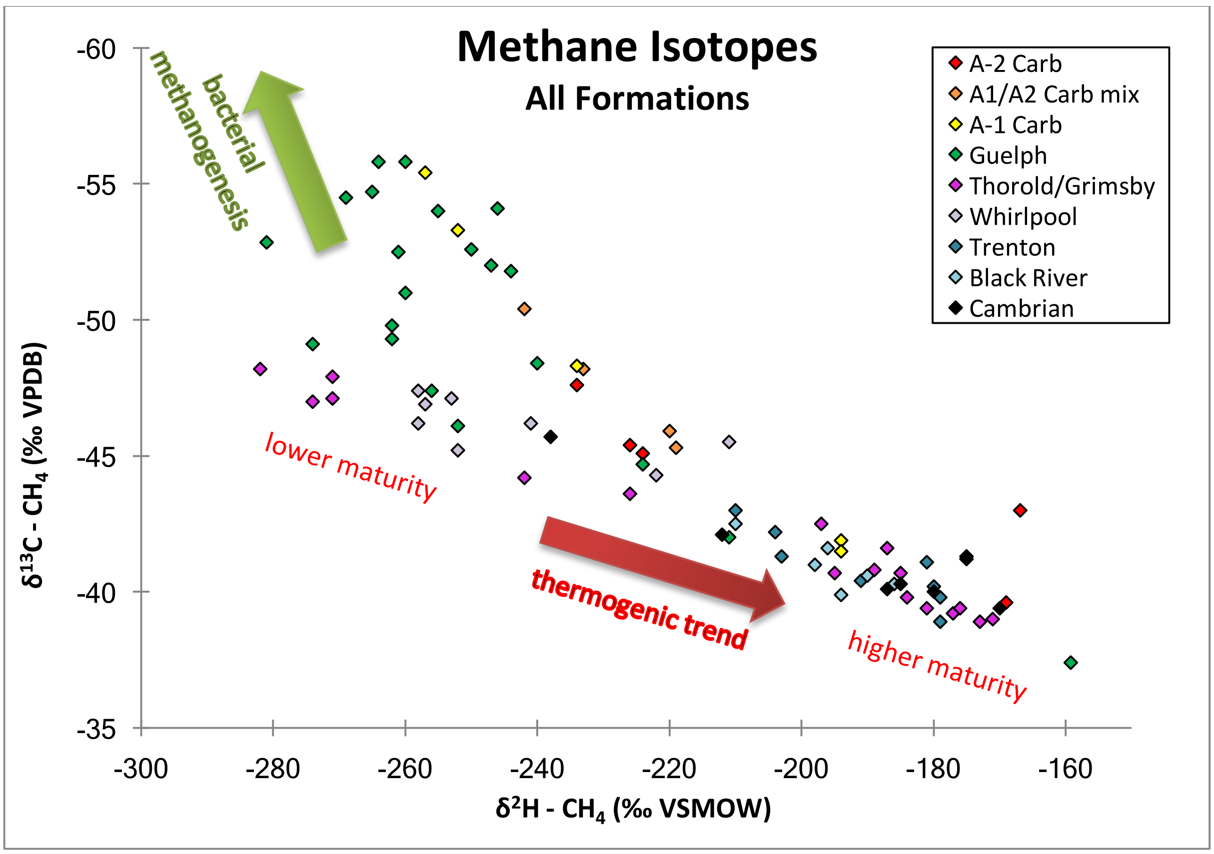


Figure 3: Methane $\delta^{13}C$ *vs.* $\delta^{2}H$ for all samples considered in this study.

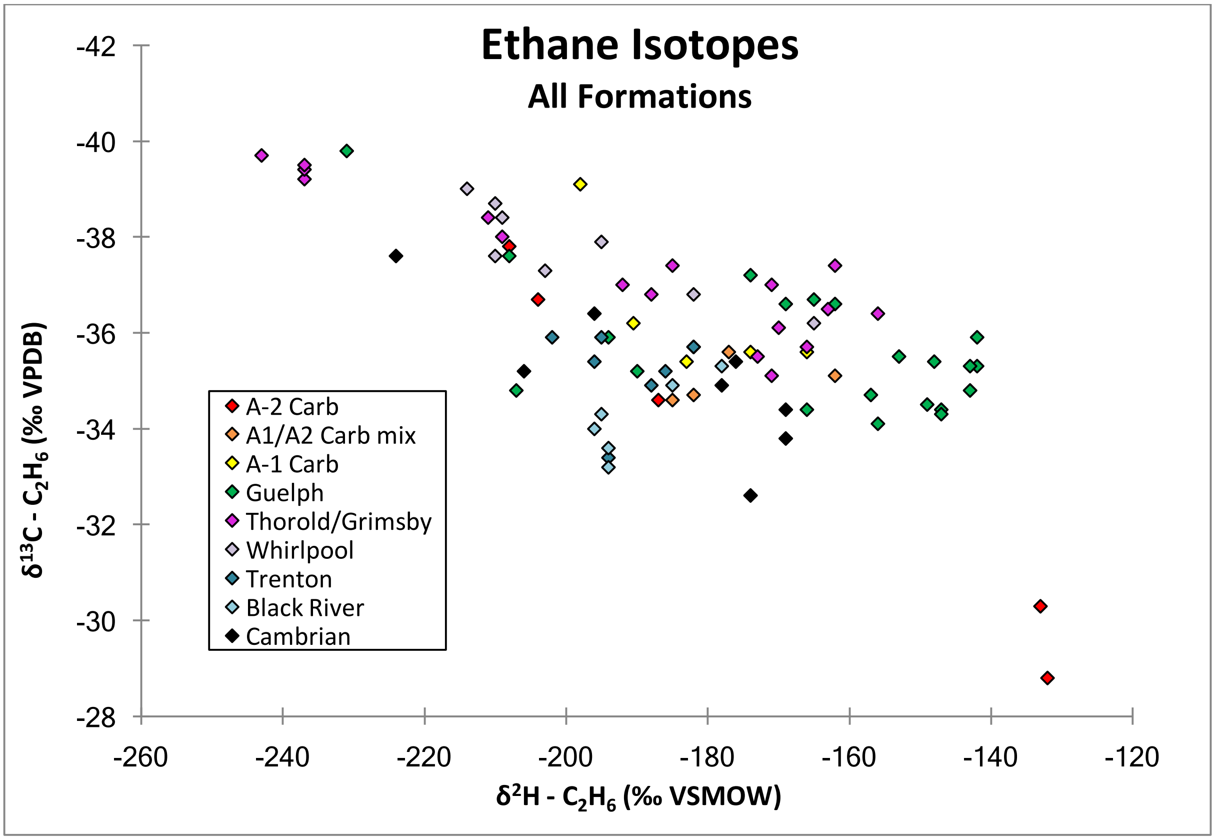


Figure 4: Ethane δ^{13}C *vs.* δ^{2}H for all samples considered in this study.

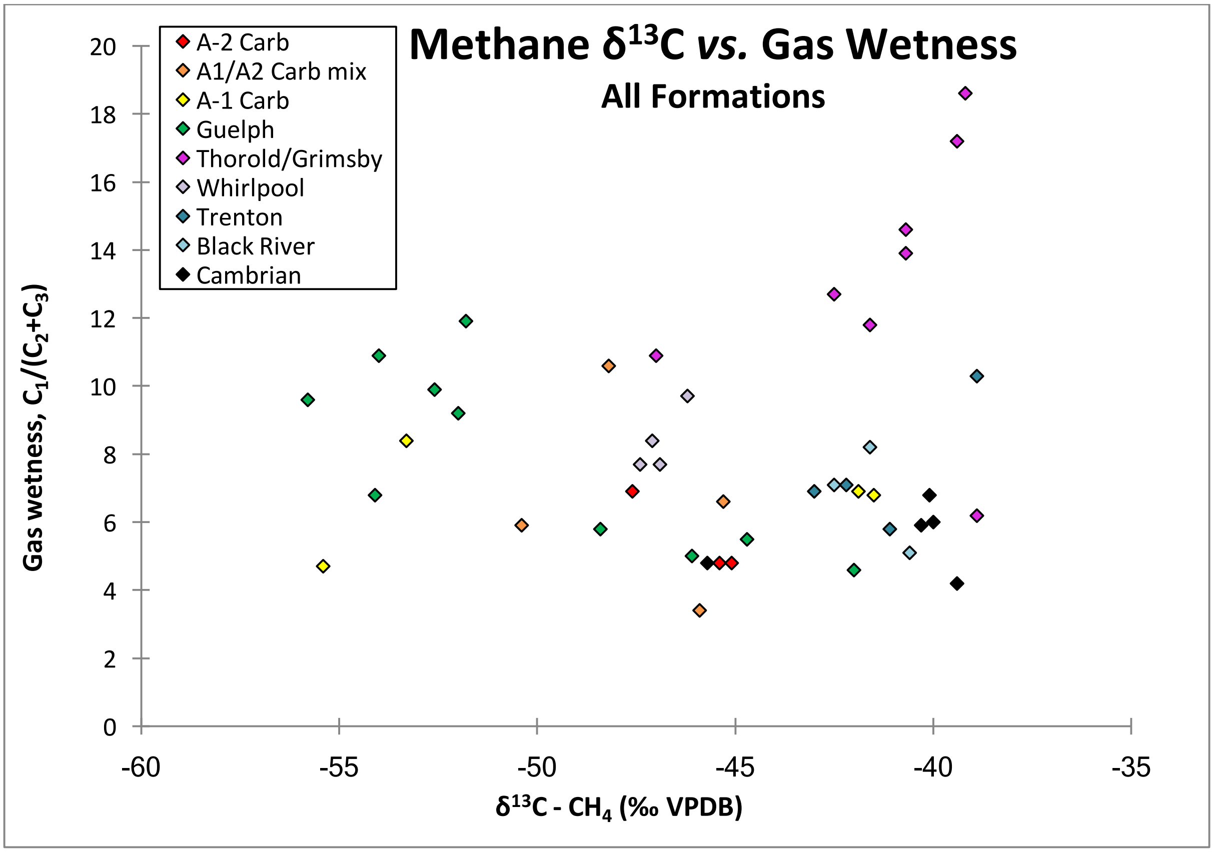


Figure 5: Methane δ^{13}C *vs.* gas wetness for all samples considered in this study.

Salina Group

Well No.	Well Location	County	Pool	Producing Formation	$\delta^{13}C$ CH_4	$\delta^{13}C$ C_2H_6	$\delta^{13}C$ C_3H_8	$\delta^{13}C$ i-C_4H_{10}	$\delta^{13}C$ n-C_4H_{10}	δ^2H CH_4	δ^2H C_2H_6	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	Wetness - $C_1/(C_2+C_3)$
T003560	Sombra 2-26-VII	Lambton	Charlemont	A-2 Carb	–47.6	–37.8	–32.5	-	-	–234	–208	87.3	8.2	4.5	6.9
T008990	Dawn 7-24-VI	Lambton	Dawn 1	A-2 Carb	–45.1	–34.6	–32.4	–30.4	–32.1	–224	–187	82.9	10.8	6.3	4.8
T007498	Camden 2-10-IXGC	Kent	Camden 6-10 Gore	A-2 Carb	–45.4	–36.7	–33.7	–31.8	–33.8	–226	–204	82.8	11.2	6.0	4.8
T008636	Howard 5-94-BFC	Kent	Morpeth	A-2 Carb	–43.0	–30.3	–28.0	-	-	–167	–133	-	-	-	-
T008638	Howard 8-93-STR	Kent	Morpeth	A-2 Carb	–39.6	–28.8	–27.2	-	-	–169	–132	-	-	-	-
T008864	Dawn 7-24-IX	Lambton	Dawn 1	A-1 + A-2 Carb (mix)	–50.4	–35.1	–30.2	–29.2	-	–242	–162	85.5	9.2	5.3	5.9
T008837	Dawn 6-21-II	Lambton	Dawn Misc	A-1 + A-2 Carb (mix)	–48.2	–34.7	–30.9	-	-	–233	–182	91.4	5.9	2.7	10.6
T008997	Dawn 2-24-VII	Lambton	Dawn 1	A-1 + A-2 Carb (mix)	–45.9	–35.6	–32.8	–30.3	–32.2	–220	–177	77.1	13.0	9.9	3.4
T008906	Camden 1-4-VIIGC	Kent	Camden Gore	A-1 + A-2 Carb (mix)	–45.3	–34.6	–32.6	-	–32.2	–219	–185	86.8	8.8	4.4	6.6
T008535	Enniskillen 1-24-II	Lambton	Enniskillen 1-24-II	A-1 Carb	–48.3	–36.2	–31.7	–27.3	–29.4	–234	–191	-	-	-	-
T007848	Moore 4-51-FC	Lambton	Moore 5-50 Front	A-1 Carb	–53.3	–39.1	–32.8	–27.2	-	–252	–198	89.4	6.3	4.3	8.4
T008611	Sombra 11-VI	Lambton	Becher West	A-1 Carb	–55.4	–35.6	–30.2	–28.8	–31.8	–257	–166	82.5	9.9	7.6	4.7
T008634	Howard 1-9-BLC	Kent	Botany	A-1 Carb	–41.9	–35.6	–32.3	–29.5	–31.3	–194	–174	87.4	8.8	3.8	6.9
T008633	Howard 7-7-I	Kent	Botany	A-1 Carb	–41.5	–35.4	–32.4	–31.9	–32.1	–194	–183	87.1	9.1	3.8	6.8

Table 1: Natural gas data for the Salina Group (δ-values in units of ‰ relative to VPDB for carbon and VSMOW for hydrogen). Results for sample names shown in **BOLD** are from Mohd Zaffa (2010).

The data for gases from the Upper Silurian Salina Group are presented in Table 1 and illustrated in Figure 6A-E. Sample locations are shown in Appendix A, Maps 1 & 2. Overall, the Salina Group has a wide range of isotopic compositions, with $\delta^{13}C_{CH4}$ varying from –55.4 to –39.6‰; $\delta^{13}C_{C2H6}$ from –39.1 to –28.8‰; $\delta^{13}C_{C3H8}$ from –32.8 to –27.2‰; $\delta^{13}C_{n\text{-}C4H10}$ from –31.9 to –27.2‰; $\delta^{13}C_{i\text{-}C4H10}$ from –33.8 to –29.4‰; $\delta^{2}H_{CH4}$ from –257 to –167‰; and $\delta^{2}H_{C2H6}$ from –208 to –132‰. Gas concentrations range from 77.1–91.4% for methane; 5.9–13.0% ethane; and 2.7–9.9% propane, with gas wetness ratios varying from 3.4–10.6.

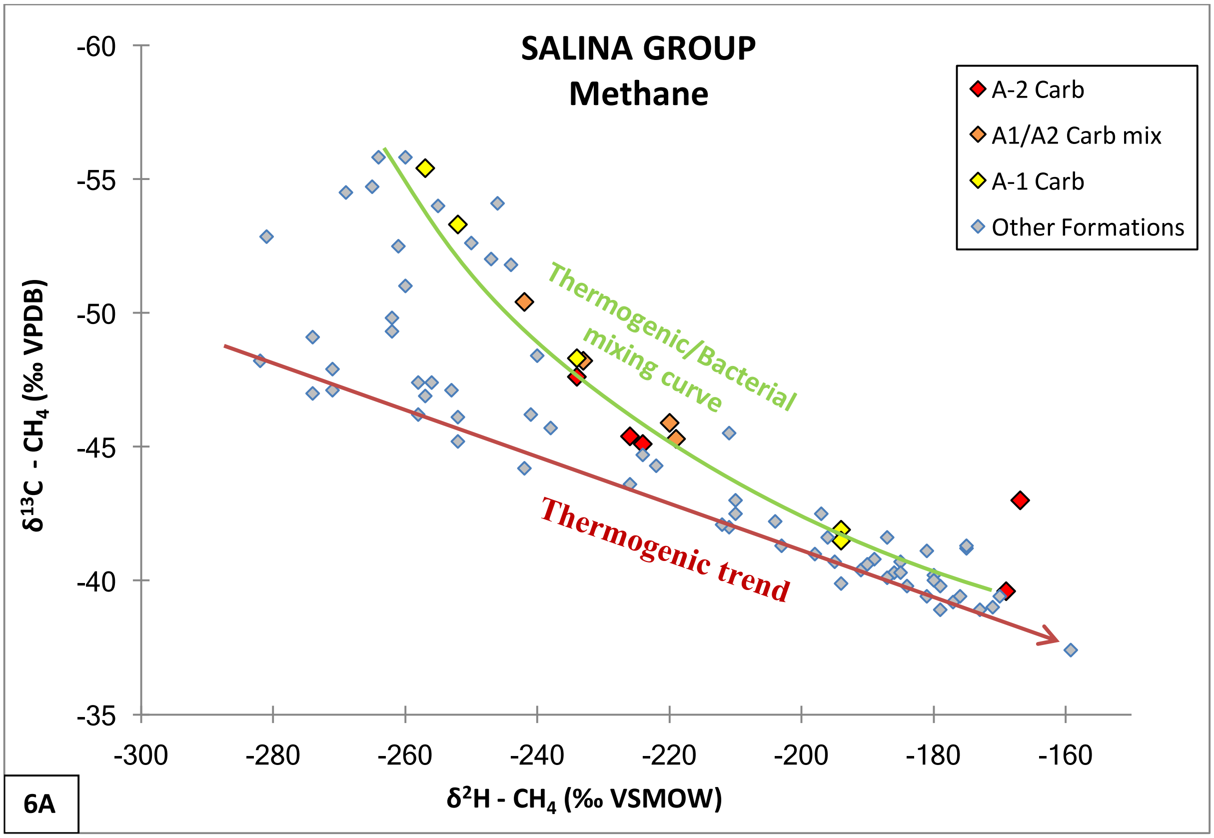
The Salina Group's isotopic compositions appear to vary from bacterial methane to very mature thermogenic gas, with intermediate compositions likely reflecting mixtures thereof. The two most thermogenically-mature samples are from wells on the shore of Lake Erie, on the Appalachian side of the Algonquin Arch, suggesting that this mature gas may have migrated up-dip from deeper in the Appalachian Basin. The next two most mature samples are near the crest of the arch, and all bacterially generated samples are on the Michigan side of the Algonquin Arch, providing further support for this theory. The bacterial methane may have been generated locally in the Salina or the underlying Guelph Formation, or have migrated in from the Michigan Basin; the latter possibility is perhaps suggested by samples with the lowest δ-values being located furthest west (closest to the Michigan Basin). Ultimately, while the A-1 and A-2 carbonate units do span different (although overlapping) isotopic ranges, it is unlikely that there is actually any significant isotopic differentiation between them, since the compositions of both units appear to be predominantly controlled by the proportions of the two gas end-members (bacterial and thermogenic), which in turn appears to be predominantly controlled by the sample's geographical position on the arch, rather than the stratigraphic unit within the Salina Group. There is no clear geochemical fingerprint for differences between gases from the A-1 versus A-2 units.

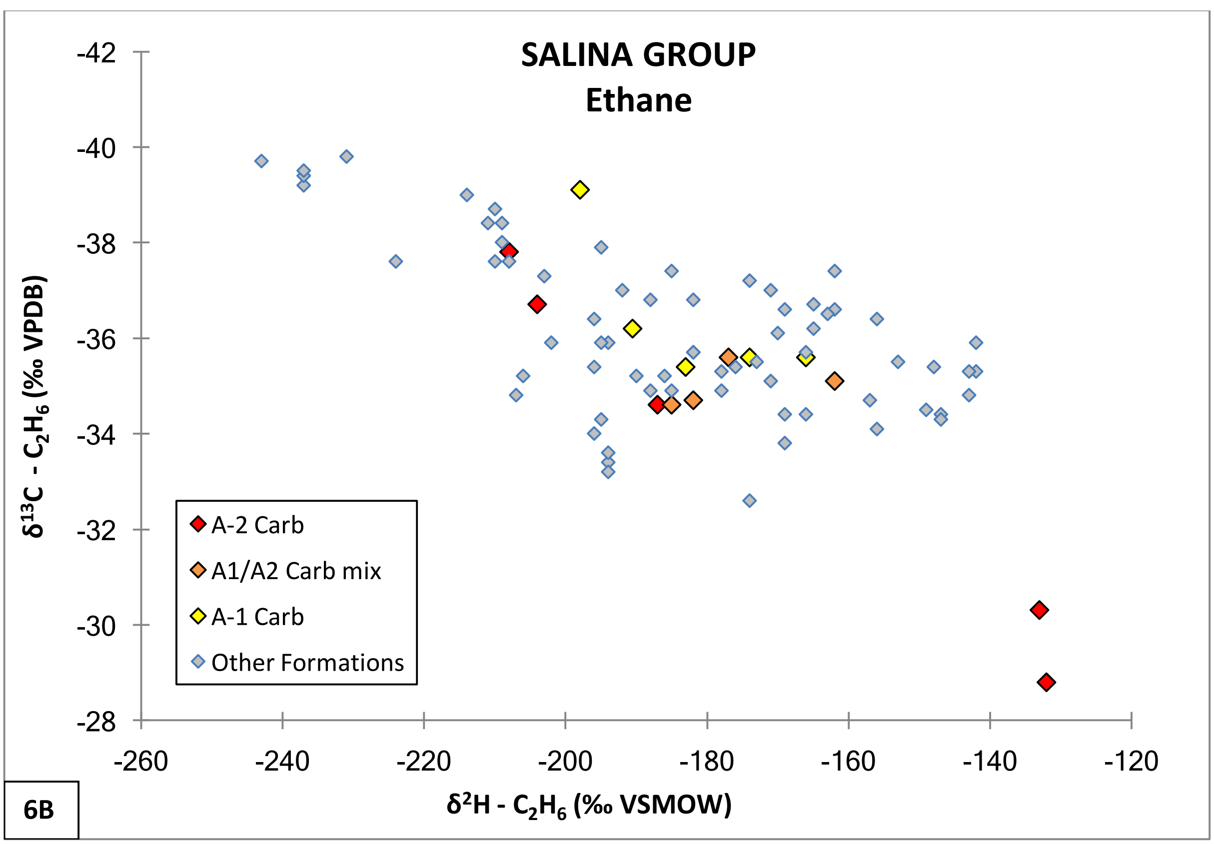
When attempting to determine the source of an unknown gas sample that could potentially contain Salina gas, one must therefore first estimate the local Salina composition, by interpolation from the available samples, based on the position of the well on the Algonquin Arch. Once that composition is determined, the ease of differentiation between it and that of other formations depends on the local Salina composition. On the western side of the Algonquin Arch, bacterial methane-dominated Salina gas has methane $\delta^{13}C$ and $\delta^{2}H$ compositions indistinguishable from those of the Guelph Formation in Lambton County (possibly also in the other western counties, but no Salina data are available) – possibly suggesting a common methane source. However, it does appear to be distinct on the basis of the ethane and propane isotopes – Salina $\delta^{13}C_{C2H6}$ (in Lambton County) ranges from –39.1 to –34.7 ‰, and $\delta^{13}C_{C3H8}$ from –32.8 to –30.2‰. In this area, the Guelph ethane and propane are slightly but distinctly higher, with $\delta^{13}C_{C2H6}$ ranging from –35.5 to –34.1‰, and $\delta^{13}C_{C3H8}$ from –31.2 to –28.0‰ (average –28.9‰), excepting two Enniskillen samples with more thermogenic signatures (which would be distinct from the Salina based on the methane $\delta^{13}C$ and $\delta^{2}H$). Methane, however, readily differentiates the Salina gases in this area from the Cambro-Ordovician gases based on their much lower isotopic signatures (being bacterial rather than thermogenic). They are also distinct from the Clinton-Cataract Group gases, which while they have overlapping $\delta^{2}H_{CH4}$ ranges, the bacterial Salina $\delta^{13}C_{CH4}$ is much lower than the (low-maturity) thermogenic Clinton-Cataract gases (although the Clinton-Cataract reservoirs are on the other side of the Algonquin Arch, and so there should be no question of attempting to differentiate them).

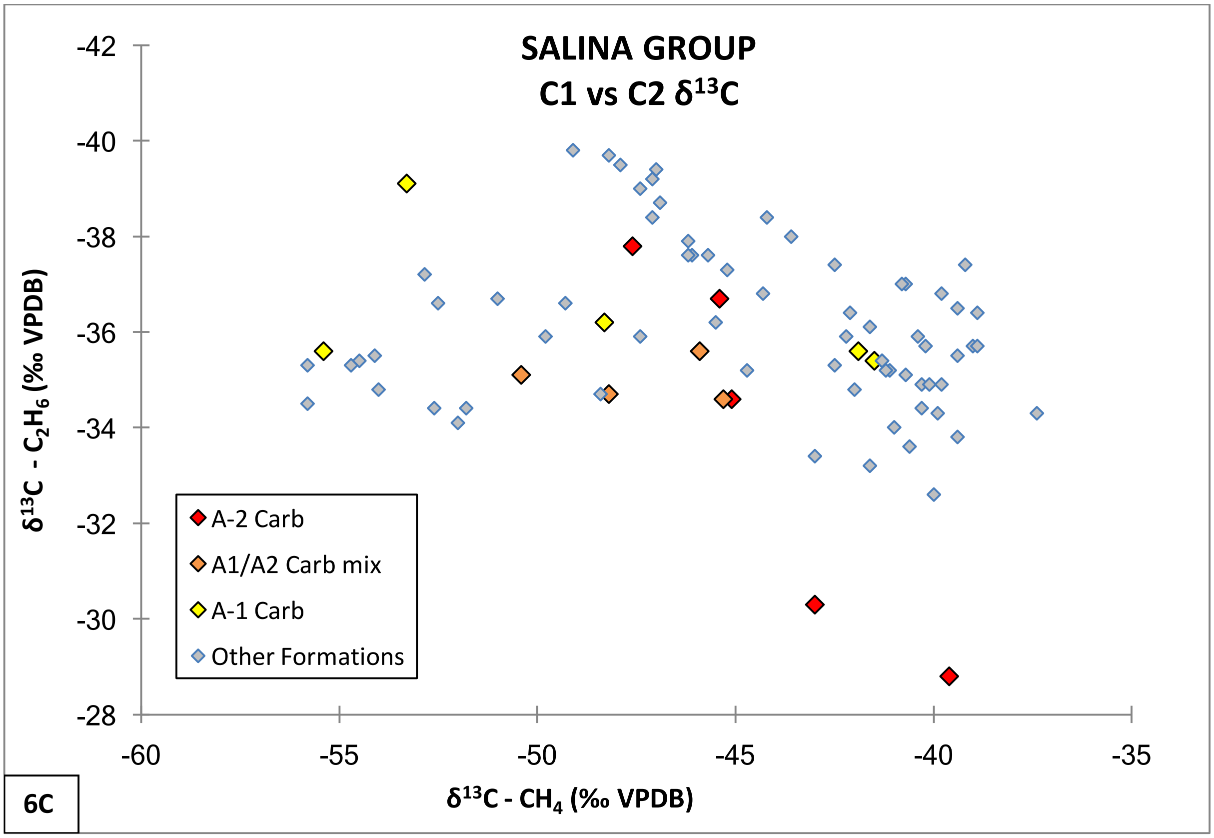
On the far eastern side of the Algonquin Arch, thermogenic Salina gas should be readily distinguishable from the thermogenic gases of the deeper formations based also on its ethane and propane isotopes. The two Salina samples from the Morpeth pool in Kent have conspicuously higher $\delta^{13}C$ and $\delta^{2}H$ than all other samples: –30.3 and –28.8‰ $\delta^{13}C_{C2H6}$; –28.0 and –27.0‰ $\delta^{13}C_{C3H8}$; –167 and –169‰ $\delta^{2}H_{CH4}$; and –132 and –133‰ $\delta^{2}H_{C2H6}$. It is unclear why these values are different from the other thermogenic gases.

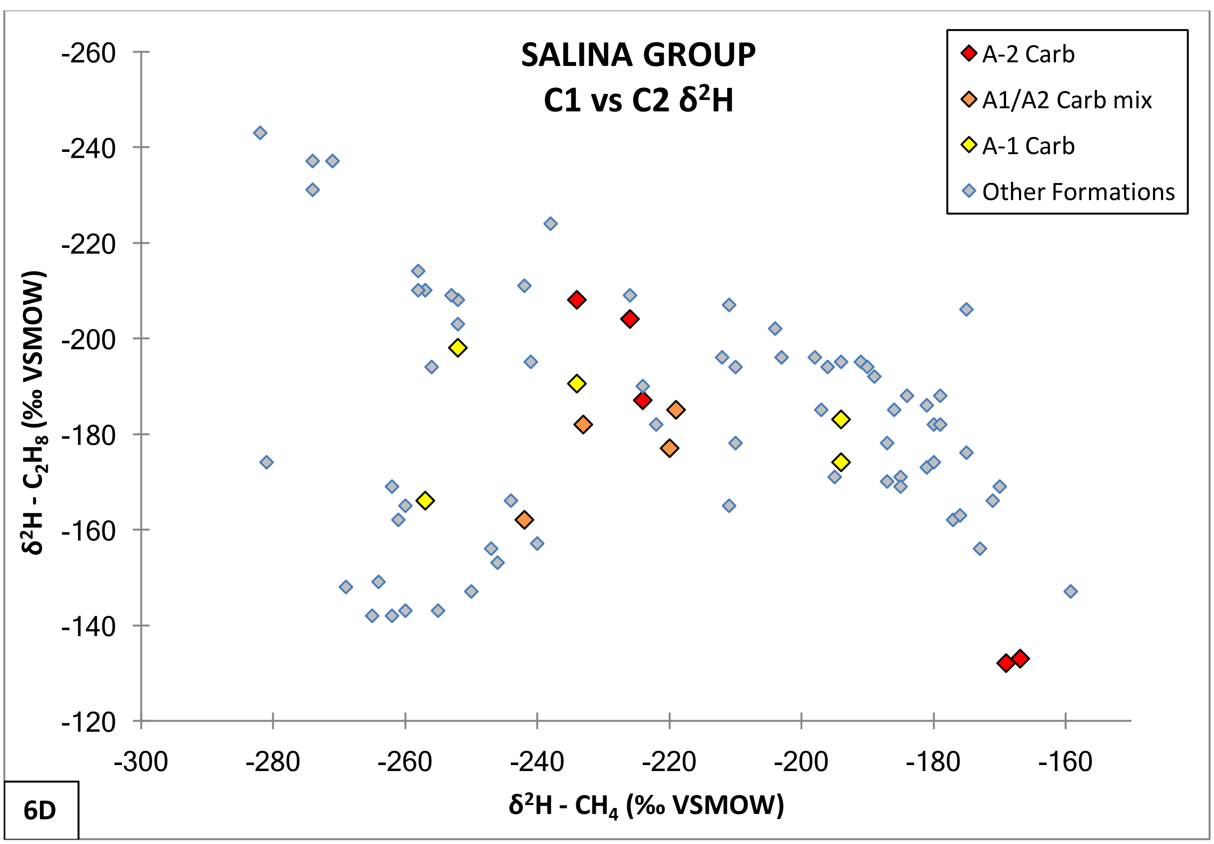
Samples between the geographical extremes of the area have intermediate compositions. They are partially differentiated from the deeper formations based on their methane isotopes, falling along a mixing curve between the thermogenic and bacterial end-members. This mixing curve plots distinctively above the general thermogenic trend on a methane $\delta^{13}C$–$\delta^{2}H$ plot (Fig. 6A).

In general, all Salina samples are also distinct from all gases below the Guelph Formation, on the basis of butane $\delta^{13}C$ isotopes – more specifically, the difference between $\delta^{13}C_{n\text{-}C4H10}$ and $\delta^{13}C_{i\text{-}C4H10}$ (or $\Delta^{13}C_{n\text{-}C4H10\,-\,i\text{-}C4H10}$). For almost all Salina samples, this difference is slightly negative (i.e., n-C_4H_{10} has lower $\delta^{13}C$ than i-C_4H_{10}), whereas all but a few sub-Guelph gases have positive $\Delta^{13}C_{n\text{-}C4H10\,-\,i\text{-}C4H10}$. This characteristic is noticeable on the Chung diagram in Figure 6E.


SALINA GROUP
Methane
A-2 Carb
A1/A2 Carb mix
A-1 Carb
Other Formations
Thermogenic/Bacterial mixing curve
Thermogenic trend
δ13C - CH4 (‰ VPDB)
δ2H - CH4 (‰ VSMOW)
-60
-55
-50
-45
-40
-35
-300
-280
-260
-240
-220
-200
-180
-160
6A


SALINA GROUP
Ethane
A-2 Carb
A1/A2 Carb mix
A-1 Carb
Other Formations
δ13C - C2H6 (‰ VPDB)
δ2H - C2H6 (‰ VSMOW)
-42
-40
-38
-36
-34
-32
-30
-28
-260
-240
-220
-200
-180
-160
-140
-120
6B


SALINA GROUP
C1 vs C2 δ13C
δ13C - C2H6 (‰ VPDB)
δ13C - CH4 (‰ VPDB)
A-2 Carb
A1/A2 Carb mix
A-1 Carb
Other Formations
-42
-40
-38
-36
-34
-32
-30
-28
-60
-55
-50
-45
-40
-35
6C


SALINA GROUP
C1 vs C2 δ2H
δ2H - C2H8 (‰ VSMOW)
δ2H - CH4 (‰ VSMOW)
A-2 Carb
A1/A2 Carb mix
A-1 Carb
Other Formations
-260
-240
-220
-200
-180
-160
-140
-120
-300
-280
-260
-240
-220
-200
-180
-160
6D

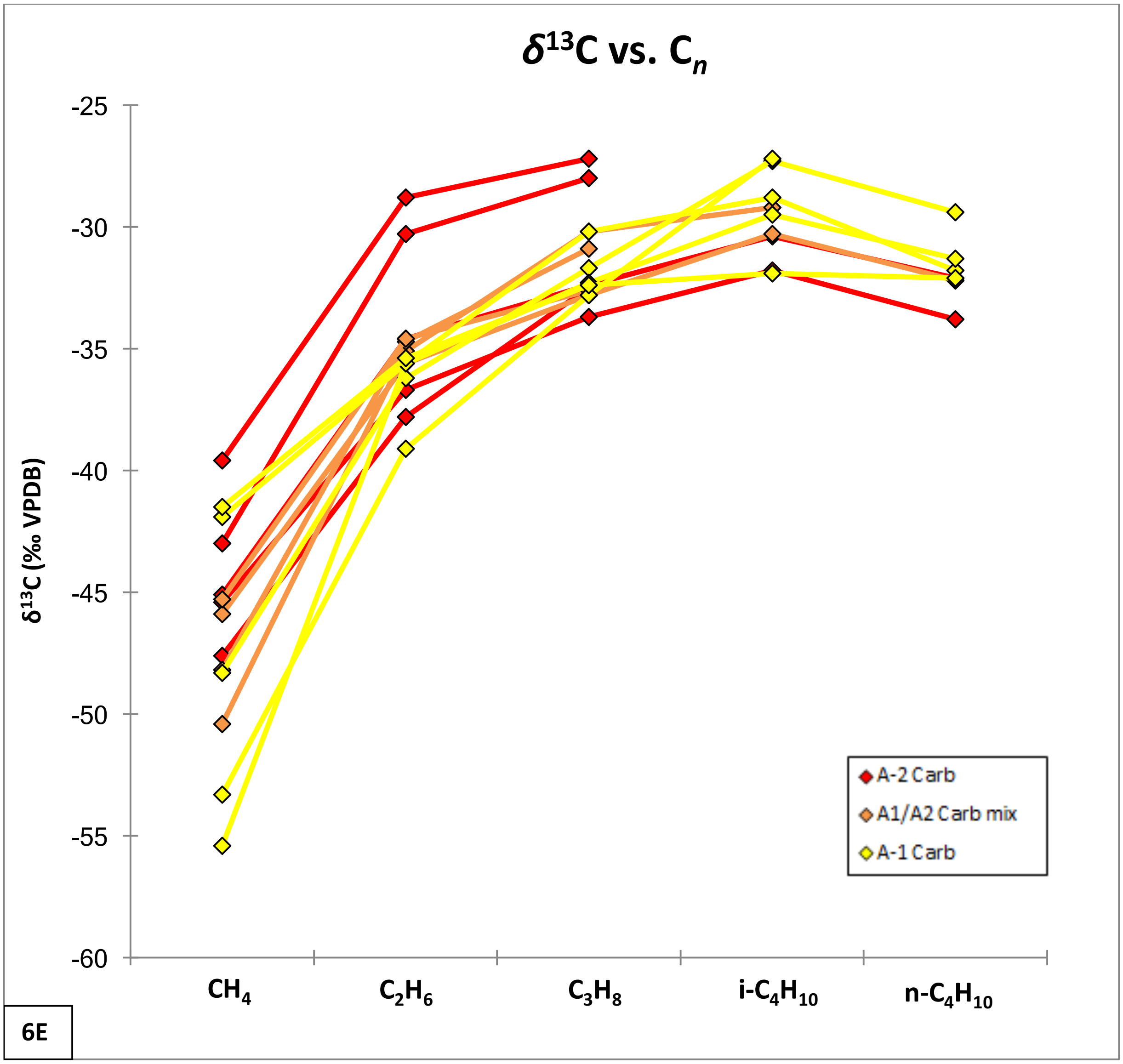


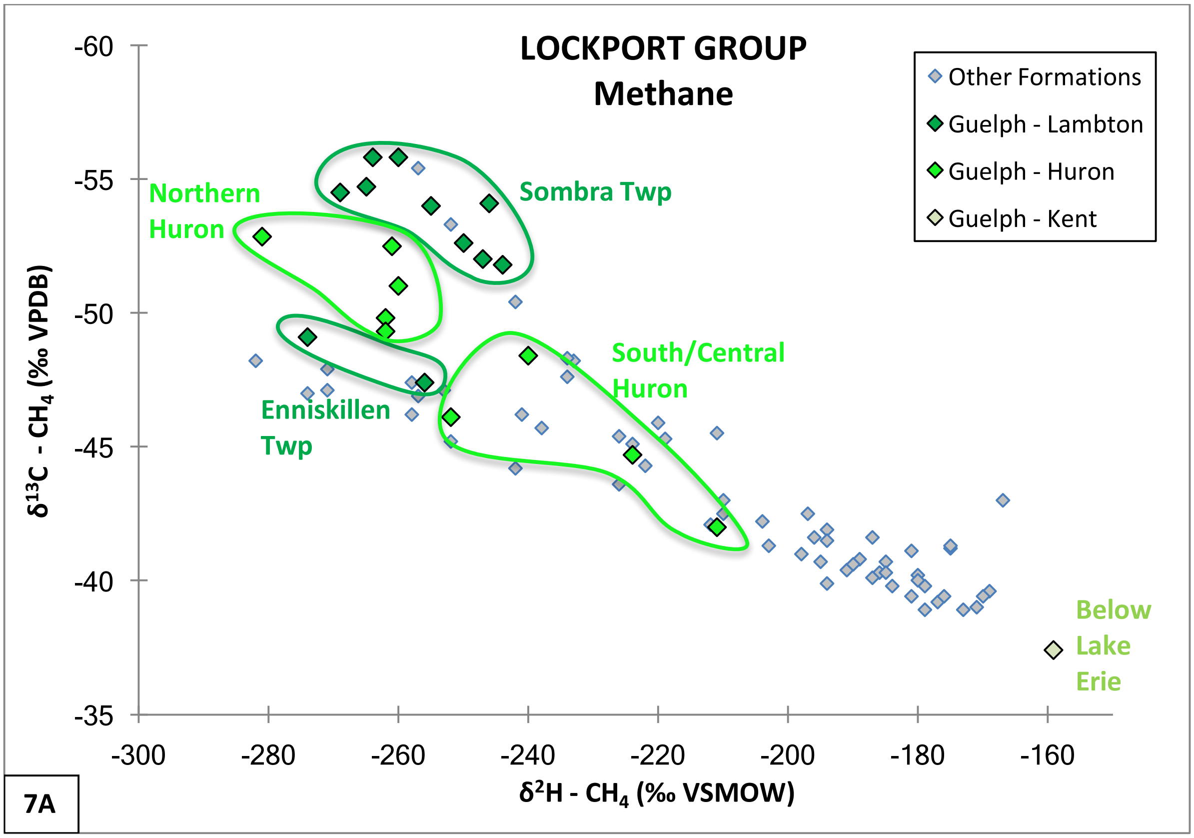
Figure 6: Isotopic compositions of gases from Salina Group units. **A** – methane δ^{13}C *vs.* δ^{2}H; **B** – ethane δ^{13}C *vs.* δ^{2}H; **C** – methane δ^{13}C *vs.* ethane δ^{13}C; **D** – methane δ^{2}H *vs.* ethane δ^{2}H; **E** – Chung diagram of δ^{13}C *vs.* C_n (after Chung et al. 1988).

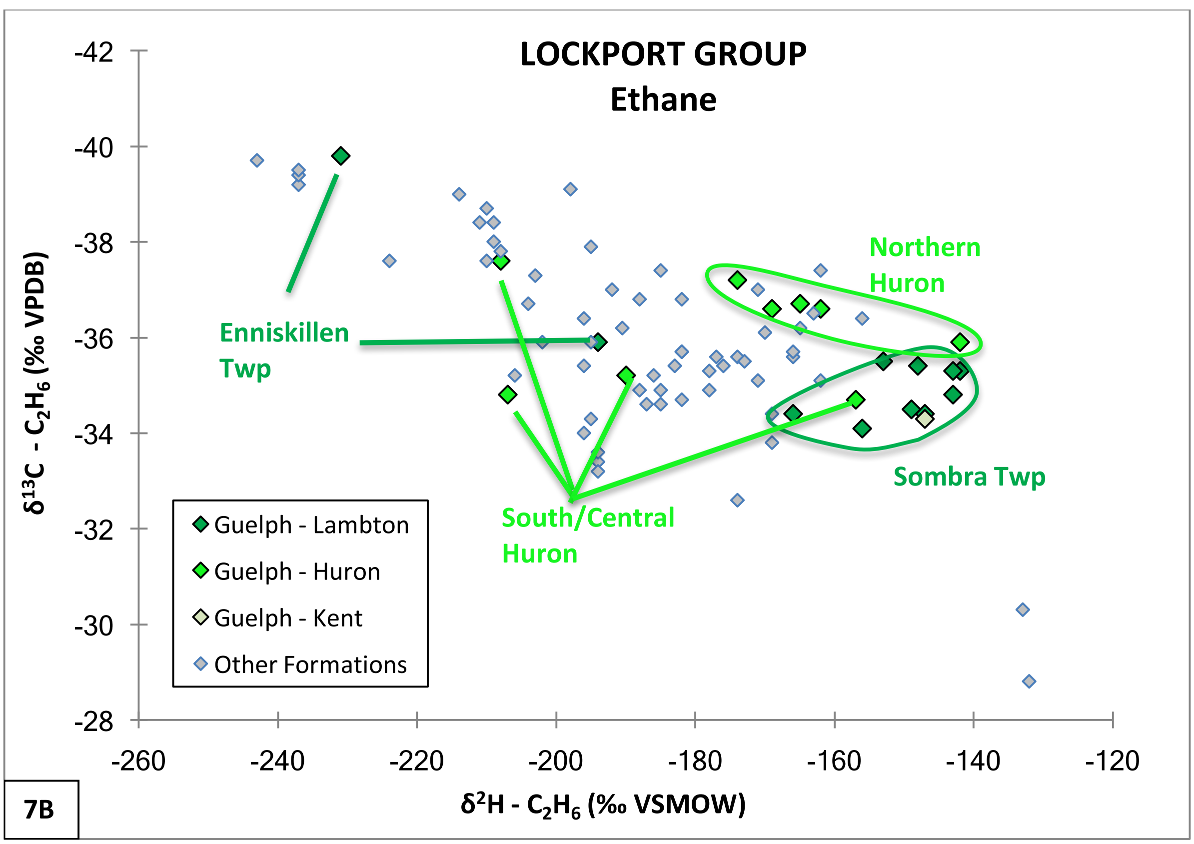
Lockport Group (Guelph Formation)

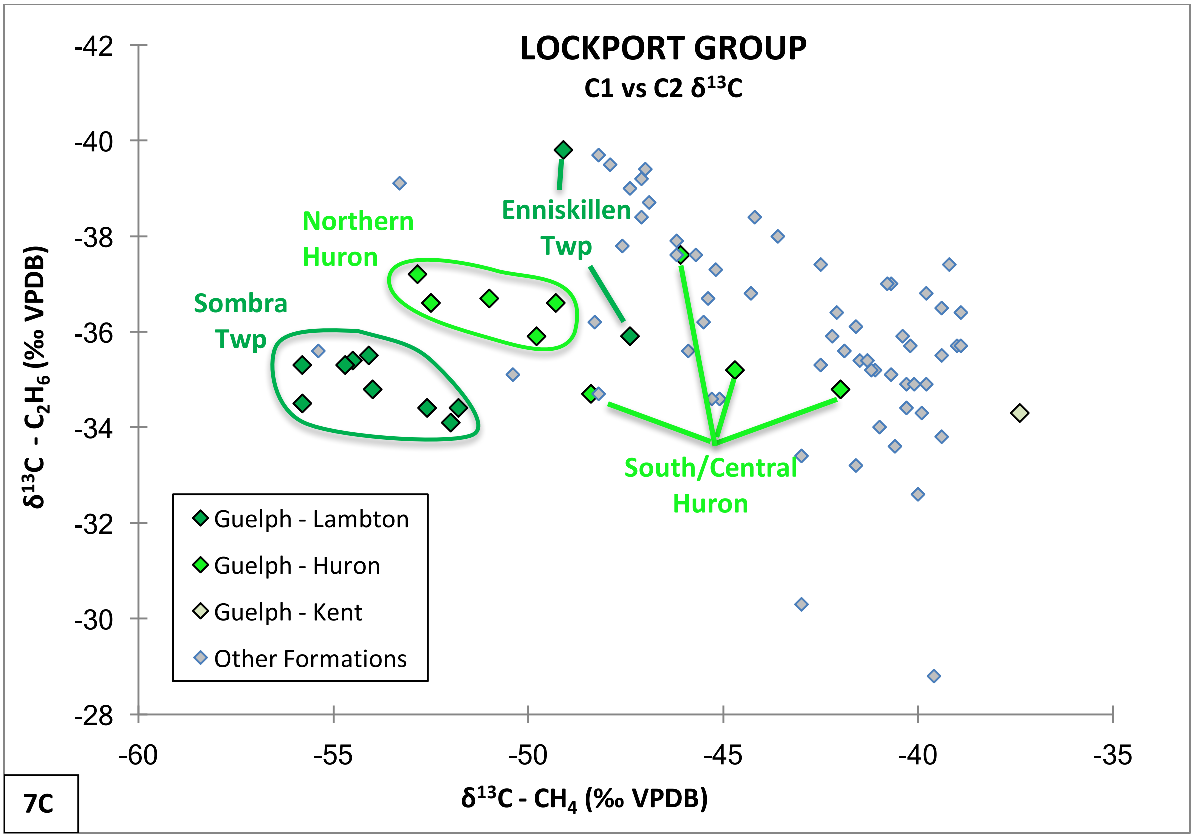
Well No.	Well Location	County	Pool	Producing Formation	$\delta^{13}C$ CH_4	$\delta^{13}C$ C_2H_6	$\delta^{13}C$ C_3H_8	$\delta^{13}C$ i-C_4H_{10}	$\delta^{13}C$ n-C_4H_{10}	δ^2H CH_4	δ^2H C_2H_6	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	Wetness - $C_1/(C_2+C_3)$
T002911	Sombra 3-24-VII	Lambton	Otter Creek E	Guelph	–51.8	–34.4	–29.1	-	-	–244	–166	92.2	5.3	2.5	11.9
T002890	Sombra 2-22-VII	Lambton	Otter Creek	Guelph	–52.0	–34.1	–28.5	-	-	–247	–156	90.2	6.4	3.5	9.2
T008617	Sombra 2-15-VI	Lambton	Becher West	Guelph	–54.1	–35.5	–31.2	–29.8	–32.2	–246	–153	87.2	8.0	4.8	6.8
T008804	Enniskillen 1-17-X	Lambton	Petrolia East	Guelph	–49.1	–39.8	–34.6	–30.6	–31.5	–274	–231	-	-	-	-
T008468	Enniskillen 2-15-VI	Lambton	Corey East	Guelph	–47.4	–35.9	–34.1	–29.8	–30.2	–256	–194	-	-	-	-
T003899	Sombra 5-17-XI	Lambton	Sombra 5-17-XI	Guelph	–54.5	–35.4	–29.1	–28.2	–27.4	–269	–148	-	-	-	-
T007243	Sombra 5-11-XII	Lambton	Sombra 5-11-XII	Guelph	–54.7	–35.3	–28.3	–27.1	–27.5	–265	–142	-	-	-	-
T010637	Sombra 8-24-VIII	Lambton	Sombra	Guelph	–52.6	–34.4	–28.7	-	-	–250	–147	90.8	5.8	3.3	9.9
T007316	Sombra 4-16-IX	Lambton	Sombra	Guelph	–54.0	–34.8	–28.6	-	-	–255	–143	91.6	5.6	2.9	10.9
T010395	Sombra 4-2-XIII	Lambton	Sombra	Guelph	–55.8	–34.5	–28.0	-	-	–264	–149	90.6	6.2	3.2	9.6
T010395	Sombra 4-2-XIII	Lambton	Sombra	Guelph	–55.8	–35.3	–28.8	–27.7	-	–260	–143	-	-	-	-
T004543	Lake Erie	Kent	Morpeth	Guelph	–37.4	–34.3	–29.4	-	-	–159	–147	-	-	-	-
T004918	Ashfield 8-1-IIIED	Huron	Ashfield 7-1-III	Guelph	–52.9	–37.2	–31.3	–30.1	–29.4	–281	–174	-	-	-	-
T011742	Ashfield 5-5-IXWD	Huron	?	Guelph	–49.8	–35.9	–30.9	–30.5	–28.7	–262	–142	-	-	-	-
T002235	W.Wawa. 6-17-VIII	Huron	Dungannon	Guelph	–52.5	–36.6	–30.8	–30.0	–28.4	–261	–162	-	-	-	-

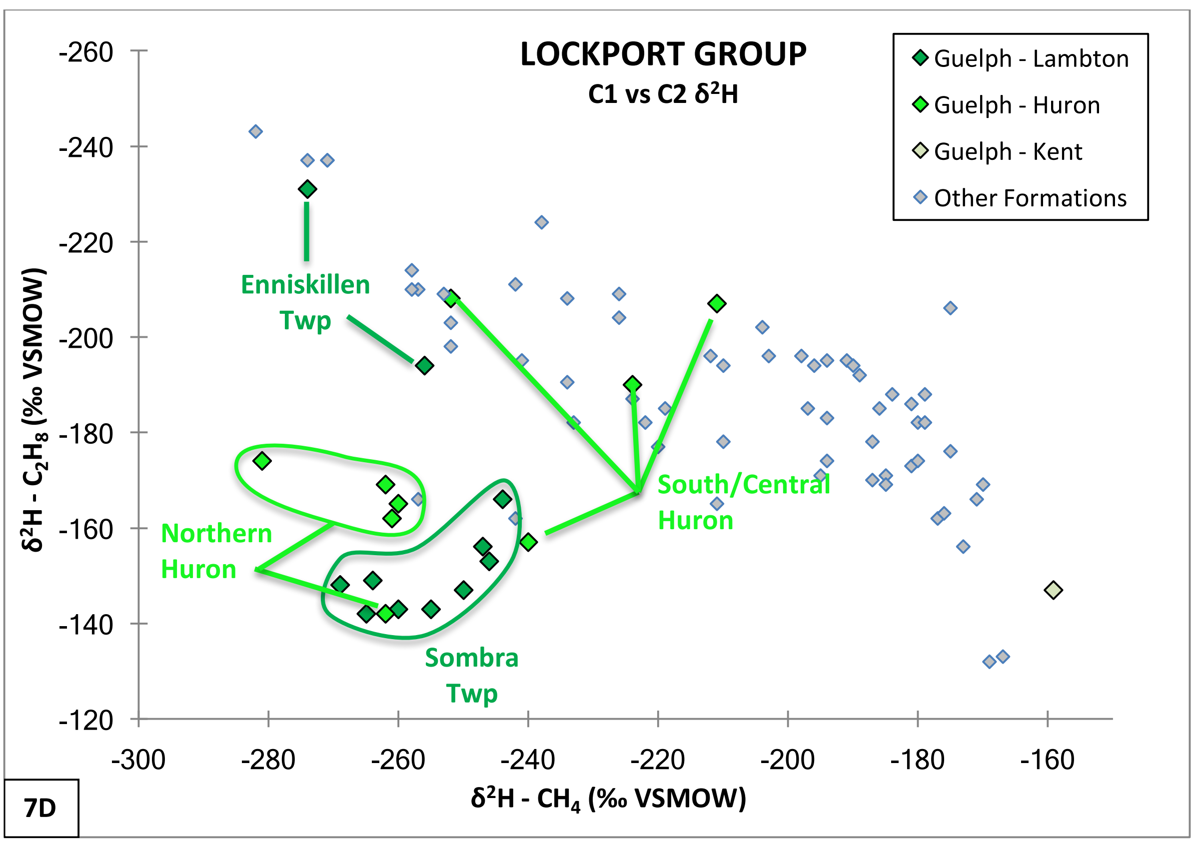
T002556	West Wawanosh	Huron	West Wawanosh	Guelph	–51.0	–36.7	–30.8	–29.9	–28.7	–260	–165	-	-	-	-
T011560	W.Wawa. 1-25-XIIWD	Huron	W.Wawa. 1-25-XII	Guelph	–49.3	–36.6	–30.7	–30.0	–28.5	–262	–169	-	-	-	-
T009602	Hay 2-11-XVI	Huron	Hay 5-12-XV	Guelph	–46.1	–37.6	–34.9	–34.1	–34.3	–252	–208	83.3	10.4	6.3	5.0
T010097	Stephen 3-22-XV	Huron	Hay 5-12-XV	Guelph	–42.0	–34.8	–32.6	–30.7	–31.2	–211	–207	82.3	10.3	7.4	4.6
T007415	Hay 3-23-XI	Huron	Zurich	Guelph	–48.4	–34.7	–29.5	–28.6	–27.9	–240	–157	85.4	9.1	5.5	5.8
T008657	Tuckersmith 2-30-IIISHR	Huron	Tuckersmith 30-III	Guelph	–44.7	–35.2	–32.2	–31.1	–30.9	–224	–190	84.7	9.5	5.8	5.5

Table 2: Natural gas data for the Guelph Formation, Lockport Group. Results for samples names in **BOLD** are from Mohd Zaffa (2010).


LOCKPORT GROUP
Methane
Other Formations
Guelph - Lambton
Guelph - Huron
Guelph - Kent
Northern Huron
Sombra Twp
Enniskillen Twp
South/Central Huron
Below Lake Erie
δ13C - CH4 (‰ VPDB)
δ2H - CH4 (‰ VSMOW)
-60
-55
-50
-45
-40
-35
-300
-280
-260
-240
-220
-200
-180
-160
7A


LOCKPORT GROUP
Ethane
Northern Huron
Enniskillen Twp
Sombra Twp
South/Central Huron
Guelph - Lambton
Guelph - Huron
Guelph - Kent
Other Formations
δ13C - C2H6 (‰ VPDB)
δ2H - C2H6 (‰ VSMOW)
-42
-40
-38
-36
-34
-32
-30
-28
-260
-240
-220
-200
-180
-160
-140
-120
7B


LOCKPORT GROUP
C1 vs C2 δ13C
Northern Huron
Enniskillen Twp
Sombra Twp
South/Central Huron
Guelph - Lambton
Guelph - Huron
Guelph - Kent
Other Formations
δ13C - C2H6 (‰ VPDB)
δ13C - CH4 (‰ VPDB)
-42
-40
-38
-36
-34
-32
-30
-28
-60
-55
-50
-45
-40
-35
7C


LOCKPORT GROUP
C1 vs C2 δ2H
Guelph - Lambton
Guelph - Huron
Guelph - Kent
Other Formations
Enniskillen Twp
Northern Huron
Sombra Twp
South/Central Huron
δ2H - C2H8 (‰ VSMOW)
δ2H - CH4 (‰ VSMOW)
-260
-240
-220
-200
-180
-160
-140
-120
-300
-280
-260
-240
-220
-200
-180
-160
7D

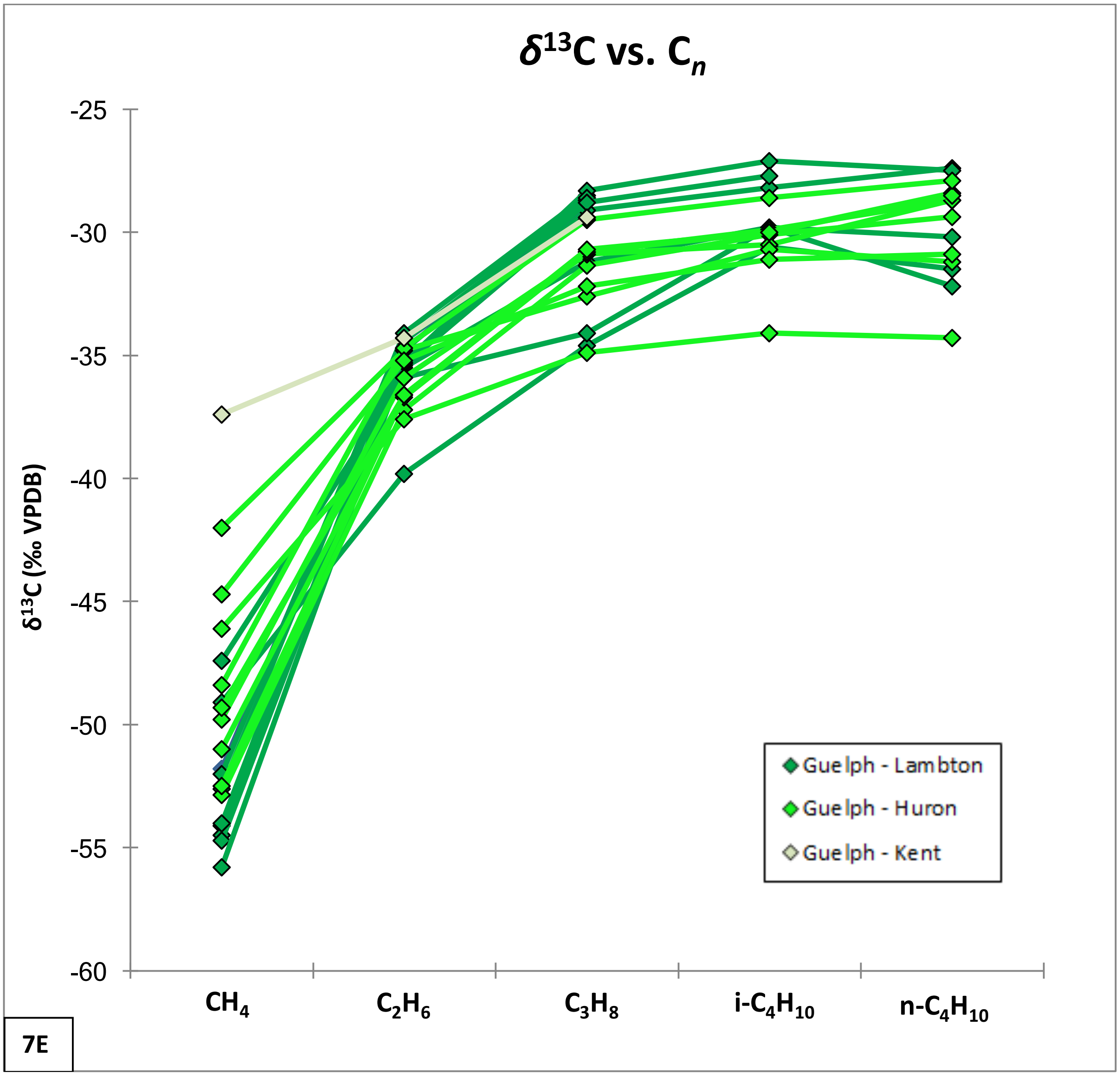


Figure 7: Isotopic compositions of gases from the Guelph Formation (Lockport Group). **A** – methane δ^{13}C *vs.* δ^{2}H; **B** – ethane δ^{13}C *vs.* δ^{2}H; **C** – methane δ^{13}C *vs.* ethane δ^{13}C; **D** – methane δ^{2}H *vs.* ethane δ^{2}H; **E** – Chung diagram of δ^{13}C *vs.* C_n (after Chung et al. 1988).

The data for gases from the Guelph Formation of the Upper Silurian Lockport Group are presented in Table 2 and illustrated in Figure 7A-E. Sample locations are shown in Appendix A, Maps 1 & 2. Overall, the Guelph Formation has isotopic compositions that span almost the full range measured for the study area. However, most samples fall within a narrower range, with $\delta^{13}C_{CH4}$ varying from –55.8 to –42.0‰; $\delta^{13}C_{C2H6}$ from –39.8 to –34.1‰; $\delta^{13}C_{C3H8}$ from –34.9 to –28.0 ‰; $\delta^{13}C_{n\text{-}C4H10}$

from –34.1 to –27.1‰; $\delta^{13}C_{i\text{-}C4H10}$ from –34.3 to –27.4‰; $\delta^{2}H_{CH4}$ from –281 to –211‰; and $\delta^{2}H_{C2H6}$ from –231 to –142‰. Gas concentrations range from 82.3–92.2% for methane; 5.3–10.4% ethane; and 2.5–7.4% propane, with gas wetness ratios varying from 4.6–11.9.

With one exception, on Lake Erie (T004543), all Guelph samples analysed are on the Michigan Basin side of the Algonquin Arch. Attempts to extrapolate compositions across the Algonquin Arch, or south towards the Chatham Sag should be made with caution.

The Guelph Formation's isotopic compositions span a fairly wide range that overlaps with numerous other formations. One important characteristic, however, is that composition is largely location-specific, with different counties and sub-county areas having significantly different compositions (Figs. 7A-D), as outlined below. This should refine attempts to differentiate it.

In Lambton County, the majority of samples are in Sombra Township, and have fairly narrow and distinctive isotopic ranges. In particular, they have very low, bacterial methane $\delta^{13}C$ values (–55.8 to –51.8‰), which set them apart from Guelph gases in other areas, and all other gases except the Salina Group gases in Lambton County (the latter can be differentiated on the basis of ethane and propane isotopes, as described earlier). The Sombra Township samples are also set conspicuously apart from other gases on plots of $\delta^{13}C_{C2H6}$ *vs.* $\delta^{2}H_{C2H6}$, $\delta^{13}C_{CH4}$ *vs.* $\delta^{13}C_{C2H6}$, and $\delta^{2}H_{CH4}$ *vs.* $\delta^{2}H_{C2H6}$. Other distinctive characteristics include: (i) a very tight range of $\delta^{13}C_{C2H6}$ (–35.5 to –34.1‰); (ii) very high $\Delta^{13}C_{C2H6\text{-}CH4}$ (17.4–21.3‰, which is higher than most Lambton Salina samples) as a result of the bacterial methane; and (iii) fairly consistent gas concentrations and gas wetness ratios (9.2–11.9, with one exception). Guelph samples in this area should thus be very easy to identify.

Two other samples in Lambton County, from Enniskillen Township, have distinctively different compositions compared to Sombra Township (and Guelph samples elsewhere). They have higher $\delta^{13}C_{CH4}$ (–49.1 and –47.4‰), indicating a low-maturity thermogenic rather than bacterial methane source. They also have distinctively lower $\delta^{13}C_{C3H8}$ than the Sombra Guelph gases (–34.6 and –34.1‰, compared to ~ –29‰), and much lower $\delta^{2}H_{C2H6}$ (–194 and –231‰, compared to –166 to –142‰). These compositions also set them apart from all Salina Group gases. While they do overlap with the Clinton-Cataract Group gases, these reservoirs are well-separated geographically. Unless the Enniskillen Guelph composition migrated across the Algonquin Arch (which it likely shouldn't), this overlap should not cause any issues with differentiation.

Further northeast, in Huron County, Guelph Formation gases are different from both types of Lambton County gases. The compositions of these gases are also area-dependant, with those in northern Huron (Ashfield and West Wawanosh Townships) being distinct from central and southern Huron (Hay, Stephen and Tuckersmith Townships). Guelph gases in northern Huron have a tight range of methane $\delta^{13}C$ (–52.9 to –49.8‰), which is intermediate between the Lambton Sombra and Enniskillen compositions (possibly a mixed thermogenic/bacterial source). They can be distinguished from all other gases simply on that basis alone, but they can also be distinguished from the Salina Group based on their ethane isotopes; they fall within a distinctive group on a plot of $\delta^{13}C_{C2H6}$ *vs.* $\delta^{2}H_{C2H6}$, separate from the Salina gases, which have generally higher $\delta^{13}C_{C2H6}$ and lower $\delta^{2}H_{C2H6}$ (Fig. 7B). They also plot in relatively distinct fields in graphs of $\delta^{13}C_{CH4}$ *vs.* $\delta^{13}C_{C2H6}$ and $\delta^{2}H_{CH4}$ *vs.* $\delta^{2}H_{C2H6}$ (Figs. 7C,D). Unlike the Sombra Guelph and Salina gases, they also have positive $\Delta^{13}C_{n\text{-}C4H10\,-\,i\text{-}C4H10}$ (1.2–1.8‰). Their $\Delta^{2}H_{C2H6-CH4}$ are also higher than almost all other gases, except those from Sombra Guelph.

The south/central Huron Guelph gases are distinctively more thermogenic than the northern Huron and Sombra Guelph gases, and more thermogenically-mature than the Enniskillen Guelph. Their isotopic compositions are more variable than the Guelph in other regions, with $\delta^{13}C_{CH4}$ between –48.4 and –42.0‰, $\delta^{2}H_{CH4}$ between –252 and –211‰, $\delta^{13}C_{C2H6}$ between –37.6 and –34.7‰, and $\delta^{2}H_{C2H6}$ between –208 and –157‰. They have lower $\Delta^{13}C_{n\text{-}C4H10\,-\,i\text{-}C4H10}$ (–0.5 to +0.7‰) than the northern Huron Guelph, as well as lower $\Delta^{2}H_{C2H6-CH4}$ (4–83‰, *vs.* 93–120‰). Their isotopic ranges overlap significantly with the Salina Group gases; there are only a few features that can be tentatively used to distinguish the two - namely that the south/central Huron Guelph gases have slight statistical differences between certain isotope pairs, as indicated in Table 3. Highlighted pairs ($\Delta^{13}C_{n\text{-}C4H10\,-\,i\text{-}C4H10}$; $\Delta^{13}C_{n\text{-}C4H10-C3H8}$; $\Delta^{13}C_{i\text{-}C4H10-C3H8}$) may be particularly useful for identification, but any pair could be potentially useful if the value of an unknown sample falls outside the range of one formation. This method should be used with caution, however, as the limited number of samples may not capture the full natural range in compositions.

Apart from a few samples, the south/central Huron Guelph gases are readily distinguishable from the more thermogenically-mature gases in the Cambro-Ordovician reservoirs, which plot in separate fields in the methane $\delta^{13}C$ *vs.* $\delta^{2}H$ graph (compare Figs. 7A & 9A).

There is one Guelph gas sample from the eastern side of the Algonquin Arch, from a well on Lake Erie (T004543). While its ethane and propane isotopes are indistinguishable from the Sombra Guelph compositions, it has highly thermogenic methane signatures (–37.4‰ $\delta^{13}C_{CH4}$, –159‰ $\delta^{2}H_{CH4}$). These are distinctively higher than all other samples, supporting the idea that the thermogenic gases originated deeper in the Appalachian Basin. It is thus possible that other Guelph gases on the eastern side of the Algonquin arch may have transitional thermogenic signatures that are similar to the Salina gases in Kent County. Further sampling of Guelph wells in that area is recommended, as it is important to determine whether or not this is the case. Extrapolating the T004543 composition as representative of the Guelph composition throughout Kent and other Appalachian Basin-side counties is likely inappropriate.

		$\Delta^{13}C$ C2-C1	$\Delta^{13}C$ C3-C2	$\Delta^{13}C$ C3-C1	$\Delta^{13}C$ nC4-iC4	$\Delta^{13}C$ iC4-C3	$\Delta^{13}C$ nC4-C3	$\Delta^{13}C$ iC4-C2	$\Delta^{13}C$ nC4-C2	$\Delta^{13}C$ iC4-C1	$\Delta^{13}C$ nC4-C1	$\Delta^{2}H$ C2-C1
Salina A-1 Carbonate	T003560	9.8	5.3	15.1								26
	T008990	10.5	2.2	12.7	-1.7	2.0	0.3	4.2	2.5	14.7	13.0	37
	T007498	8.7	3.0	11.7	-2.0	1.9	-0.1	4.9	2.9	13.6	11.6	22
	T008636	12.7	2.3	15.0								34
	T008638	10.8	1.6	12.4								37
Sal.A1-A2 mix	T008864	15.3	4.9	20.2		1.0		5.9		21.2		80
	T008837	13.5	3.8	17.3								51
	T008997	10.3	2.8	13.1	-1.9	2.5	0.6	5.3	3.4	15.6	13.7	43
	T008906	10.7	2.0	12.7								34
Salina A-2 Carbonate	T008535	12.1	4.5	16.6	-2.1	4.4	2.3	8.9	6.8	21.0	18.9	44
	T007848	14.2	6.3	20.5		5.6		11.9		26.1		54
	T008611	19.8	5.4	25.2	-3.0	1.4	-1.6	6.8	3.8	26.6	23.6	91
	T008634	6.3	3.3	9.6	-1.8	2.8	1.0	6.1	4.3	12.4	10.6	20
	T008633	6.1	3.0	9.1	-0.2	0.5	0.3	3.5	3.3	9.6	9.4	58
Overall	**average**	**11.5**	**3.6**	**15.1**	**-1.8**	**2.5**	**0.4**	**6.4**	**3.9**	**17.9**	**14.4**	**45**
	min	**6.1**	**1.6**	**9.1**	**-3.0**	**0.5**	**-1.6**	**3.5**	**2.5**	**9.6**	**9.4**	**20**
	max	**19.8**	**6.3**	**25.2**	**-0.2**	**5.6**	**2.3**	**11.9**	**6.8**	**26.6**	**23.6**	**91**
Guelph – South / Central Huron County	T009602	8.5	2.7	11.2	-0.2	0.8	0.6	3.5	3.3	12.0	11.8	44
	T010097	7.2	2.2	9.4	-0.5	1.9	1.4	4.1	3.6	11.3	10.8	4
	T007415	13.7	5.2	18.9	0.7	0.9	1.6	6.1	6.8	19.8	20.5	83
	T008657	9.5	3.0	12.5	0.2	1.1	1.3	4.1	4.3	13.6	13.8	34
	average	**9.7**	**3.3**	**13.0**	**0.1**	**1.2**	**1.2**	**4.5**	**4.5**	**14.2**	**14.2**	**41**
	min	**7.2**	**2.2**	**9.4**	**-0.5**	**0.8**	**0.6**	**3.5**	**3.3**	**11.3**	**10.8**	**4**
	max	**13.7**	**5.2**	**18.9**	**0.7**	**1.9**	**1.6**	**6.1**	**6.8**	**19.8**	**20.5**	**83**

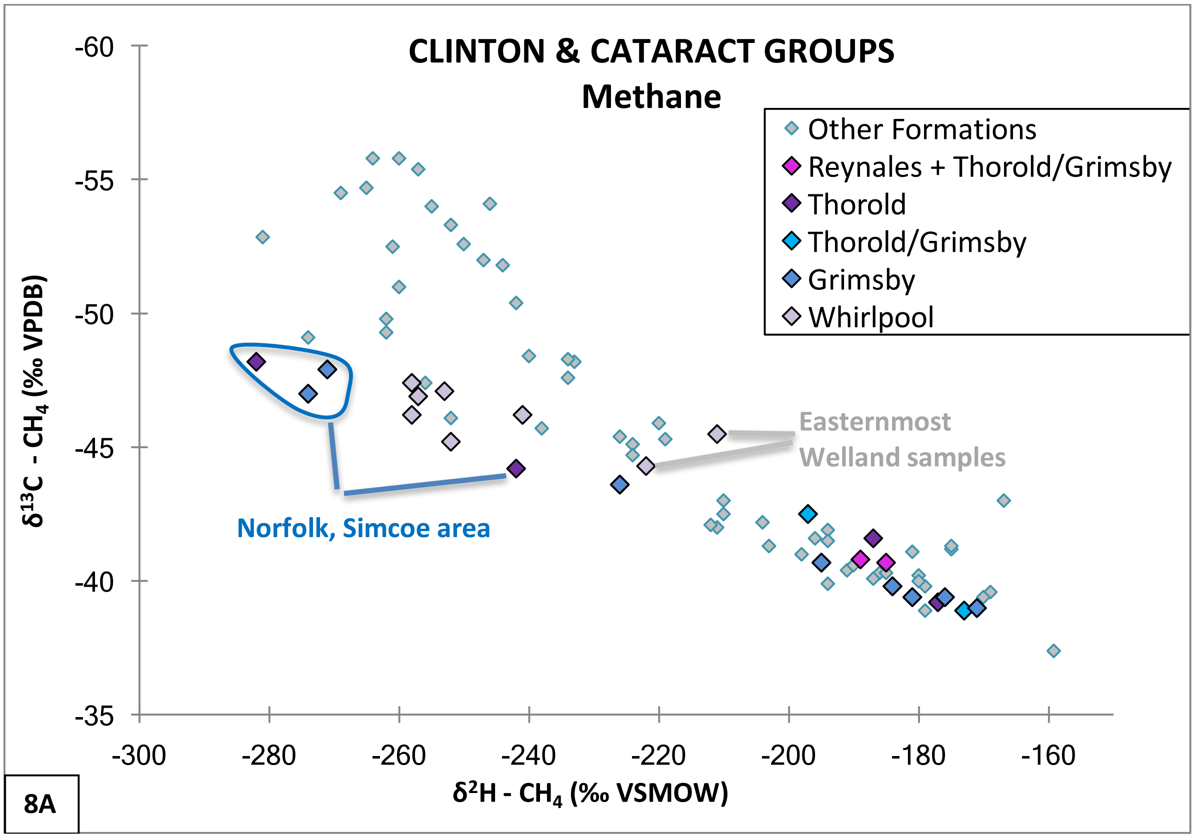
Table 3: Isotope difference pairs for Salina Group and south/central Huron County Guelph gases.

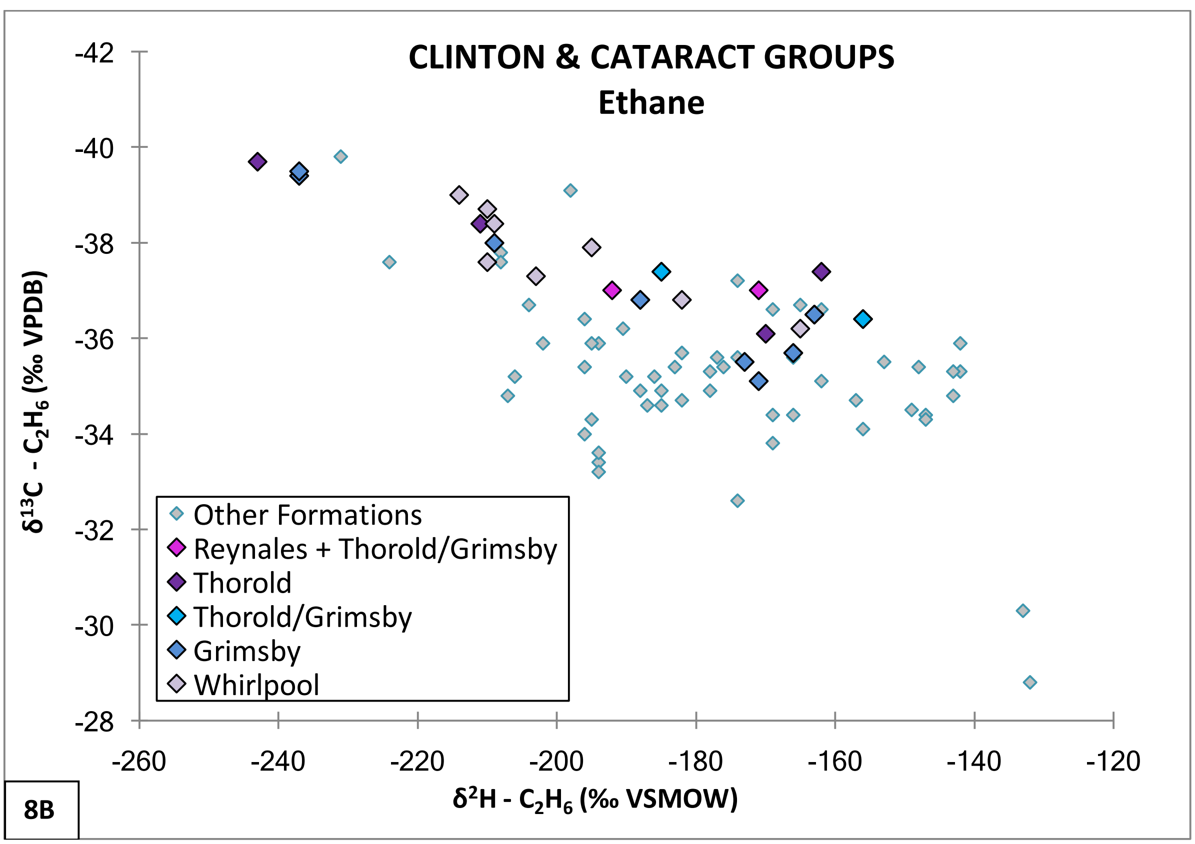
Clinton & Cataract Groups

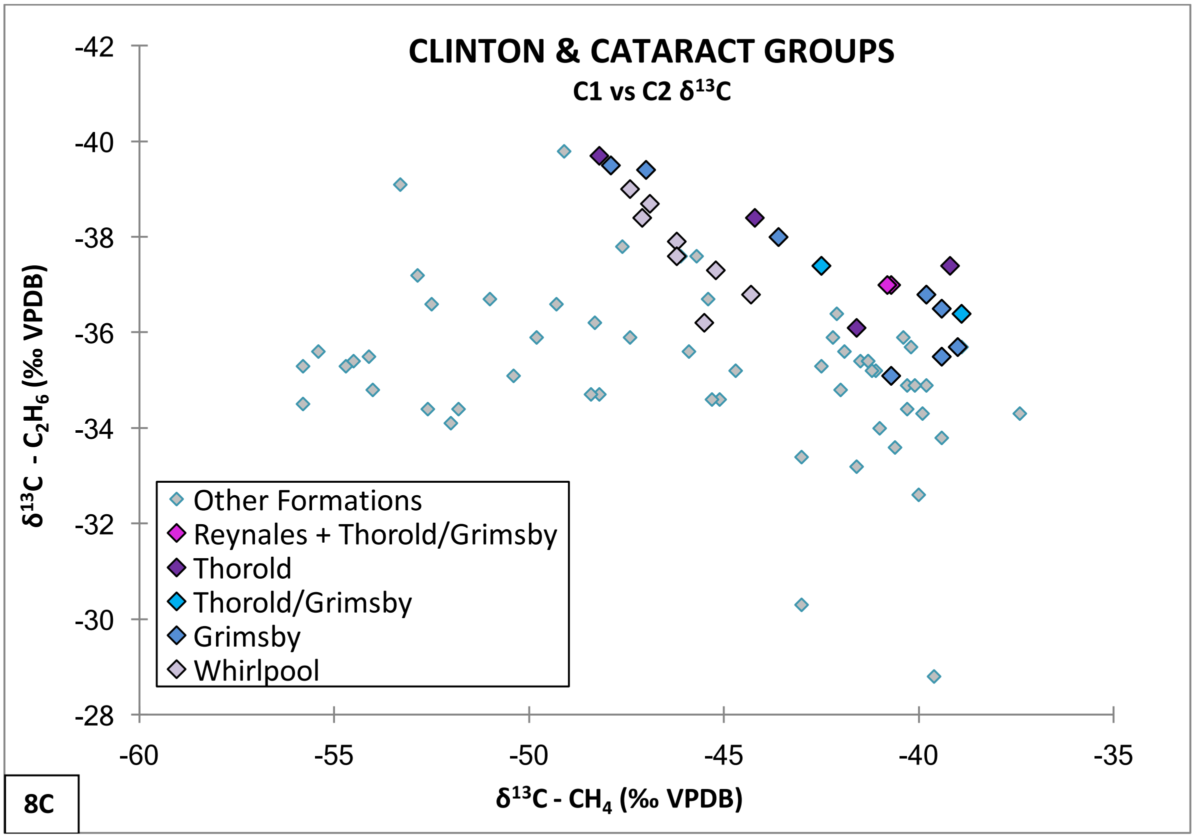
Well No.	Well Location	County	Pool	Producing Formation	$\delta^{13}C$ CH_4	$\delta^{13}C$ C_2H_6	$\delta^{13}C$ C_3H_8	$\delta^{13}C$ i-C_4H_{10}	$\delta^{13}C$ n-C_4H_{10}	δ^2H CH_4	δ^2H C_2H_6	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	Wetness - $C_1/(C_2+C_3$
T008932	N. Walsh-ingham 7	Norfolk	S. Walsh-ingham 5-6-	Reynales+ Thorold	–40.7	–37.0	–32.2	–30.9	–29.3	–185	–171	93.6	4.7	1.7	14.6
T011830	Walpole 7-17-IX	Haldi-mand	Haldimand	Reynales+ Grimsby	–43.6	–38.0	–32.1	-	-	–226	–209				
T011828	Walpole 3-13-VIII	Haldi-mand	Haldimand	Reynales+ Grimsby	–40.8	–37.0	–31.3		-	–189	–192				
T004185	Charlotte 6-1-III	Norfolk	Norfolk	Thorold	–39.2	–37.4	–32.0	–32.5	-	–177	–162	94.9	4.0	1.1	18.6
T010691	Houghton 2-138-STR	Norfolk	Bayham	Thorold	–41.6	–36.1	–32.2	–25.2	–30.6	–187	–170	92.2	5.2	2.6	11.8
T011584	Windham 8-1-IX	Norfolk	Norfolk	Thorold	–44.2	–38.4	–33.4	–29.9	–29.3	–242	–211				
T011554	Windham 6-10-XII	Norfolk	Norfolk	Thorold	–48.2	–39.7	–34.5	–32.1	–30.7	–282	–243				
T011280	Townsend 3-7-XIV	Norfolk	Norfolk	Thor./Grim./ Whirlpool	–47.1	–39.2	–32.5	–31.1	–28.9	–271	–237				
T011549	Houghton 4-11-II	Norfolk	Houghton 5-8-ENR	Thorold/ Grimsby	–42.5	–37.4	–32.7	-	-	–197	–185	92.7	5.2	2.1	12.7
T008812	S. Walsh-ingham 4	Norfolk	S. Walsingham 5-6-VI	Thorold/ Grimsby	–38.9	–36.4	–31.6	-	-	–173	–156	94.7	3.9	1.4	6.2
T011190	Aldborough 4-15-IV	Elgin	Aldborough 4-15-IV	Grimsby	–39.4	–35.5	–31.9	–31.3	–30.5	–181	–173				
T006762	Lake Erie	Norfolk	Clear Creek	Grimsby	–39.0	–35.7	–30.9	-	-	–171	–166				
T005741	S. Walsh-ingham 1	Norfolk	Venison Creek	Grimsby	–39.4	–36.5	–31.6	-	-	–176	–163	94.5	4.0	1.5	17.2
T010610	Aldborough 6-Gore-IV	Elgin	Aldborough 1-21-IV	Grimsby	–40.7	–35.1	–32.4	–29.3	–29.5	–195	–171	93.3	5.1	1.6	13.9
T011814	Charlottevi lle 5-22-V	Norfolk	Norfolk	Grimsby	–47.0	–39.4	–33.4	-	-	–274	–237	91.6	5.4	3.0	10.9

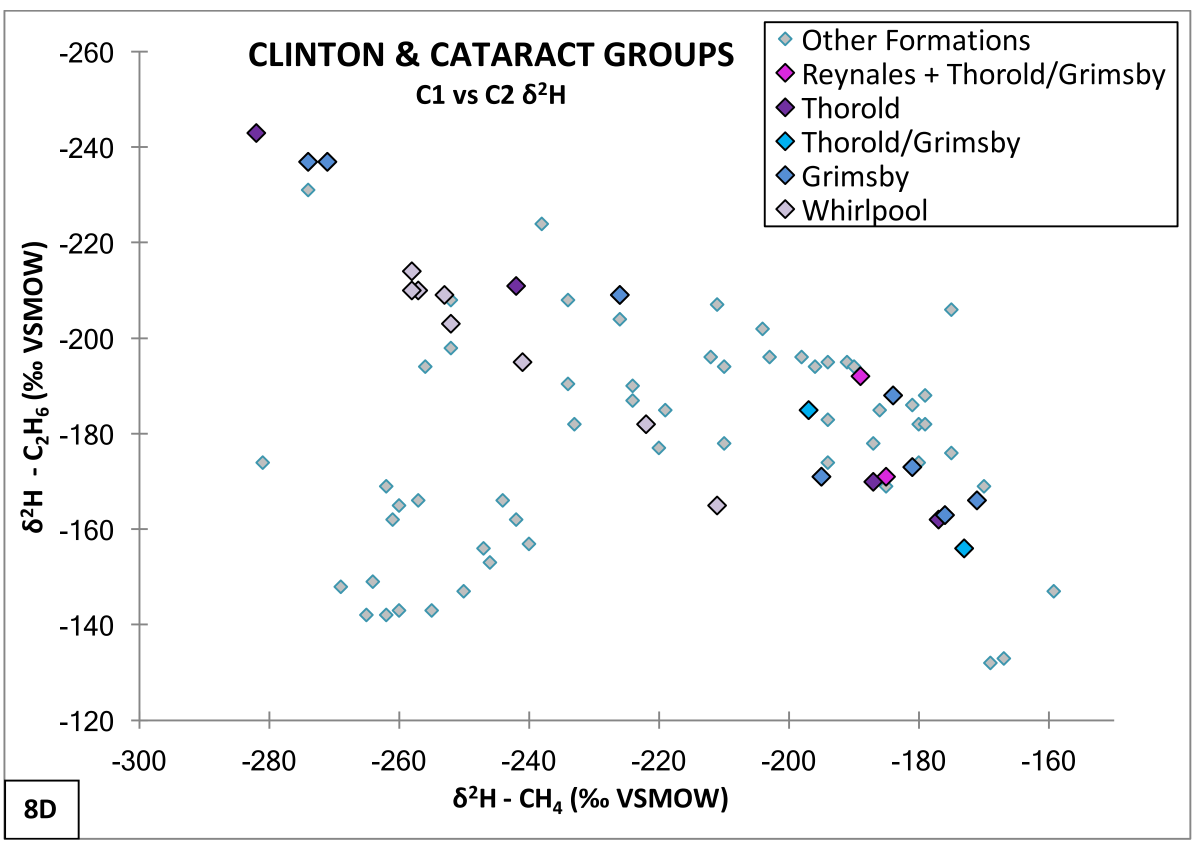
T002374	Charlottevi lle 8-9-IX	Norfolk	Norfolk	Grimsby	–47.9	–39.5	–33.7	-	-	–271	–237				
T003188	Charlottevi lle 12-10-	Norfolk	Norfolk	Grimsby	–39.8	–36.8	–31.9	-	-	–184	–188				
T012287	Humberst-one 7-5-V	Welland	Welland	Whirlpool	–45.5	–36.2	–30.1	-	-	–211	–165				
T011199	Sherbrooke 2-2-I	Haldi-mand	Haldimand	Whirlpool	–46.2	–37.9	–32.7	–30.9	–28.8	–241	–195	90.6	7.2	2.2	9.7
T011200	Sherbrooke 4-3-I	Haldi-mand	Haldimand	Whirlpool	–46.9	–38.7	–33.4	–31.9	–29.6	–257	–210	88.5	7.9	3.6	7.7
T011201	Sherbrooke 3-3-I	Haldi-mand	Haldimand	Whirlpool	–47.1	–38.4	–33.4	–31.5	–30.1	–253	–209	89.3	7.6	3.1	8.4
T011365	Sherbrooke 3-2-I	Haldi-mand	Haldimand	Whirlpool	-47.4	–39.0	–33.9	–32.4	–30.5	–258	–214	88.5	7.7	3.8	7.7
T008194	Gainsborough 6 24 -IV	Lincoln	Welland	Whirlpool	–46.2	–37.6	–31.8	-	-	–258	–210				
T009877	Wainfleet 9 - 31 - VII	Welland	Welland	Whirlpool	–45.2	–37.3	–32.5	-	-	–252	–203				
T012264	Thorold 2 - 237 -	Welland	Welland	Whirlpool	–44.3	–36.8	–31.1	-	-	–222	–182				

Table 4: Natural gas data for the Clinton and Cataract groups. All data are from this study.


CLINTON & CATARACT GROUPS
Methane
Other Formations
Reynales + Thorold/Grimsby
Thorold
Thorold/Grimsby
Grimsby
Whirlpool
Easternmost
Welland samples
Norfolk, Simcoe area
-60
-55
-50
-45
-40
-35
-300
-280
-260
-240
-220
-200
-180
-160
δ13C - CH4 (‰ VPDB)
δ2H - CH4 (‰ VSMOW)
8A


CLINTON & CATARACT GROUPS
Ethane
Other Formations
Reynales + Thorold/Grimsby
Thorold
Thorold/Grimsby
Grimsby
Whirlpool
-42
-40
-38
-36
-34
-32
-30
-28
-260
-240
-220
-200
-180
-160
-140
-120
δ13C - C2H6 (‰ VPDB)
δ2H - C2H6 (‰ VSMOW)
8B


CLINTON & CATARACT GROUPS
C1 vs C2 δ13C
Other Formations
Reynales + Thorold/Grimsby
Thorold
Thorold/Grimsby
Grimsby
Whirlpool
δ13C - C2H6 (‰ VPDB)
δ13C - CH4 (‰ VPDB)
-42
-40
-38
-36
-34
-32
-30
-28
-60
-55
-50
-45
-40
-35
8C


CLINTON & CATARACT GROUPS
C1 vs C2 δ2H
Other Formations
Reynales + Thorold/Grimsby
Thorold
Thorold/Grimsby
Grimsby
Whirlpool
δ2H - C2H6 (‰ VSMOW)
δ2H - CH4 (‰ VSMOW)
-260
-240
-220
-200
-180
-160
-140
-120
-300
-280
-260
-240
-220
-200
-180
-160
8D

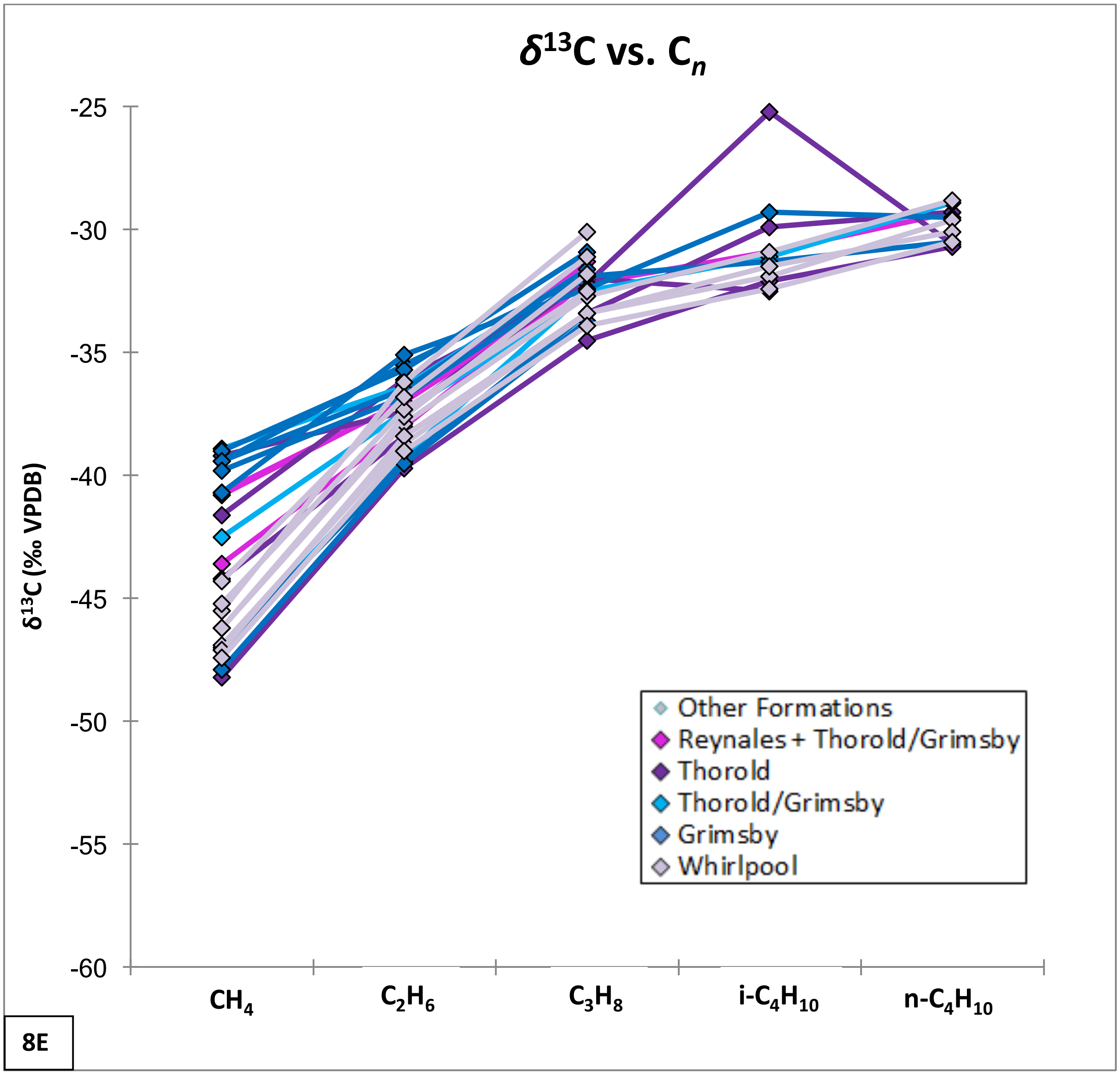


Figure 8: Isotopic compositions of gases from the Clinton and Cataract groups. **A** – methane δ^{13}C *vs.* δ^{2}H; **B** – ethane δ^{13}C *vs.* δ^{2}H; **C** – methane δ^{13}C *vs.* ethane δ^{13}C; **D** – methane δ^{2}H *vs.* ethane δ^{2}H; **E** – Chung diagram of δ^{13}C *vs.* C_n (after Chung et al. 1988).

The data for gases from the Lower Silurian Clinton and Cataract Groups are presented in Table 4 and illustrated in Figure 8A-E. Sample locations are shown in Appendix A, Maps 1 & 3. These groups include samples from the Reynales, Thorold, Grimsby, and Whirlpool formations. The former three are all apparently indistinguishable from each other in terms of isotopic composition, while there are some compositional differences in the Whirlpool Formation. Overall, the Clinton-Cataract gases span almost the full range of thermogenic isotopic compositions, from –48.2 to –

38.9‰ $\delta^{13}C_{CH4}$ and –282 to –171‰ $\delta^{2}H_{CH4}$, and there are some spatial variations. Ethane isotopes are also quite variable and not very distinctive, with $\delta^{13}C_{C2H6}$ from –39.7 to –35.1‰ and $\delta^{2}H_{C2H6}$ from –243 to –156‰. Gas concentrations range from 88.5–94.9% for methane; 3.9–7.9% ethane; and 1.1–3.8% propane. Gas wetness ratios vary from 6.2–18.6; on average, these samples have the highest wetness ratios of all formation gases (see Figure 3).

All Clinton-Cataract reservoirs are located on the Appalachian Basin side of the Algonquin Arch. The samples in this study are from Elgin, Norfolk, Haldimand, Welland and Lincoln Counties. The Reynales, Thorold, and Grimsby formation samples are from the former three counties, and the Whirlpool Formation samples are from the latter three.

As mentioned above, the Reynales, Thorold, and Grimsby formation gases are apparently indistinguishable from each other, but that may be an artifact arising from the mixed nature of the reservoirs sampled. Further sampling of unmixed reservoirs might identify some differences. These gases have a wide isotopic range, but the compositional extremes seem to be regionally-defined.

The lighter, more thermogenically-immature end of the range (–48.2 to –47.0‰ $\delta^{13}C_{CH4}$ and –282 to –271‰ $\delta^{2}H_{CH4}$) is formed by a group of four samples in an area in north-east Norfolk County, surrounding Simcoe; a fifth sample in the area (T011584), seems to have a large component of this immature gas, but it is also mixed with the more mature gas found in Reynales/Thorold/Grimsby formation samples elsewhere. The cause of the unusual compositions in this area is unclear.

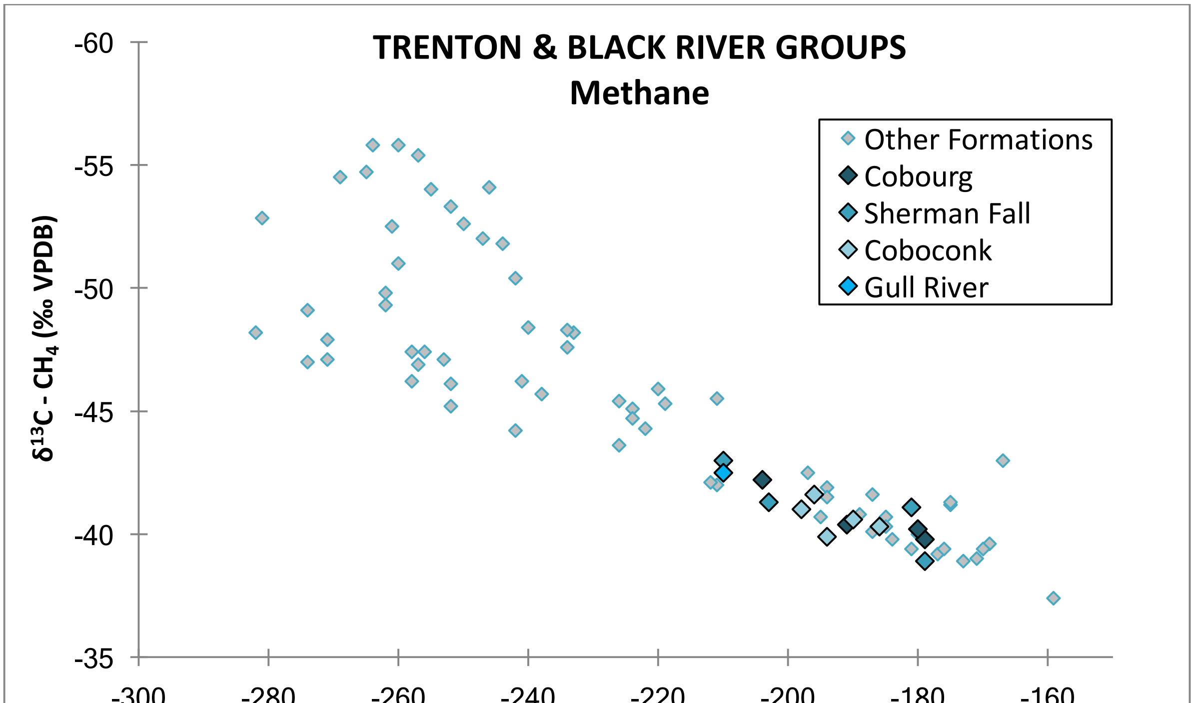
With one exception, all Reynales/Thorold/Grimsby formation gases outside the Simcoe area fall within a relatively tight range with mature thermogenic signatures (–42.5 to –38.9‰ $\delta^{13}C_{CH4}$ and –197 to –171 ‰ $\delta^{2}H_{CH4}$). The main distinguishing characteristic of these gases is their wetness, with $C_1/(C_2+C_3)$ greater than 10 (except for one sample), which higher than almost every sample from other formations. These samples, in general, also have lower ethane isotopic compositions (average –36.4‰ $\delta^{13}C_{C2H6}$ and –172.5‰ $\delta^{2}H_{C2H6}$) compared to the similarly-mature Cambro-Ordovician reservoirs (average –34.9‰ $\delta^{13}C_{C2H6}$ and –189‰ $\delta^{2}H_{C2H6}$). The one exception (T011830) has intermediate-maturity compositions (–43.6‰ $\delta^{13}C_{CH4}$ and –226‰ $\delta^{2}H_{CH4}$). These compositions are similar to T011584 (from the Simcoe area), but these two samples are geographically widely separated.

The Whirlpool Formation gases are distinct from the Reynales/Thorold/Grimsby gases. Their methane isotopic compositions are intermediate (–47.4 to –44.3‰ $\delta^{13}C_{CH4}$ and –258 to –211‰ $\delta^{2}H_{CH4}$) between the two groups at the extreme ends of the thermogenic spectrum. Most in fact fall within a considerably narrower $\delta^{2}H_{CH4}$ range (–258 to –241‰); the two most thermogenic samples (T012287 and T012264) are the easternmost (furthest-basinward) Whirlpool samples (Welland County). As well as their differences in methane isotopes, the Whirlpool gases can also be differentiated from the Reynales/Thorold/Grimsby gases by their lower $C_1/(C_2+C_3)$ values (7.7–9.7), and their higher and narrower range of $\Delta^{2}H_{C2H6\text{-}CH4}$ (40–49‰, vs. –4 to +39‰). While the Whirlpool gases are largely distinct from the Cambro-Ordovician gases based on their lower methane isotope compositions, this $\Delta\delta^{2}H_{C2H6\text{-}CH4}$ range can be used to further differentiate them; the Cambro-Ordovician gases also have lower $\Delta^{2}H_{C2H6\text{-}CH4}$ (–31 to +32‰). The Whirlpool gases are distinct from the mixed bacterial/thermogenic eastern Salina gases based on their methane isotopes, which fall along a different trend – see Figure 6A.

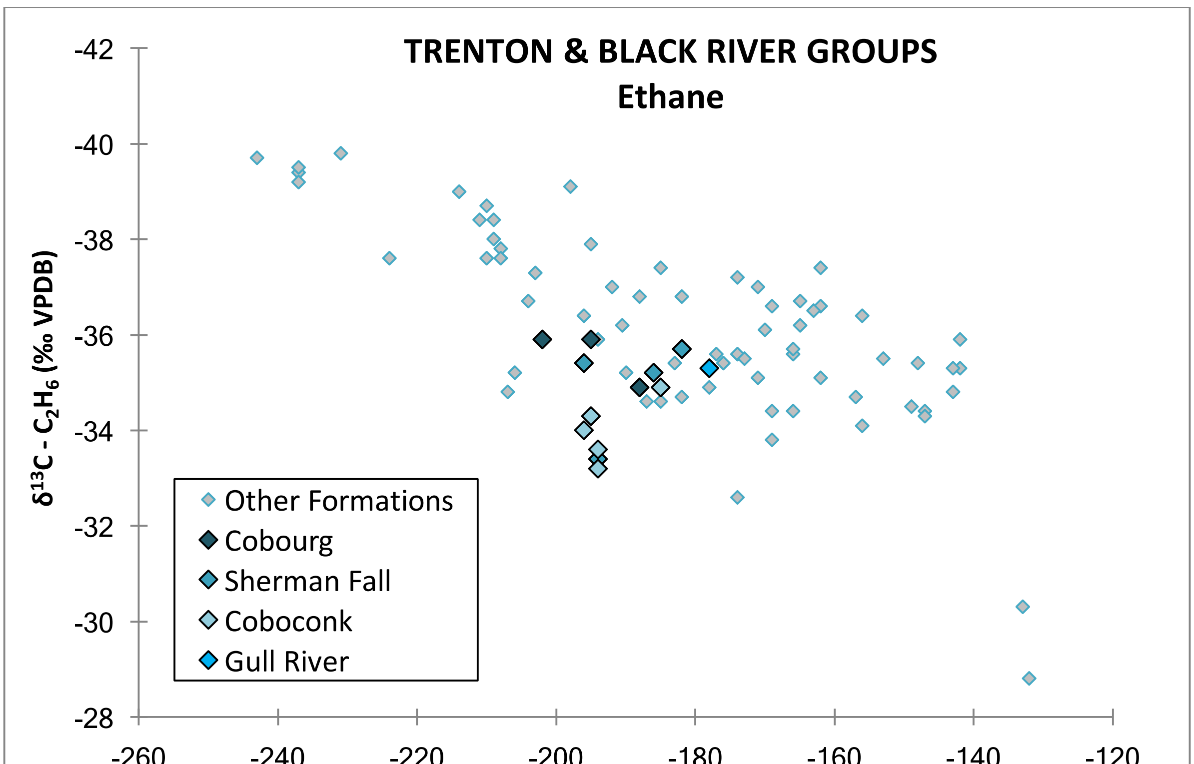
Trenton & Black River Groups

Well No.	Well Location	County	Pool	Producing Formation	$\delta^{13}C$ CH_4	$\delta^{13}C$ C_2H_6	$\delta^{13}C$ C_3H_8	$\delta^{13}C$ i-C_4H_{10}	$\delta^{13}C$ n-C_4H_{10}	δ^2H CH_4	δ^2H C_2H_6	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	Wetness - $C_1/(C_2+C_3)$
T007357	Raleigh 2-14-XIV	Kent	Raleigh	Cobourg	–42.2	–35.9	–33.4	–31.9	–31.4	–204	–202	87.7	7.8	4.5	7.1
T007954	Rochester 8-17-IIIEBR	Essex	Rochester	Cobourg	–39.8	–34.9	–32.4	–30.9	–29.5	–179	–188	-	-	-	-
T009605	Mersea 1-2-VI	Essex	Mersea	Cobourg	–40.2	–35.7	–31.7	-	-	–180	–182	-	-	-	-
T008358	Mersea 4-5-V	Essex	Mersea	Cobourg	–40.4	–35.9	–33.1	-	-	–191	–195	-	-	-	-
T007793	Dover 3-4-IVE	Kent	Dover	Sherman Fall	–41.1	–35.2	–33.2	-	–33.1	–181	–186	85.4	9.5	5.1	5.8
T007743	Sombra 7-6-VI	Lambton	Sombra	Sherman Fall	–43.0	–33.4	–32.2	-	-	–210	–194	87.4	7.6	5.0	6.9
T003803	Aldborough 7-18-IV	Elgin	Aldborough	Sherman Fall	–38.9	–35.7	–32.8	–31.4	–30.5	–179	–182	91.2	5.9	2.9	10.3
T008057	Tilbury North 1-11-	Lambton	Tilbury North	Sherman Fall	–41.3	–35.4	–32.5	-	-	–203	–196	-	-	-	-
T006983	Dawn 7-20-III	Lambton	Dawn	Coboconk	–40.6	–33.6	–32.5	-	-	–190	–194	83.7	12.5	3.9	5.1
T011597	Esquesing 6 - 15 - IV	Halton	Esquesing	Coboconk	–39.9	–34.3	–31.2	-	-	–194	–195	-	-	-	-
T006907	Sombra 3-26-VI	Lambton	Sombra	Coboconk	–41.6	–33.2	–32.1	-	-	–196	–194	89.2	7.4	3.5	8.2
T006907	Sombra 3-26-VI	Lambton	Sombra	Coboconk	–41.0	–34.0	–32.3	–30.9	–29.3	–198	–196	-	-	-	-
T008313	Rochester 3-15-IIEBR	Essex	Rochester	Coboconk	–40.3	–34.9	–32.5	–29.4	–28.7	–186	–185	-	-	-	-
T008974	Blenheim 3-10-VI	Oxford	Blenheim	Gull River	–42.5	–35.3	–31.8	-	-	–210	–178	87.7	8.5	3.8	7.1

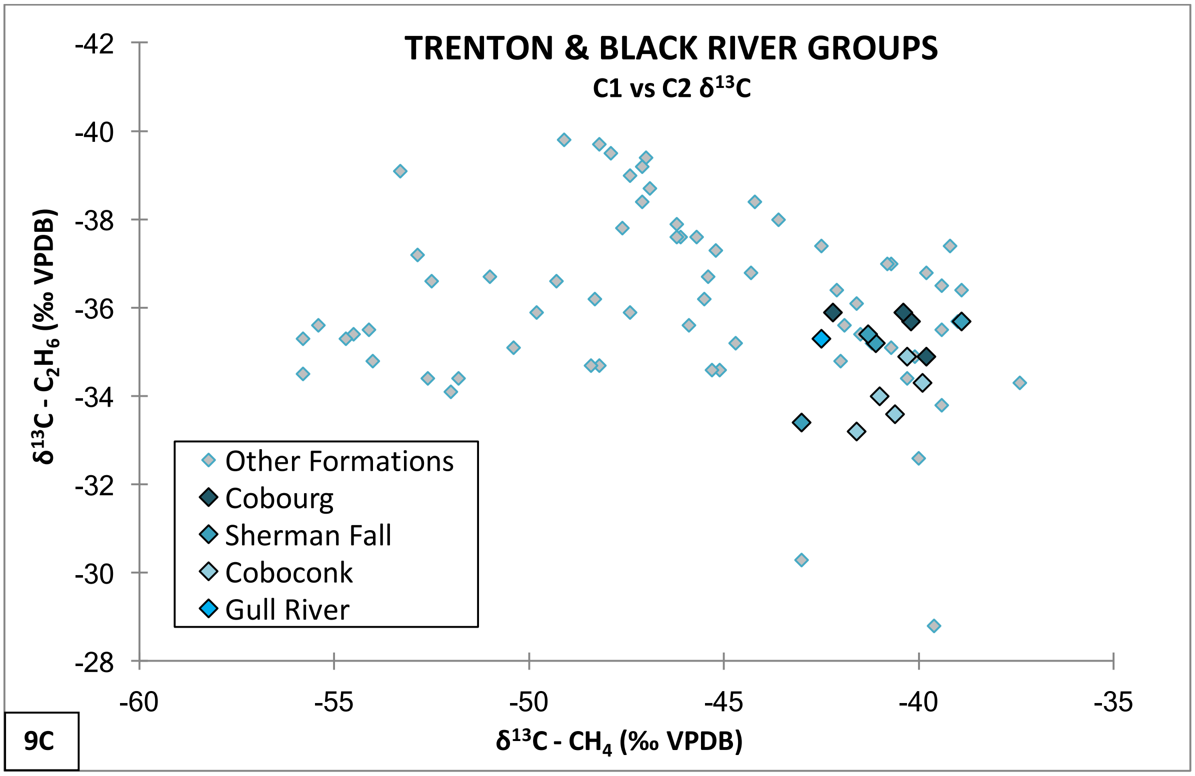
Table 5: Natural gas data for the Trenton and Black River Groups. Samples names shown in **BOLD** are from Mohd Zaffa (2010).

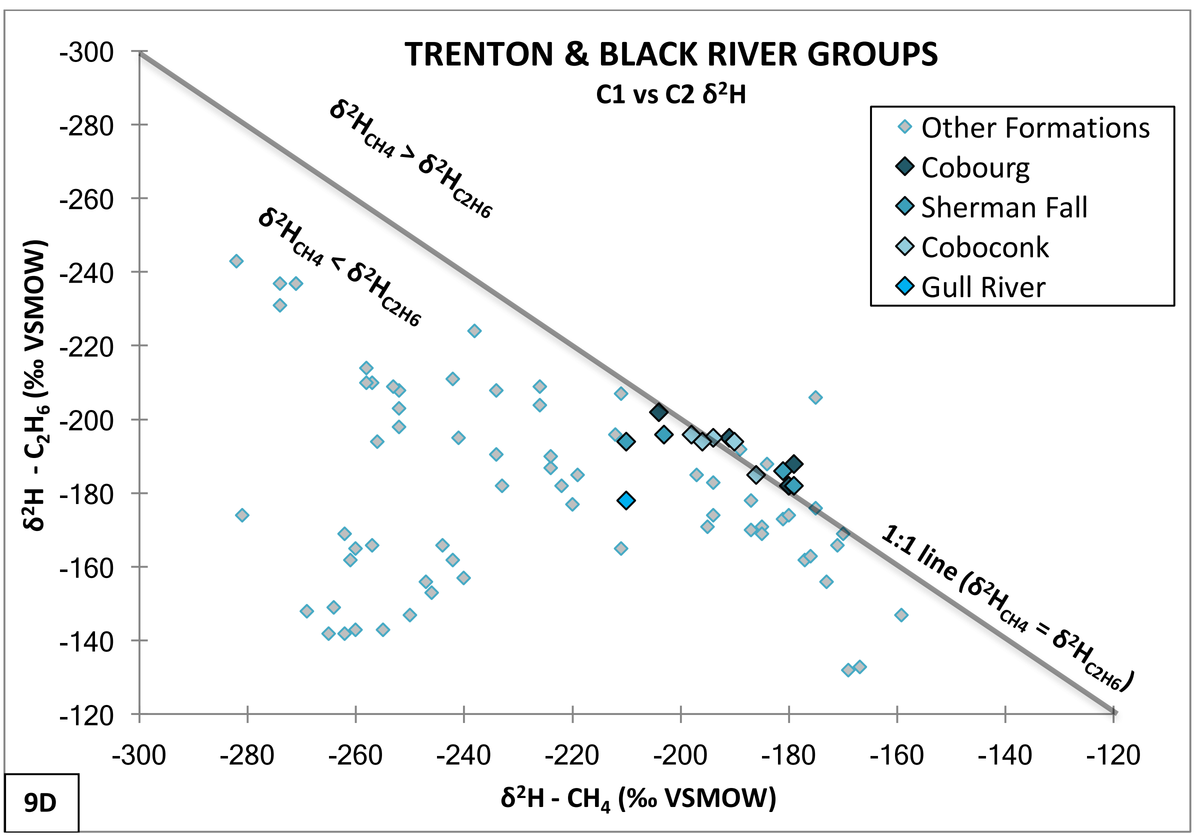

TRENTON & BLACK RIVER GROUPS
Methane
Other Formations
Cobourg
Sherman Fall
Coboconk
Gull River
δ13C - CH4 (‰ VPDB)
δ2H - CH4 (‰ VSMOW)
-60
-55
-50
-45
-40
-35
-300
-280
-260
-240
-220
-200
-180
-160

9A


TRENTON & BLACK RIVER GROUPS
Ethane
Other Formations
Cobourg
Sherman Fall
Coboconk
Gull River
δ13C - C2H6 (‰ VPDB)
δ2H - C2H6 (‰ VSMOW)
-42
-40
-38
-36
-34
-32
-30
-28
-260
-240
-220
-200
-180
-160
-140
-120

9B


TRENTON & BLACK RIVER GROUPS
C1 vs C2 $\delta^{13}C$
$\delta^{13}C$ - C_2H_6 (‰ VPDB)
$\delta^{13}C$ - CH_4 (‰ VPDB)
-42
-40
-38
-36
-34
-32
-30
-28
-60
-55
-50
-45
-40
-35
Other Formations
Cobourg
Sherman Fall
Coboconk
Gull River
9C


TRENTON & BLACK RIVER GROUPS
C1 vs C2 δ^2H
$\delta^2H_{CH4} > \delta^2H_{C2H6}$
$\delta^2H_{CH4} < \delta^2H_{C2H6}$
1:1 line ($\delta^2H_{CH4} = \delta^2H_{C2H6}$)
δ^2H - C_2H_6 (‰ VSMOW)
δ^2H - CH_4 (‰ VSMOW)
-300
-280
-260
-240
-220
-200
-180
-160
-140
-120
Other Formations
Cobourg
Sherman Fall
Coboconk
Gull River
9D

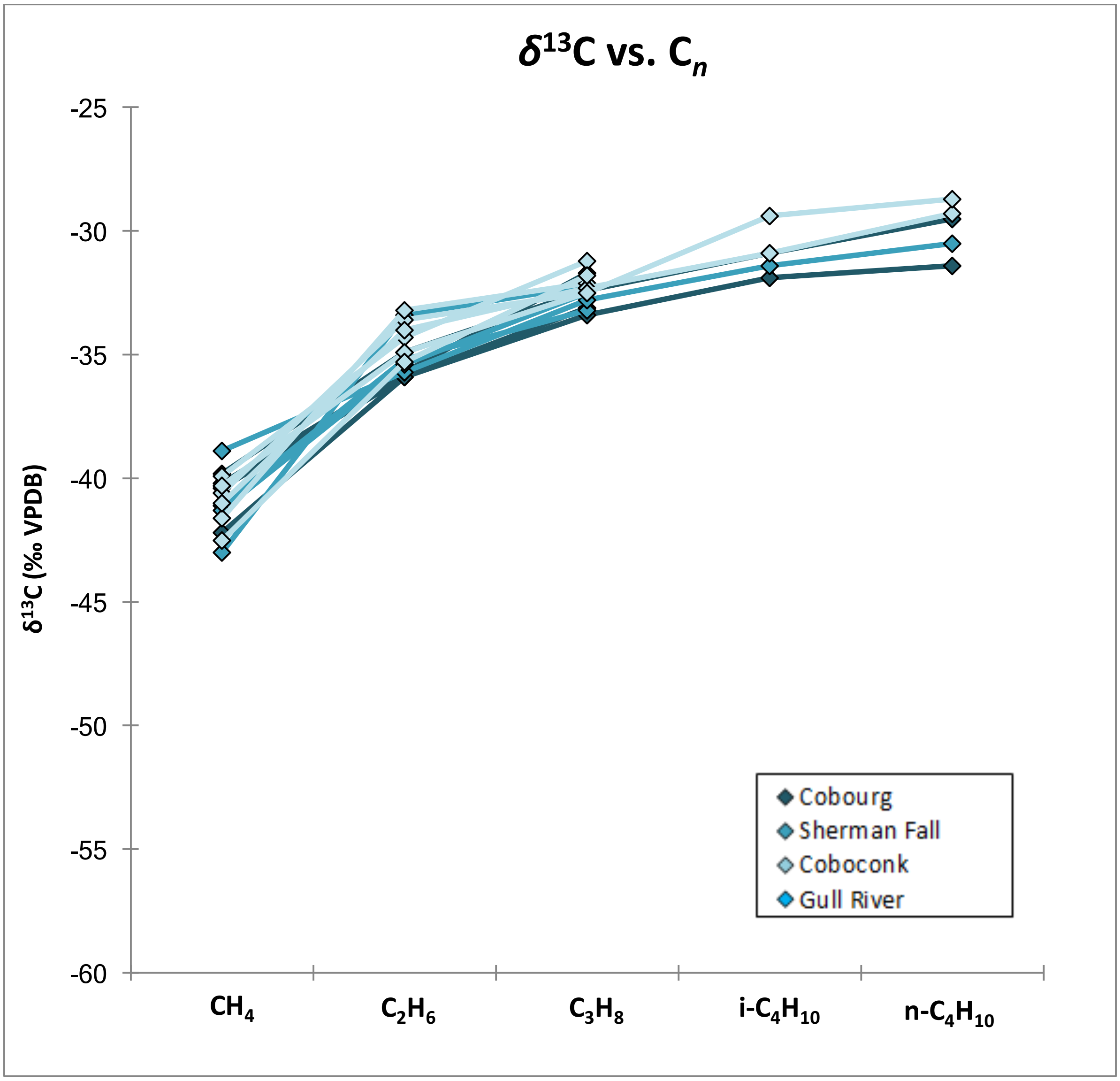


Figure 9: Isotopic compositions of gases from the Clinton and Cataract groups. **A** – methane $\delta^{13}C$ *vs.* $\delta^{2}H$; **B** – ethane $\delta^{13}C$ *vs.* $\delta^{2}H$; **C** – methane $\delta^{13}C$ *vs.* ethane $\delta^{13}C$; **D** – methane $\delta^{2}H$ *vs.* ethane $\delta^{2}H$; **E** – Chung diagram of $\delta^{13}C$ *vs.* C_n (after Chung et al. 1988).

The data for gases from the Upper Ordovician Trenton and Black River groups are presented in Table 5 and illustrated in Figure 9A-E. Sample locations are shown in Appendix A, Maps 1 & 4. These groups include samples from the Cobourg and Sherman Fall (Trenton) and Coboconk and Gull River formations (Black River). Overall, the Trenton-Black River gases span a fairly narrow range of mature thermogenic isotopic compositions (–43.0 to –38.9‰ $\delta^{13}C_{CH4}$ and –210 to –179‰ $\delta^{2}H_{CH4}$; –35.9 to –33.2‰ $\delta^{13}C_{C2H6}$ and –202 to –178‰ $\delta^{2}H_{C2H6}$). Gas concentrations range from

83.7–91.2% for methane; 5.9–12.2% ethane; and 2.1–5.1% propane, with gas wetness ratios varying from 5.1–10.3.

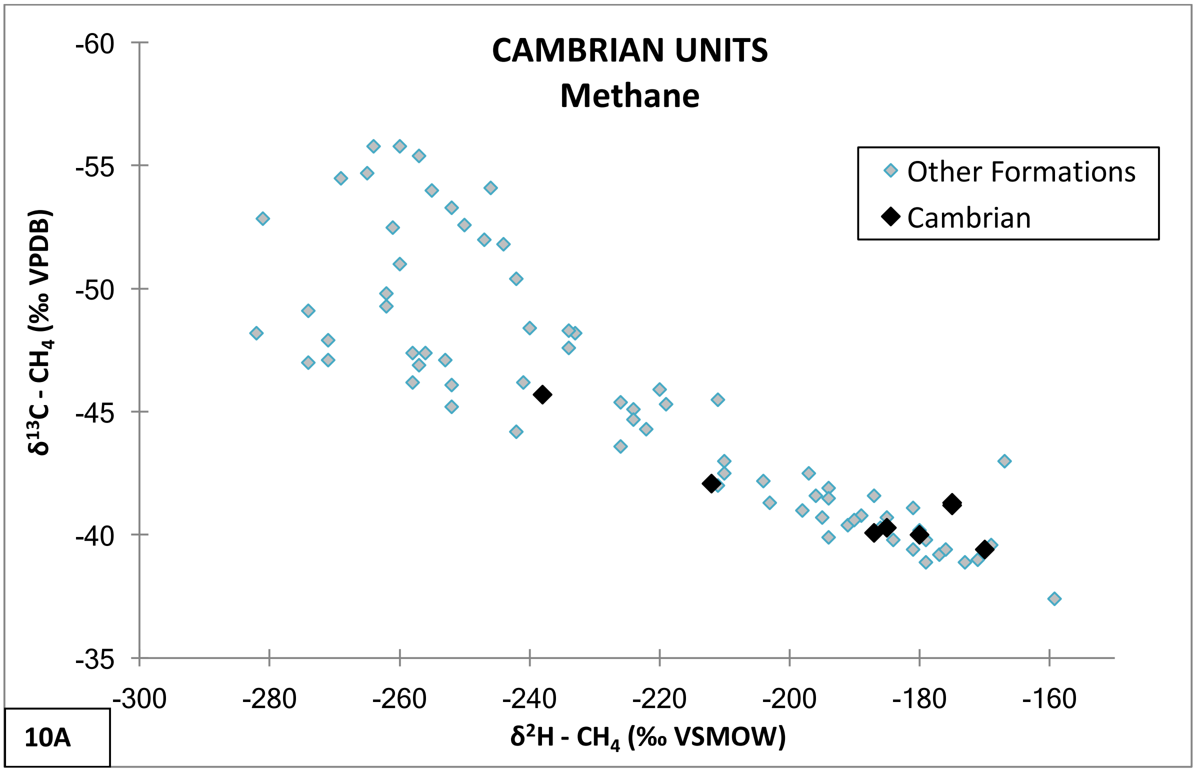
There are no apparent spatial trends in the data and, with the exception of the sole Gull River sample, there do not seem to be any significant compositional differences between the gases in the different Trenton-Black River formations. The main diagnostic feature of the Trenton-Black River gases (which overlap somewhat with the Clinton-Cataract and Cambrian gases in terms of their methane isotopes), is their unusual hydrogen isotope compositions. Most thermogenic gases have $\delta^2H_{CH4} < \delta^2H_{C2H6}$, but the Trenton-Black River gases (with the notable exception of the Gull River) have $\delta^2H_{CH4} \sim \delta^2H_{C2H6}$, with almost all samples within a tight range of $\Delta\delta^2H_{C2H6-CH4}$ from –9 to +7‰. Only a few samples from other formations have this characteristic. There are few other characteristics that differentiate the Trenton-Black River from other thermogenic gases. They do have positive $\Delta^{13}C_{n-C4H10\,-\,i-C4H10}$ (+0.5 to +1.6‰), which may be useful in differentiating them from the thermogenic, eastern Salina Group gases (all Salina gases have negative $\Delta^{13}C_{n-C4H10\,-\,i-C4H10}$ values).

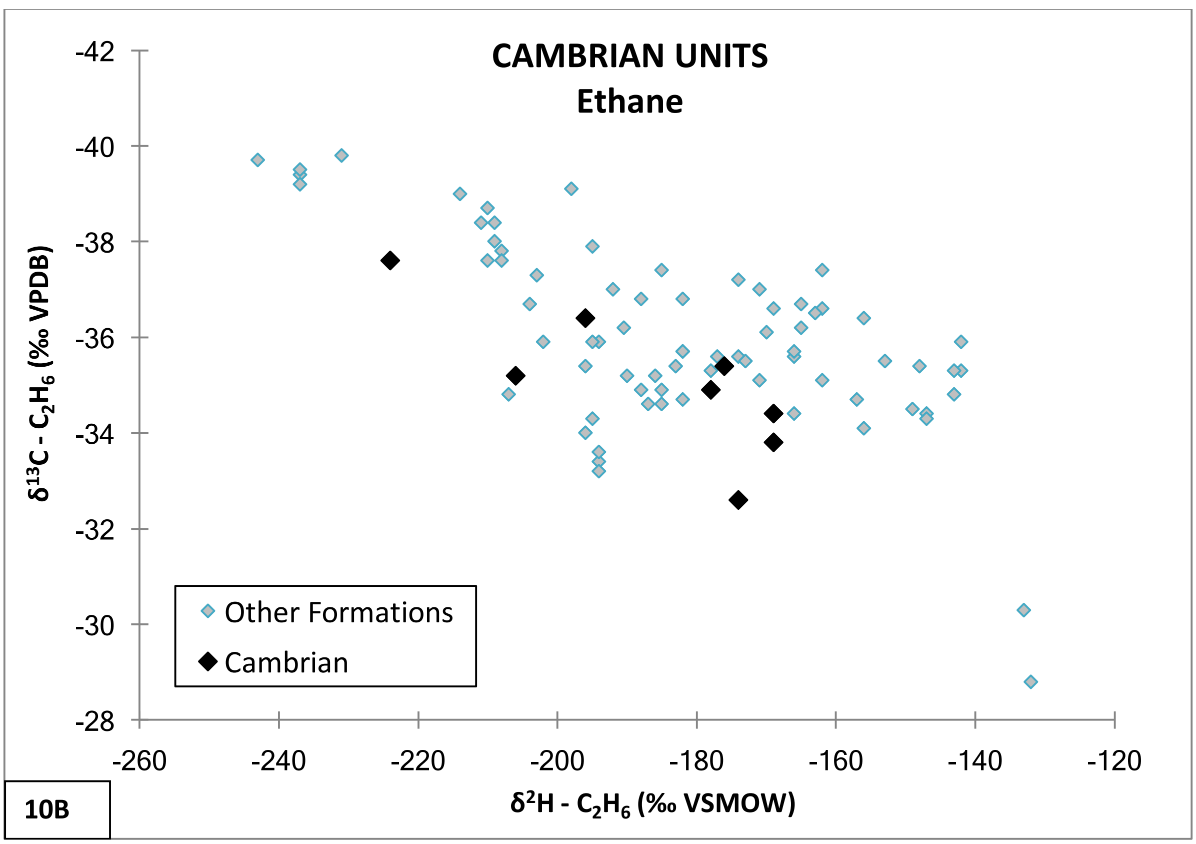
The Gull River sample (T008974) is very similar to the other Trenton-Black River gases in most respects, but it is distinctly differentiated from them by its relatively high ethane δ^2H (–178‰), leading it to have a high positive $\Delta^2H_{C2H6-CH4}$ (+32‰). This also distinguishes the Gull River from the other thermogenic gases – Cambrian gases have considerably lower $\Delta^2H_{C2H6-CH4}$, whereas values for Whirlpool Formation gases are higher, and gases from other Clinton-Cataract formations are lower.

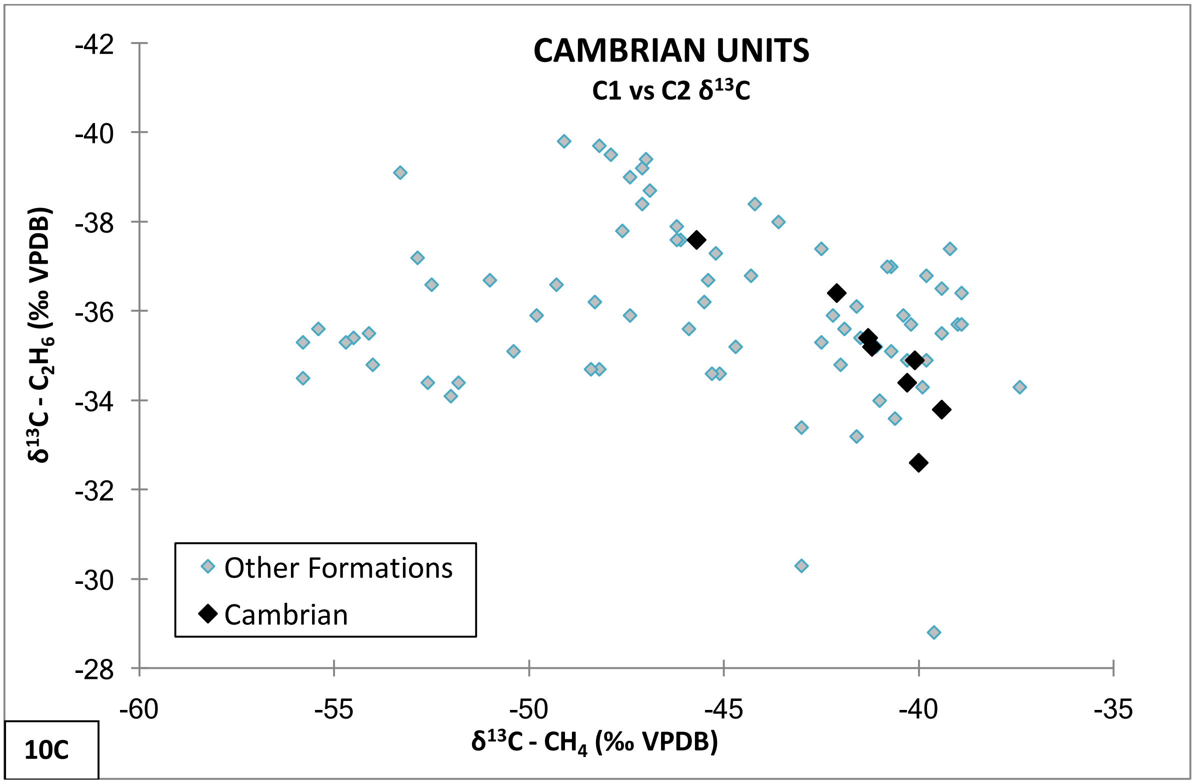
Cambrian units

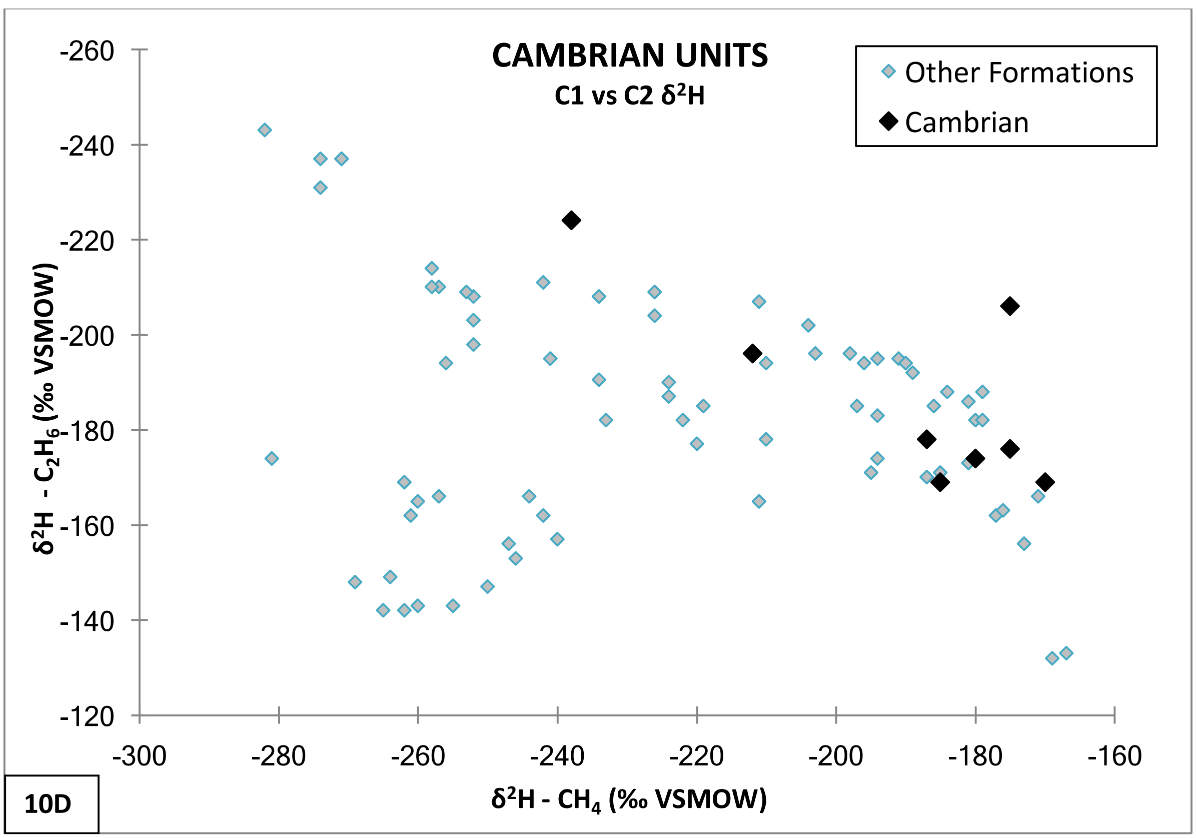
Well No.	Well Location	County	Pool	$\delta^{13}C$ CH_4	$\delta^{13}C$ C_2H_6	$\delta^{13}C$ C_3H_8	$\delta^{13}C$ i-C_4H_{10}	$\delta^{13}C$ n-C_4H_{10}	δ^2H CH_4	δ^2H C_2H_6	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	Wetness - $C_1/(C_2+C_3)$
T008532	South Easthope 4-35-II	South Easthope	Innerkip	–40.0	–32.6	–31.5	–30.5	–29.7	–180	–174	85.7	9.2	5.1	6.0
T007369	Raleigh 1-17-XIII	Raleigh	Raleigh 1-17-XIII	–40.1	–34.9	–33.0	–32.2	–32.1	–187	–178	87.2	8.5	4.3	6.8
T007956	Blenheim 8-24-VII	Blenheim	Innerkip	–40.3	–34.4	–31.7	–30.9	–30.8	–185	–169	85.5	8.8	5.7	5.9
T008094	East Zorra 2-25-XVI	East Zorra	Innerkip	–39.4	–33.8	–32.2	–31.2	–30.8	–170	–169	80.6	10.7	8.7	4.2
T008045	Blenheim 1-15-IV	Blenheim	Innerkip	–45.7	–37.6	–34.0	–32.7	–33.6	–238	–224	82.7	10.4	6.9	4.8
T010638	Burford 17-IV	Burford	Burford 17-IV	–41.2	–35.2	–30.9	-	-	–175	–206	-	-	-	-
T001910	Burford 15-II	Burford	Gobles	–41.3	–35.4	–31.2	-	-	–175	–176	-	-	-	-
T000823	Blenheim 19-II	Blenheim	Gobles	–42.1	–36.4	–32.6	-	-	–212	–196	-	-	-	-

Table 6: Natural gas data for the Cambrian strata (undifferentiated). All samples are from this study.


CAMBRIAN UNITS
Methane
Other Formations
Cambrian
δ13C - CH4 (‰ VPDB)
δ2H - CH4 (‰ VSMOW)
-60
-55
-50
-45
-40
-35
-300
-280
-260
-240
-220
-200
-180
-160
10A


CAMBRIAN UNITS
Ethane
Other Formations
Cambrian
δ13C - C2H6 (‰ VPDB)
δ2H - C2H6 (‰ VSMOW)
-42
-40
-38
-36
-34
-32
-30
-28
-260
-240
-220
-200
-180
-160
-140
-120
10B


CAMBRIAN UNITS
C1 vs C2 δ13C
δ13C - C2H6 (‰ VPDB)
δ13C - CH4 (‰ VPDB)
Other Formations
Cambrian
-42
-40
-38
-36
-34
-32
-30
-28
-60
-55
-50
-45
-40
-35
10C


CAMBRIAN UNITS
C1 vs C2 δ2H
δ2H - C2H6 (‰ VSMOW)
δ2H - CH4 (‰ VSMOW)
Other Formations
Cambrian
-260
-240
-220
-200
-180
-160
-140
-120
-300
-280
-260
-240
-220
-200
-180
-160
10D

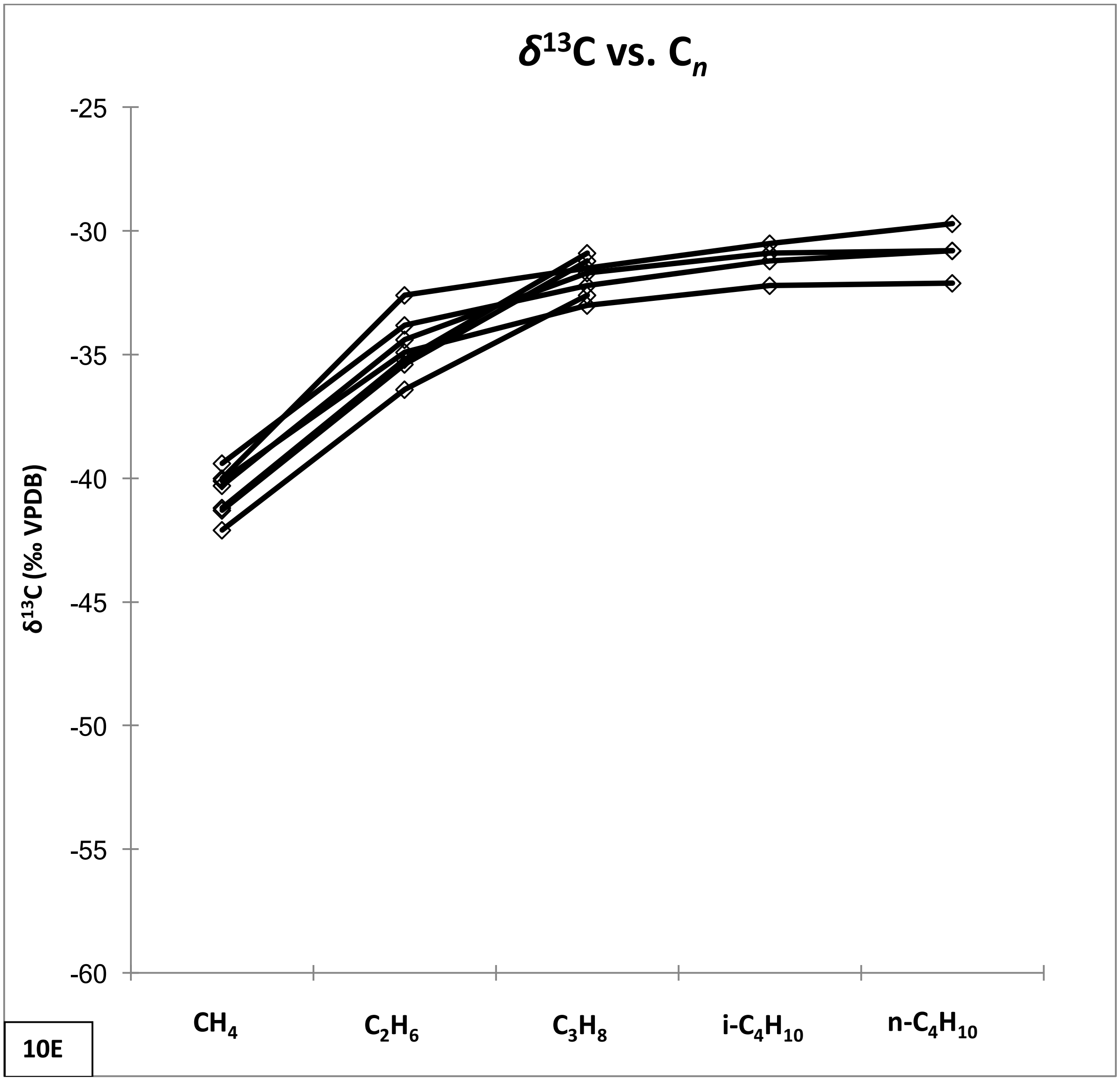


Figure 10: Isotopic compositions of gases from the Cambrian units. **A** – methane δ^{13}C *vs.* δ^{2}H; **B** – ethane δ^{13}C *vs.* δ^{2}H; **C** – methane δ^{13}C *vs.* ethane δ^{13}C; **D** – methane δ^{2}H *vs.* ethane δ^{2}H; **E** – Chung diagram of δ^{13}C *vs.* C_n (after Chung et al. 1988).

The data for gases from the (undifferentiated) Cambrian units are presented in Table 6 and illustrated in Figure 10A-E. Sample locations are shown in Appendix A, Maps 1 & 5. These samples are mostly from the Innerkip pool and surrounding area, plus one sample to the south-west in Kent County (T007369). Overall, the Cambrian gases span a fairly wide range of moderate- to highly-mature thermogenic isotopic compositions (–45.7 to –39.4‰ $\delta^{13}C_{CH4}$ and –238 to –170‰ $\delta^{2}H_{CH4}$; –37.6 to –32.6‰ $\delta^{13}C_{C2H6}$ and –224 to 169‰ $\delta^{2}H_{C2H6}$); however, with the exception of two samples (T008045 and T000823), most gases plot within a considerably narrower range (–41.3 to –39.4‰ $\delta^{13}C_{CH4}$ and –187 to –170‰ $\delta^{2}H_{CH4}$). Gas concentrations range from 80.6–87.2% for methane; 8.5–10.7% ethane; and 4.3–8.7% propane, with gas wetness ratios varying from 4.2–6.8.

Most Cambrian samples show no spatial variations in their isotopic compositions, with the exceptions of the two lower-maturity gases mentioned above, which are found in the south-east corner of the Innerkip pool (T008045) and directly south of it in the small Gobles pool (T000823). It is unclear why these two samples have compositions so different from the other gases, but presumably they contain a component of immature gas, likely sourced either *in-situ* or closer to the basin margins than the other, highly thermogenic samples.

The main distinguishing feature of the majority of the Cambrian samples is their high thermogenic maturity, although the range does overlap with the Trenton-Black River and most Reynales/Thorold/Grimsby gases, as well as the more eastern Salina gases. As mentioned above, however, the Cambrian gases largely do not share the near-zero $\Delta^{2}H_{C2H6\text{-}CH4}$ values of the Trenton-Black River gases. They have significantly lower gas wetness values than all Clinton-Cataract gases (4.2 to 6.8), and have more propane than most Trenton-Black River gases. The two lower-maturity samples are largely indistinguishable from many of the other formation gases, although their relatively low $\Delta^{2}H_{C2H6\text{-}CH4}$ (+14 and +16‰) should differentiate them from most, with the possible exception of the Reynales/Thorold/Grimsby gases.

Finally, it is perhaps noteworthy that one sample (T010638) from the small, isolated Burford 17-IV pool, to the south of the Innerkip pool, has distinctively 'reversed' $\delta^{2}H_{CH4}$ and $\delta^{2}H_{C2H6}$ values (–175 and –206‰, respectively). It is otherwise identical to the other mature Cambrian samples (except for a slightly higher $\delta^{13}C_{C3H8}$). The reason for the unusual hydrogen compositions in this pool is unclear.

Conclusions and Recommendations for Further Work

This project has significantly improved the characterization of the isotopic compositions of the natural gases in southwestern Ontario. It should be useful – together with formation water chemistry and isotopic compositions described by Skuce (2014a,b), Skuce et al. (2014a-c; 2015a,b) – for identifying the sources of gases leaking from abandoned wells. It could also be useful in other situations, where interests arise concerning the origin of natural gases appearing at the surface or in the shallow subsurface of southwestern Ontario.

The multi-isotope approach has proven quite powerful in identifying unique signatures for the various formation gases in the region. A summary of their features is outlined below:

Unit	Sub-region/ formation	Isotopic Features
Salina Group	OVERALL	Methane isotope compositions vary considerably across the region in an apparently systematic way → light bacterial isotopic signatures to the west progressing to increasingly thermogenic signatures to the east
		Bacterial/thermogenic mixing trend has most samples plotting above the thermogenic trend of other formations
		$\Delta^{13}C_{nC4-iC4}$ generally significantly negative (most below -1‰) - distinct from almost all other gases except Sombra Guelph
	Lambton County	Light, bacterial methane isotope signatures
		Generally lower ethane and propane $\delta^{13}C$ than local Sombra Guelph
	Morpeth Pool (eastern Kent)	Highly thermogenic gas
		Ethane $\delta^{13}C$ and $\delta^{2}H$ substantially higher than all other gases
Guelph Formation (Lockport Group)	OVERALL	Highly variable isotopic compositions; may share general spatial bacterial/thermogenic trend with Salina (but more eastern samples needed)
		Different regions have much narrower, distinctive isotopic compositions
	Lambton County - Sombra Township	Very light, bacterial methane isotope compositions - lower $\delta^{13}C$ than all other Guelph, and every formation except some (Lambton) Salina
		Highest $\Delta^{2}H_{C2-C1}$ of all samples - plots in a distinct group on a $\delta^{2}H_{C2}$ *vs.* $\delta^{2}H_{C1}$ graph
		Very tight range of $\delta^{13}C_{C2H6}$ (–35.5 to –34.1‰)
		Very high $\Delta^{13}C_{C2-C1}$ (17.4 – 21.3‰ – higher than most Lambton Salina samples
		Fairly consistent gas concentrations and gas wetness ratios (9.2–11.9, with one exception); gas wetness ratios higher than most Salina and many other units
		$\Delta^{13}C_{nC4-iC4}$ generally significantly negative (most below -1‰) – distinct from almost all except Salina

	Lambton County - Enniskillen Township	Low-maturity thermogenic methane - higher $\delta^{13}C_{CH4}$ than Sombra Guelph
		Lower $\delta^{13}C_{C3H8}$ and $\delta^{2}H_{C2H6}$ than Sombra Guelph ($\delta^{13}C_{C3H8}$ also lower than all Salina)
		$\Delta^{13}C_{nC4\text{-}iC4}$ generally significantly negative (most below -1‰) – distinct from almost all gases except Salina
	Huron County (north)	Mixed bacterial/thermogenic? Methane $\delta^{13}C$ intermediate between Sombra and Enniskillen Guelph gases
		Ethane isotope compositions plot in a different region from other Guelph, Salina gases (generally lower $\delta^{13}C_{C2H6}$ and/or higher $\delta^{2}H_{C2H6}$)
		Also plot in distinct fields on graphs of methane *vs.* ethane $\delta^{13}C$ and $\delta^{2}H$
		Positive $\Delta^{13}C_{nC4\text{-}iC4}$ (1.2–1.8‰) – distinct from Salina and Lambton Guelph gases
		Higher $\Delta^{2}H_{C2\text{-}C1}$ than almost all other samples except Sombra Guelph gases
	Huron County (south/central)	Wider range of compositions than other Guelph gases
		Distinctively more thermogenic than the northern Huron and Sombra Guelph gases, and more thermogenically-mature than the Enniskillen Guelph
		Moderate thermogenic maturity - methane isotope compositions lower than most Cambro-Ordovician samples
		Lower $\Delta^{13}C_{nC4\text{-}iC4}$ (–0.5 to +0.7‰) than the northern Huron Guelph
		Some slight differences in several isotope pairs compared to Salina gases ($\Delta^{13}C_{nC4\text{-}iC4}$; $\Delta^{13}C_{nC4\text{-}C3}$; $\Delta^{13}C_{iC4\text{-}C3}$) – see Table 3.
	Kent County (Lake Erie)	Highly mature thermogenic gas - higher methane isotope compositions than all other gases ($\delta^{13}C$ and $\delta^{2}H$ of C_2+ not particularly distinctive)
		Lower $\Delta^{2}H_{C2\text{-}C1}$ than other Guelph and Salina (with one exception)
Clinton & Cataract Groups	OVERALL	Highly variable, low to high maturity thermogenic gases
		Almost all have lower ethane isotope compositions than Cambro-Ordovician gases
	Reynales/Thorold/ Grimsby Formations (Simcoe area)	Low thermogenic maturity (low methane isotope compositions) - more immature than all other gases found on the Appalachian Basin side of the Algonquin Arch
		High (10+) gas wetness values (higher than most other formations, including Whirlpool)
		Higher $\Delta^{2}H_{C2\text{-}C1}$ than other Reynales/Thorold/Grimsby and Cambro-Ordovician gases; lower than Whirlpool and most Guelph and Salina gases
		Generally lower ethane isotope compositions than Salina and Guelph gases
	Reynales/Thorold/ Grimsby Formations (all other areas)	High thermogenic maturity (high methane isotope compositions); similar maturity to Cambro-Ordovician gases
		High (10+) gas wetness values (above most other formations, including Whirlpool)
		Lower $\Delta^{2}H_{C2\text{-}C1}$ than all other gases except Cambro-Ordovician gases
	Whirlpool Formation	Intermediate-maturity thermogenic gas; two most thermogenic samples are the easternmost, but otherwise no spatial trend. More mature than Simcoe (Norfolk County) area Reynales/Thorold/ Grimsby; less mature than Reynales/Thorold/ Grimsby elsewhere, and Cambro-Ordovician gases
		Lower gas wetness than Reynales/Thorold/Grimsby (<10)
		Among the highest $\Delta^{13}C_{nC4\text{-}iC4}$ (+1.4 to +2.3‰); higher than all Cambrian gases

		Narrow range of δ^2H_{CH4} (–258 to –241‰); Δ^2H_{C2-C1} distinctively between 40–50‰, higher than Cambro-Ordovician and Reynales/Thorold/Grimsby, lower than Salina and Guelph
Trenton & Black River Groups	OVERALL	Highly-mature thermogenic gases
	Cobourg/Sherman Fall/ Coboconk Fmns (all areas)	Very distinctive hydrogen isotope compositions: $\delta^2H_{CH4} \approx \delta^2H_{C2H6}$, with almost all samples having $\Delta^2H_{C2H6\text{-}CH4}$ in a tight range between –9 and +7‰.
		Moderately positive $\Delta^{13}C_{nC4\text{-}iC4}$ (+0.5 to +1.6‰) differentiate from eastern, thermogenic Salina (and possibly Guelph) gases
	Gull River Formation	Relatively high ethane δ^2H (–178‰), leading it to have a high, positive $\Delta^2H_{C2H6\text{-}CH4}$ (+32‰) – higher than Cambrian gases
Cambrian units	OVERALL	Moderate- to highly-mature thermogenic gases (mostly the latter)
	Southeast Innerkip/ North Gobles pools	Lower thermogenic maturity (distinctly lower δ^2H_{CH4}) than other Cambrian samples
	Burford 17-IV pool	Distinctively 'reversed' δ^2H_{CH4} and δ^2H_{C2H6} (–175 and –206‰, respectively)
		Slightly higher $\delta^{13}C_{C3H8}$ than other Cambrian and Trenton-Black River gases; otherwise identical to other mature Cambrian gases
	All other samples	Highly-mature thermogenic gases
		Generally higher $\Delta^2H_{C2H6\text{-}CH4}$ than the Trenton-Black River gases
		Lower gas wetness ratios than all Clinton-Cataract gases (4.2 to 6.8)
		Higher propane concentrations than most Trenton-Black River gases (average 6.1% vs 4.1%)

Further sampling efforts could be of value for improving this characterization and filling in gaps where areas and formations are under-represented. Some such areas are summarized below.

- Most importantly, samples from the Salina and Guelph formations should be collected from the eastern parts of the peninsula, since most current samples are from the west.
- Further investigation of the Simcoe (Norfolk County) area 'anomaly' in the Clinton-Cataract Groups is needed, to determine its borders relative to the 'main' Clinton-Cataract composition. The Whirlpool Formation is under-represented to the south-west; further samples would be useful to assess any spatial changes in thermogenic maturity
- The Trenton-Black River Groups are under-represented to the north-east, and the Gull River Formation needs further characterization
- The Cambrian has few samples outside the Innerkip area, and further investigation of the anomalous compositions in the vicinity of the Gobles pool would be beneficial.

References

Armstrong, D.A., and Carter, T.R., 2010. The subsurface Paleozoic stratigraphy of southern Ontario. *Ontario Geological Survey*, Special Volume **7**, 301 p.

Armstrong, D.A., and Dodge, J.E.P., 2007. Paleozoic geology of southern Ontario. *Ontario Geological Survey*, Miscellaneous Release-Data **219**.

Barker, J.F., and Pollack, S.J., 1984. Geochemistry and origin of natural gases in southern Ontario. *Bulletin of Canadian Petroleum Geology* **32**: 313-326.

Carter, T.R., Clark, J., Colquhoun, I., Dorland, M., and Phillips, A., 2016. Ontario oil and gas plays: exploration, production and geology. Canadian Society of Petroleum Geologists, *CSPG Reservoir* **43(8)**: 19-24.

Chung, H.M., Gormly, J.R., and Squires, R.M., 1988. Origin of gaseous hydrocarbons in subsurface environments: Theoretical considerations of carbon isotope distribution. *Chemical Geology* **71**: 97-103.

Hut, G., 1987. Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations. Report to the Director General, *International Atomic Energy Agency*, Vienna, September 16-18, 1985), 42p.

Lazorek, M., and Carter, T.R., 2008. The oil and gas plays of Ontario. Ontario Petroleum Institute, Ontario, *Oil & Gas Magazine* **June 2008**: 18-27. June-Warren Publishing.

Mohd Zaffa, F., 2010. Isotope Fingerprinting of Natural Gas Wells in Southwestern Ontario. BSc Thesis, Department of Earth Sciences, *The University of Western Ontario*, 128p.

NIST, 2007. National Institute of Standards & Technology Report of Investigation, Reference Materials 8559, 8560, 856. Prepared by S.A. Wise and R.L. Watters, Jr., 7p.

Potter, J., and Longstaffe F.J., 2011. The isotopic characterisation of water and natural gas seepage from abandoned wells in southwestern Ontario. Unpublished Report for Stage 1 (Feasibility) Study, *Ontario Ministry of Natural Resources and Forestry*, 26p.

Potter, J., and Siemann, M.G., 2004. A new method for determining $\delta^{13}C$ and δD simultaneously for CH_4 by gas chromatography/continuous-flow isotope-ratio mass spectrometry. *Rapid Communications in Mass Spectrometry* **18**: 175-180.

Potter, J., Salvi, S., and Longstaffe, F.J., 2013. Abiogenic hydrocarbon isotopic signatures in granitic rocks: Identifying pathways of formation. *Lithos* **182-183**: 114-124.

Sherwood Lollar, B., Weise, S.M., Frape, S.K., and Barker, J.F., 1994. Isotopic constraints on the migration of hydrocarbon and helium gases of southwestern Ontario. *Bulletin of Canadian Petroleum Geology* **42**: 283-295.

Skuce, M., 2014a. Isotopic Fingerprinting of Shallow and Deep Groundwaters in Southwestern Ontario and its Applications to Abandoned Well Remediation. MSc Thesis, *The University of Western Ontario*, Electronic thesis and dissertation repository, Paper 1926, 267 p., http://ir.lib.uwo.ca/do/search/?q=skuce&start=0&context=686929

Skuce, M., 2014b. Volume VI. Ancillary electronic documents – Abandoned Works Program. Unpublished Report, *Ontario Ministry of Natural Resources and Forestry*, test csv and R files for SIAR.

Skuce, M., Potter, J., and Longstaffe, F.J. (2014a) Volume I. Water geochemistry – Abandoned Works Program. Unpublished Report, *Ontario Ministry of Natural Resources and Forestry*, 51p.

Skuce, M., Potter, J., and Longstaffe, F.J. (2014b) Volume II. Guide to the geochemical tool – Abandoned Works Program. Unpublished Report, *Ontario Ministry of Natural Resources and Forestry*, 25p.

Skuce, M., Potter, J., and Longstaffe, F.J. (2014c) Volume III. Water Geochemistry database – Abandoned Works Program. Unpublished Report, *Ontario Ministry of Natural Resources and Forestry*, Excel Spreadsheet.

Skuce, M., Potter, J., and Longstaffe, F.J., 2015a. The Isotopic Characterization of Water in Paleozoic Bedrock Formations in Southwestern Ontario. *Oil, Gas and Salt Resources Library*, Open File Data Release 2015-3.

Skuce, M., Longstaffe, F.J., Carter, T.R., and Potter, J., 2015b. Isotopic fingerprinting of groundwaters in southwestern Ontario: Applications to abandoned well remediation. *Applied Geochemistry* **58**: 1-13.

APPENDIX A

Table A1: Sample location details

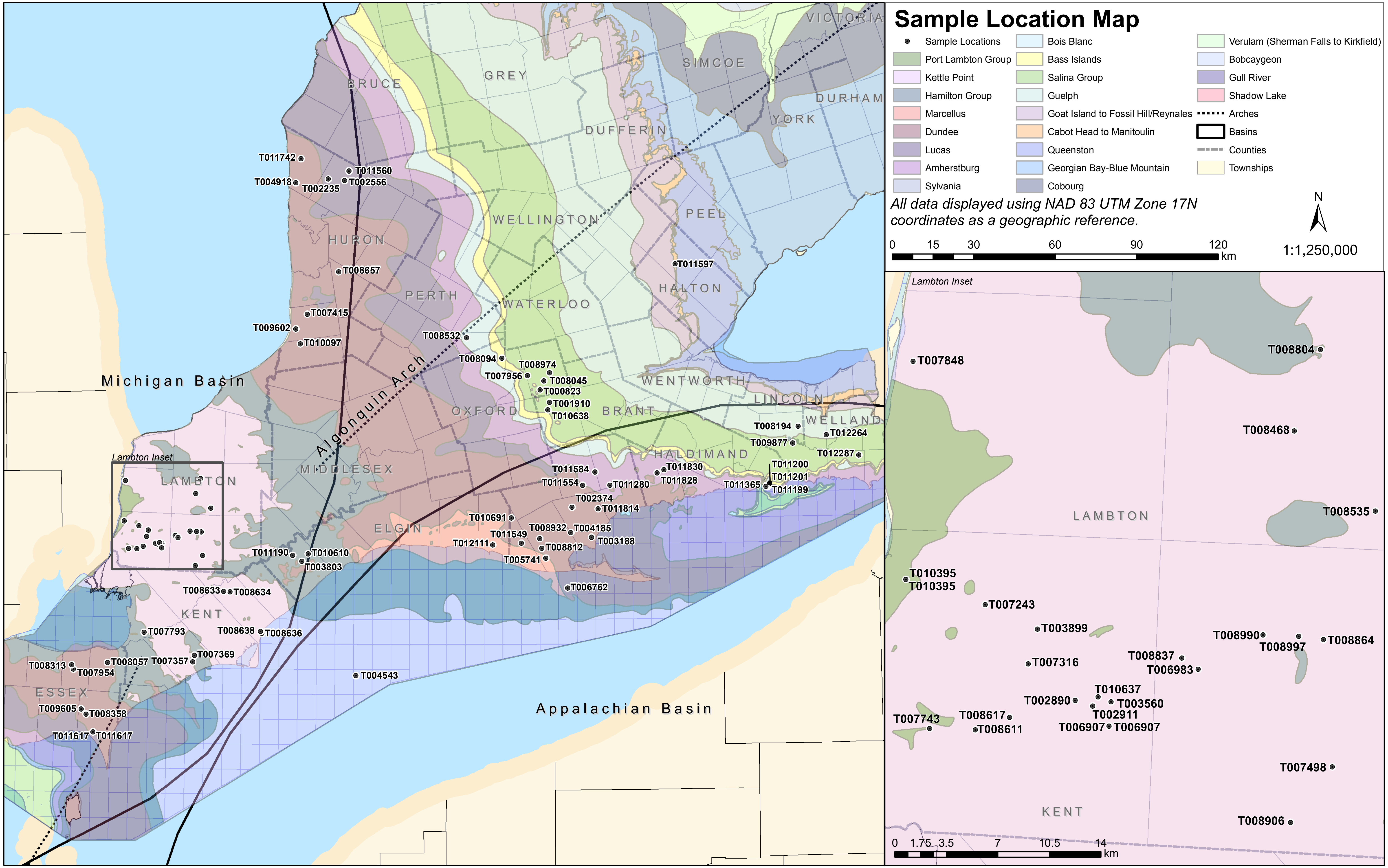
Well No.	Well Location	Well Name	County	Twp	Lat	Long	Pool	Producing Fm	Depth (m)
T003560	Sombra 2-26-VII	Baslen #16	Lambton	Sombra	42.6630	-82.2796	Charlemont	A-2 Carb	400
T008990	Dawn 7-24-VI	Union Gas Dawn 116	Lambton	Dawn	42.7054	-82.1544	Dawn 1	A-2 Carb	500
T007498	Camden 2-10-IXGC	Twin Star #6	Kent	Camden	42.6251	-82.0955	Camden 6-10 Gore	A-2 Carb	450
T008636	Howard 5-94-BFC	Imperial 495A	Kent	Howard	42.3687	-81.8271	Morpeth	A-2 Carb	495
T008638	Howard 8-93-STR	Langstaff No.1	Kent	Howard	42.3754	-81.8339	Morpeth	A-2 Carb	495
T008864	Dawn 7-24-IX	Union Gas Dawn 67	Lambton	Dawn	42.7028	-82.1042	Dawn 1	A-1 + A-2 Carb	520
T008837	Dawn 6-21-II	Salinia-Colonial 2	Lambton	Dawn	42.6904	-82.2214	Dawn Misc	A-1 + A-2 Carb	580
T008997	Dawn 2-24-VII	Union Gas Dawn 1	Lambton	Dawn	42.7047	-82.1248	Dawn 1	A-1 + A-2 Carb	480
T008906	Camden 1-4-VIIGC	Union #13	Kent	Camden	42.5908	-82.1295	Camden Gore	A-1 + A-2 Carb	475
T008535	Enniskillen 1-24-II	Midway	Lambton	Enniskillen	42.7820	-82.0624	Enniskillen 1-24-II	A-1 Carb	553
T007848	Moore 4-51-FC	Sungold #4	Lambton	Moore	42.8693	-82.4484	Moore 5-50 Front	A-1 Carb	750
T008611	Sombra 11-VI	Imperial Oil #109	Lambton	Sombra	42.6445	-82.3916	Becher West	A-1 Carb	565
T008634	Howard 1-9-BLC	Cameron-P #1	Kent	Howard	42.5059	-81.9718	Botany	A-1 Carb	500
T008633	Howard 7-7-I	Cameron Smids	Kent	Howard	42.5069	-81.9996	Botany	A-1 Carb	510
T002911	Sombra 3-24-VII	Brett-Baslen	Lambton	Sombra	42.6603	-82.2947	Otter Creek E	Guelph	455
T002890	Sombra 2-22-VII	Shawnee Lencourt	Lambton	Sombra	42.6636	-82.3092	Otter Creek	Guelph	590
T008617	Sombra 2-15-VI	Becher No. 73	Lambton	Sombra	42.6525	-82.3633	Becher West	Guelph	585
T008804	Enniskillen 1-17-X	CanEnerco #10	Lambton	Enniskillen	42.8802	-82.1098	Petrolia East	Guelph	688
T008468	Enniskillen 2-15-VI	CanEnerco #2	Lambton	Enniskillen	42.8304	-82.1306	Corey East	Guelph	550
T003899	Sombra 5-17-XI	Ram No. 33	Lambton	Sombra	42.7068	-82.3415	Sombra 5-17-XI	Guelph	615
T007243	Sombra 5-11-XII	Hadley-Midway	Lambton	Sombra	42.7212	-82.3851	Sombra 5-11-XII	Guelph	645
T010637	Sombra 8-24-VIII	CQE #1	Lambton	Sombra	42.6659	-82.2904	Sombra	Guelph	580
T007316	Sombra 4-16-IX	Raen Smith	Lambton	Sombra	42.6855	-82.3486	Sombra	Guelph	600
T010395	Sombra 4-2-XIII	Kinetic #5	Lambton	Sombra	42.7358	-82.4512	Sombra	Guelph	690
T010395	Sombra 4-2-XIII*	Kinetic #5	Lambton	Sombra	42.7358	-82.4512	Sombra	Guelph	690
T004543	Lake Erie	Consumers 13262	Kent	Lake Erie	42.2306	-81.4063	Morpeth	Guelph	501
T004918	Ashfield 8-1-IIIED	SHELL	Huron	Ashfield	43.8650	-81.6912	Ashfield 7-1-III	Guelph	593
T011742	Ashfield 5-5-IXWD	NCE Fitzgerald	Huron	Ashfield	43.9453	-81.6694	-	Guelph	442
T002235	West Wawanosh 6-17-VIII	ALTAIR ET AL	Huron	West Wawanosh	43.8783	-81.5438	Dungannon	Guelph	410
T002556	West Wawanosh 26-X	Belmore No. 1	Huron	West Wawanosh	43.8737	-81.4679	West Wawanosh 26-X	Guelph	412

T011560	WestWawanosh 1-25-XIIWD	NCE Fordyce N	Huron	West Wawanosh	43.9049	-81.4480	West Wawanosh 1-25-XII	Guelph	400
T009602	Hay 2-11-XVI	Tribute et al. #26	Huron	Hay	43.3803	-81.6857	Hay 5-12-XV	Guelph	555
T010097	Stephen 3-22-XV	Tribute et al. #28	Huron	Stephen	43.3307	-81.6648	Hay 5-12-XV	Guelph	525
T007415	Hay 3-23-XI	Ansell Lake Res #1	Huron	Hay	43.4285	-81.6344	Zurich	Guelph	575
T008657	Tuckersmith 2-30-IIISHR	Clearwood etal #12	Huron	Tuckersmith	43.5703	-81.4927	Tuckersmith 30-III	Guelph	500
T008932	North Walshingham 7	GGOL #12	Norfolk	North Walsingham	42.6852	-80.5822	S. Walsingham 5-6-VI	Reynales+Thorold	405
T011828	Walpole 3-13-VIII	Devine #1	Haldimand	Walpole	42.9007	-80.0513	Haldimand	Reynales+Grimsby	220-260
T004185	Charlotte 6-1-III	Craven-Union #12	Norfolk	Charlotteville	42.7046	-80.4419	Norfolk	Thorold	390
T010691	Houghton 2-138-STR	GGOL-Huron #3	Norfolk	Houghton	42.7543	-80.7094	Bayham	Thorold	410
T011549	Houghton 4-11-II	GGOL #50	Norfolk	Houghton	42.6702	-80.6643	Houghton 5-8-ENR	Thorold/Grimsby	425
T008812	South Walshingham 4	GGOL #10	Norfolk	South Walsingham	42.6535	-80.5726	S. Walsingham 5-6-VI	Thorold/Grimsby	410
T011190	Aldborough 4-15-IV	GGOL #65	Elgin	Aldborough	42.6285	-81.6917	Aldborough 4-15-IV	Grimsby	555
T006762	Lake Erie	Consumers 13888	Norfolk	Lake Erie	42.5207	-80.4585	Clear Creek	Grimsby	445
T005741	South Walshingham 1	Explorer #5	Norfolk	South Walsingham	42.6208	-80.5547	Venison Creek	Grimsby	420
T010610	Aldborough 6-Gore-IV	REC #16	Elgin	Aldborough	42.6338	-81.6228	Aldborough 1-21-IV	Grimsby	540
T003188	Charlotteville 12-10-A	New Metalore No.39	Norfolk	Charlotteville	42.6888	-80.3489	Norfolk	Grimsby	380
T011830	Walpole 7-17-IX	G. Williamson #1	Haldimand	Walpole	42.9103	-80.0203	Haldimand	Reynales+Grimsby	225
T011814	Charlotteville 5-22-V	Metalore No.93	Norfolk	Charlotteville	42.7832	-80.3192	Norfolk	Grimsby	360
T002374	Charlotteville 8-9-IX	New Metalore No.23	Norfolk	Charlotteville	42.7886	-80.4364	Norfolk	Grimsby	360
T011584	Windham 8-1-IX	NOG #13	Norfolk	Windham	42.9054	-80.3315	Norfolk	Thorold	282
T011554	Windham 6-10-XII	NOG #6	Norfolk	Windham	42.8617	-80.3875	Norfolk	Thorold	317
T011280	Townsend 3-7-XIV	NFK #1	Norfolk	Townsend	42.8610	-80.2645	Norfolk	Thorold/Grimsby/ Whirpool	328
T012287	Humberstone 7 - 5 - V	Bruce Sider #2	Welland	Humberstone	42.9485	-79.1404	Welland	Whirlpool	181
T011199	Sherbrooke 2-2-I	L. Kinsey 3	Haldimand	Sherbrooke	42.8536	-79.5605	Haldimand	Whirlpool	259
T011200	Sherbrooke 4-3-I	Niece Brothers #2	Haldimand	Sherbrooke	42.8495	-79.5550	Haldimand	Whirlpool	260
T011201	Sherbrooke 3-3-I	R. Niece 3	Haldimand	Sherbrooke	42.8520	-79.5564	Haldimand	Whirlpool	260
T011365	Sherbrooke 3-2-I	L. Kinsey 2	Haldimand	Sherbrooke	42.8511	-79.5613	Haldimand	Whirlpool	260
T008194	Gainsborough 6 24 -IV	Comfort No. 1	Lincoln	Gainsborough	43.0480	-79.4109	Welland	Whirlpool	132
T009877	Wainfleet 9 - 31 - VII	Heise No.1	Welland	Wainfleet	42.9930	-79.4375	Welland	Whirlpool	166
T012264	Thorold 2 - 237 -	J. Jackson #1	Welland	Thorold	43.0188	-79.2841	Welland	Whirlpool	165
T007357	Raleigh 2-14-XIV	Ram/BP 4	Kent	Raleigh	42.2714	-82.1344	Raleigh 2-14-XIV	Cobourg	925

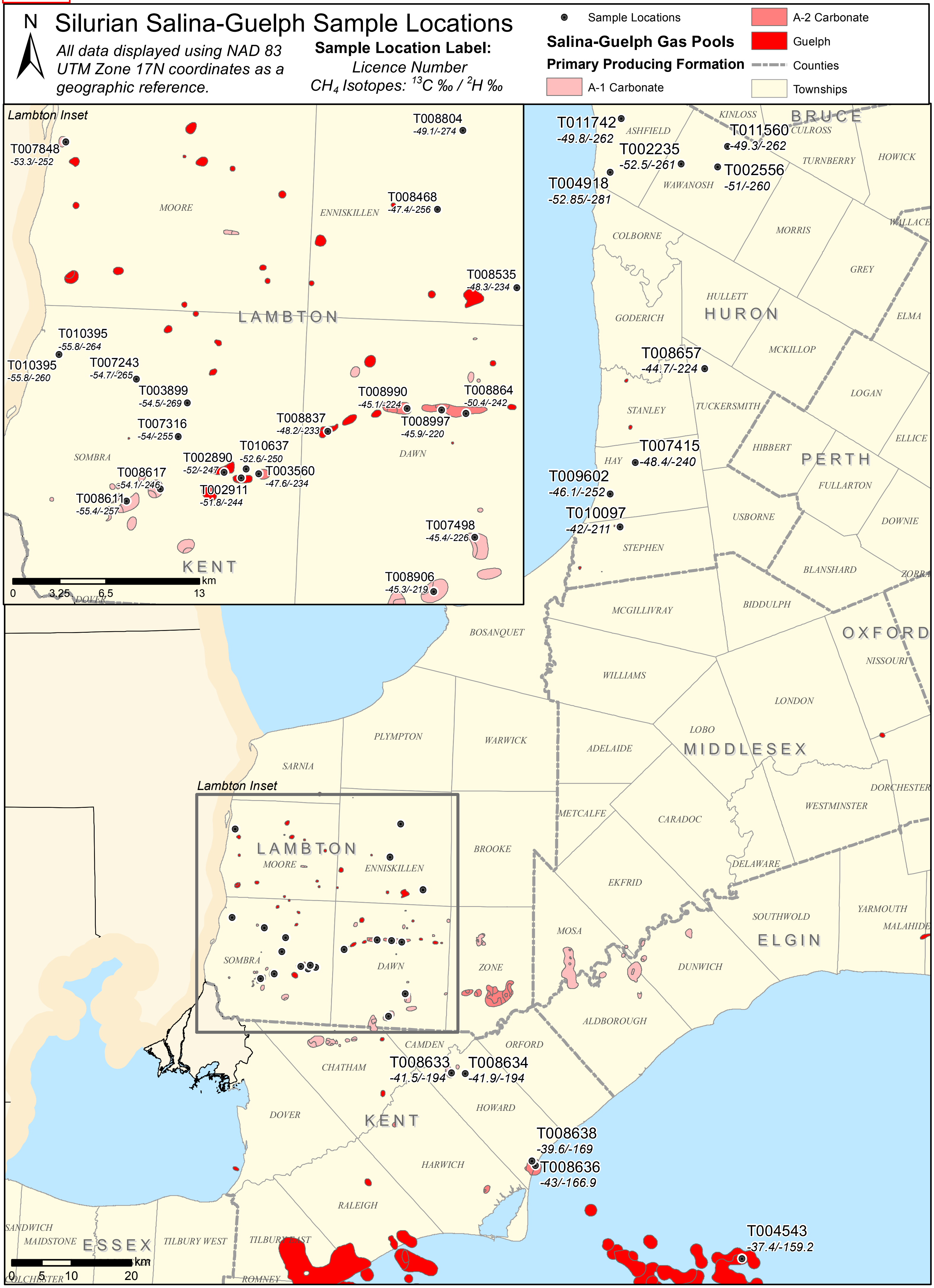
T007954	Rochester 8-17-IIIEBR	PPC Rochester #4	Essex	Rochester	42.2413	-82.6663	Rochester 1-17-II	Cobourg	821
T009605	Mersea 1-2-VI	Talisman Horiz #1	Essex	Mersea	42.1095	-82.6287	Mersea 3-4-IV	Cobourg	770
T008358	Mersea 4-5-V	REC #4A	Essex	Mersea	42.0923	-82.6060	Mersea 3-6-V	Cobourg	775
T007793	Dover 3-4-IVE	PPC/Ram 29	Kent	Dover	42.3674	-82.3532	Dover 7-5-VE	Sherman Fall	940
T007743	Sombra 7-6-VI	Torgary et al 2	Lambton	Sombra	42.6449	-82.4293	Sombra 7-6-VI	Sherman Fall	960
T003803	Aldborough 7-18-IV	Pounder Harmon	Elgin	Aldborough	42.6088	-81.6512	Aldborough 7-18-IV	Sherman Fall	960
T008057	Tilbury North 1-11-IV	Ram/Talisman #29	Lambton	Tilbury North	42.2657	-82.5151	Tilbury North 1-11-IV	Sherman Fall	860
T006983	Dawn 7-20-III	Ram #91	Lambton	Dawn	42.6836	-82.2078	Dawn 7-20-III	Coboconk	1060
T011597	Esquesing 6 - 15 - IV	No.12-Acton-1	Halton	Esquesing	43.5937	-79.9586	Acton	Coboconk	565
T006907	Sombra 3-26-VI	Ram #84	Lambton	Sombra	42.6482	-82.2808	Sombra 3-26-VI	Coboconk	1060
T006907	Sombra 3-26-VI*	Ram #84	Lambton	Sombra	42.6482	-82.2808	Sombra 3-26-VI	Coboconk	1060
T008313	Rochester 3-15-IIEBR	Paragon No. 20	Essex	Rochester	42.2552	-82.6744	Rochester 7-17-IV	Coboconk	928
T008974	Blenheim 3-10-VI	Cambright #60	Oxford	Blenheim	43.2349	-80.5338	Blenheim 3-10-VI	Gull River	810
T008532	South Easthope 4-35-II	Cambright #63	Perth	South Easthope	43.3526	-80.9106	Innerkip	Cambrian	920
T007369	Raleigh 1-17-XIII	Ram BP 5	Kent	Raleigh	42.2933	-82.1281	Raleigh 1-17-XIII	Cambrian	1150
T007956	Blenheim 8-24-VII	Gason et al #1	Oxford	Blenheim	43.2259	-80.6349	Innerkip	Cambrian	890
T008094	East Zorra 2-25-XVI	DGC #7	Oxford	East Zorra	43.2843	-80.7496	Innerkip	Cambrian	880
T008045	Blenheim 1-15-IV	DGC P2-8	Oxford	Blenheim	43.2091	-80.5598	Innerkip	Cambrian	870
T010638	Burford 17-IV	CQE #2	Brant	Burford	43.1123	-80.5424	Burford 17-IV	Cambrian	900
T001910	Burford 15-II	Imperial 892	Brant	Burford	43.1382	-80.5344	Gobles	Cambrian	875
T000823	Blenheim 19-II	Paris Petroleum No.11	Oxford	Blenheim	43.1788	-80.5778	Gobles	Cambrian	880

Table A1: Sample location details. Sample names shown in **BOLD** are from Mohd Zaffa (2010).

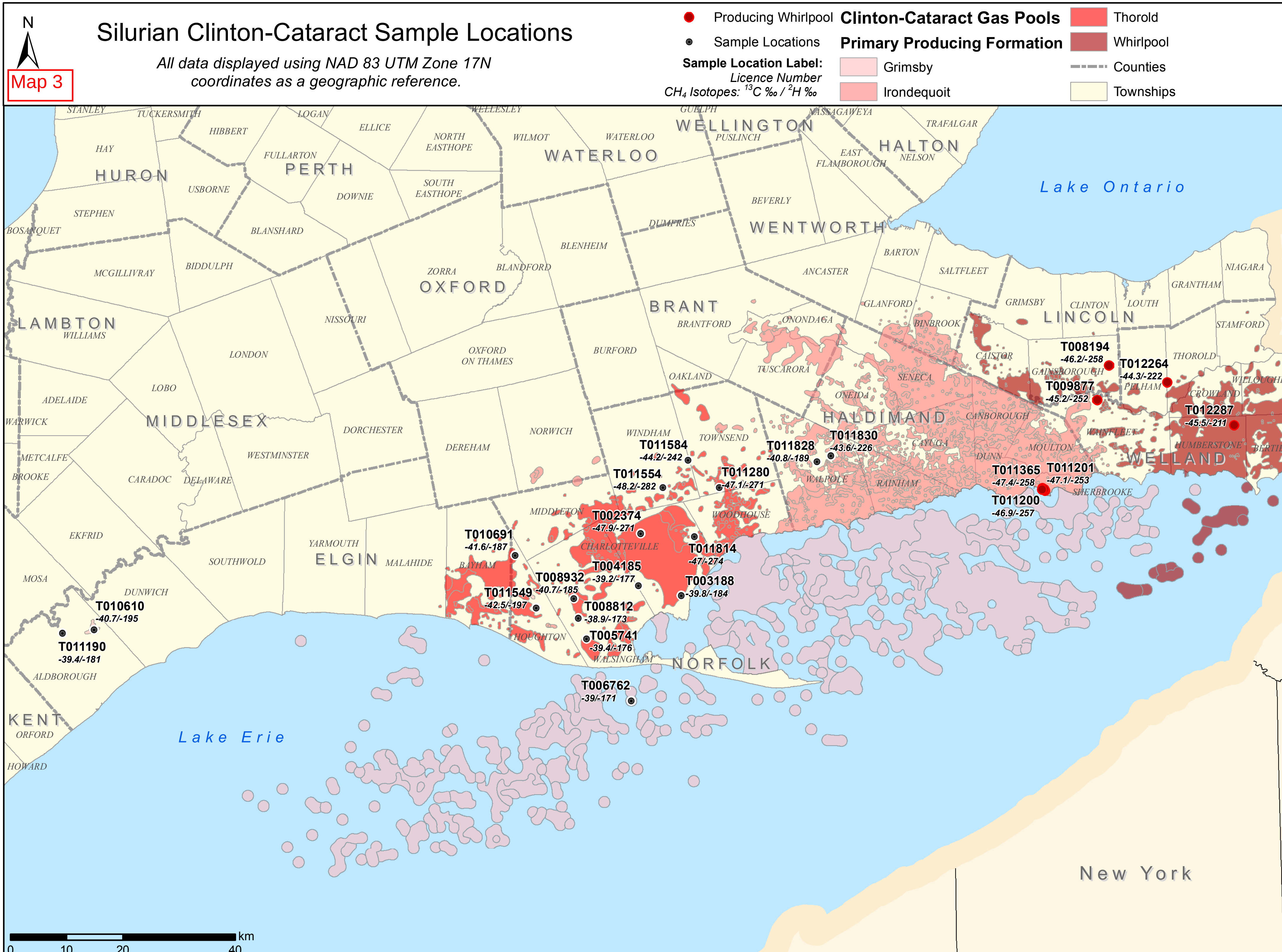
Map 1


Sample Location Map
Sample Locations
Port Lambton Group
Kettle Point
Hamilton Group
Marcellus
Dundee
Lucas
Amherstburg
Sylvania
Bois Blanc
Bass Islands
Salina Group
Guelph
Goat Island to Fossil Hill/Reynales
Cabot Head to Manitoulin
Queenston
Georgian Bay-Blue Mountain
Cobourg
Verulam (Sherman Falls to Kirkfield)
Bobcaygeon
Gull River
Shadow Lake
Arches
Basins
Counties
Townships
All data displayed using NAD 83 UTM Zone 17N coordinates as a geographic reference.
0 15 30 60 90 120 km
N
1:1,250,000
Michigan Basin
Appalachian Basin
Algonquin Arch
Lambton Inset
BRUCE
GREY
SIMCOE
VICTORIA
DURHAM
YORK
DUFFERIN
WELLINGTON
PEEL
HURON
HALTON
PERTH
WATERLOO
WENTWORTH
LINCOLN
WELLAND
OXFORD
BRANT
HALDIMAND
MIDDLESEX
LAMBTON
ELGIN
KENT
ESSEX
T011742
T011560
T004918
T002235
T002556
T008657
T011597
T007415
T009602
T010097
T008532
T008094
T008974
T007956
T008045
T000823
T001910
T010638
T008194
T012264
T009877
T012287
T011584
T011830
T011200
T011554
T011280
T011828
T011201
T011365
T011199
T002374
T011814
T010691
T008932
T004185
T011549
T003188
T012111
T008812
T005741
T011190
T010610
T003803
T006762
T008633
T008634
T007793
T008638
T008636
T007369
T008313
T008057
T007357
T007954
T004543
T009605
T008358
T011617
T011617
T007848
T008804
T008468
T008535
T010395
T010395
T007243
T003899
T008990
T008997
T008864
T007316
T008837
T006983
T010637
T002890
T003560
T002911
T008617
T007743
T008611
T006907
T006907
T007498
T008906
0 1.75 3.5 7 10.5 14 km

Map 2



N
Silurian Salina-Guelph Sample Locations
All data displayed using NAD 83 UTM Zone 17N coordinates as a geographic reference.
Sample Location Label:
Licence Number
CH4 Isotopes: 13C ‰ / 2H ‰
Sample Locations
Salina-Guelph Gas Pools
Primary Producing Formation
A-1 Carbonate
A-2 Carbonate
Guelph
Counties
Townships
Lambton Inset
T008804 -49.1/-274
T007848 -53.3/-252
T008468 -47.4/-256
T008535 -48.3/-234
T010395 -55.8/-264
T010395 -55.8/-260
T007243 -54.7/-265
T003899 -54.5/-269
T007316 -54/-255
T008990 -45.1/-224
T008864 -50.4/-242
T008837 -48.2/-233
T008997 -45.9/-220
T010637 -52.6/-250
T002890 -52/-247
T003560 -47.6/-234
T008617 -54.1/-246
T002911 -51.8/-244
T008611 -55.4/-257
T007498 -45.4/-226
T008906 -45.3/-219
T011742 -49.8/-262
T011560 -49.3/-262
T002235 -52.5/-261
T002556 -51/-260
T004918 -52.85/-281
T008657 -44.7/-224
T007415 -48.4/-240
T009602 -46.1/-252
T010097 -42/-211
T008633 -41.5/-194
T008634 -41.9/-194
T008638 -39.6/-169
T008636 -43/-166.9
T004543 -37.4/-159.2
LAMBTON
KENT
HURON
BRUCE
PERTH
OXFORD
MIDDLESEX
ELGIN
ESSEX
MOORE
ENNISKILLEN
SOMBRA
DAWN
SARNIA
PLYMPTON
WARWICK
BOSANQUET
BROOKE
ZONE
CAMDEN
CHATHAM
DOVER
HOWARD
HARWICH
RALEIGH
ORFORD
ALDBOROUGH
DUNWICH
SOUTHWOLD
YARMOUTH
MALAHIDE
MOSA
EKFRID
METCALFE
CARADOC
DELAWARE
WESTMINSTER
DORCHESTER
LONDON
LOBO
ADELAIDE
WILLIAMS
MCGILLIVRAY
BIDDULPH
NISSOURI
BLANSHARD
ZORRA
DOWNIE
USBORNE
STEPHEN
HAY
STANLEY
TUCKERSMITH
HIBBERT
FULLARTON
LOGAN
ELLICE
MCKILLOP
HULLETT
GODERICH
COLBORNE
ASHFIELD
KINLOSS
CULROSS
TURNBERRY
HOWICK
WAWANOSH
MORRIS
WALLACE
GREY
ELMA
SANDWICH
MAIDSTONE
TILBURY WEST
TILBURY EAST
ROMNEY
COLCHESTER
km


Map 3
N
Silurian Clinton-Cataract Sample Locations
All data displayed using NAD 83 UTM Zone 17N coordinates as a geographic reference.
Producing Whirlpool
Sample Locations
Sample Location Label:
Licence Number
CH_4 Isotopes: ^{13}C ‰ / ^{2}H ‰
Clinton-Cataract Gas Pools
Primary Producing Formation
Grimsby
Irondequoit
Thorold
Whirlpool
Counties
Townships
HURON
PERTH
WATERLOO
WELLINGTON
HALTON
WENTWORTH
OXFORD
BRANT
LAMBTON
MIDDLESEX
HALDIMAND
LINCOLN
WELLAND
ELGIN
NORFOLK
KENT
Lake Ontario
Lake Erie
New York
T008194
-46.2/-258
T012264
-44.3/-222
T009877
-45.2/-252
T012287
-45.5/-211
T011830
-43.6/-226
T011828
-40.8/-189
T011584
-44.2/-242
T011554
-48.2/-282
T011280
-47.1/-271
T011365
-47.4/-258
T011201
-47.1/-253
T011200
-46.9/-257
T002374
-47.9/-271
T010691
-41.6/-187
T011814
-47/-274
T004185
-39.2/-177
T003188
-39.8/-184
T008932
-40.7/-185
T011549
-42.5/-197
T008812
-38.9/-173
T005741
-39.4/-176
T006762
-39/-171
T010610
-40.7/-195
T011190
-39.4/-181
km
0
10
20
40

Ordovician Sample Locations

Map 4

N

0 20 40 80 km

All data displayed using NAD 83 UTM Zone 17N coordinates as a geographic reference.

Sample Location Label:
Licence Number
CH_4 Isotopes: ^{13}C ‰ / ^{2}H ‰

● Sample Locations

Ordovician Gas Pools

TYPE

Natural Gas

Oil

Counties

Townships

Cambrian Sample Locations

Map 5