Microbial methane generation in organic-rich shales linked to Pleistocene glacial recharge: southwestern Ontario, Canada

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ABSTRACT
This study utilizes solute chemistry, stable isotopes (C, H, O) and dissolved gases in groundwaters in fractured Upper Devonian organic-rich shales (Kettle Point Formation) and underlying Devonian carbonates, along the arches region between the Michigan and Appalachian basins in southwestern Ontario, to investigate the impact of Pleistocene glaciation on freshwater recharge and microbial generation of natural gas.

RÉSUMÉ
Cette étude utilise la chimie solute, les isotopes fermes (C, H, O) et les gaz dissous dans les nappes phréatiques dans les argiles schisteuses riches-organiques dévoniennes Supérieures fracturées (Kettle Point Formation) et le fait de sous-tendre des carbonates dévoniens, le long de la région d'arcs entre le Michigan et les cuvettes Appalachian dans Ontario sud-ouest, pour enquêter sur l'impact de glaciation de Pléistocène sur d'eau douce rechargent et la génération microbienne de gaz naturel.

1 INTRODUCTION

Economic accumulations of microbial methane are associated with Pleistocene glacial recharge in Upper Devonian organic-rich shales along the northern margins of the Michigan and Illinois basins (Fig. 1) (Martini et al., 1998; McIntosh et al., 2002). Here, infiltration of glacial meltwaters likely stimulated microbial methanogenesis in fractured shales by transporting in near-surface microorganisms and significantly diluting saline formation waters at depth to levels conducive for methanogenesis.

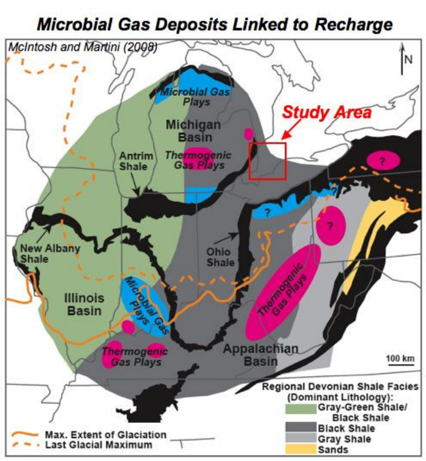

Figure 1. Microbial and thermogenic natural gas plays in the Michigan, Illinois and Appalachian basins in relation to the maximum extent of Pleistocene glaciation. This study focuses on the origin of natural gas in organic-rich shales and history of glacial recharge in southwestern Ontario (study area highlighted in red box). Figure modified from McIntosh and Martini (2008).

Methane has been reported in groundwater wells screened in age-equivalent organic-rich shales (Kettle Point Formation) in southwestern Ontario, in the arches region between the Michigan and Appalachian basins, yet there is no commercial production to date.

This study combines solute chemistry, stable isotopes (O,H,C) and dissolved gases in groundwaters from fractured shales and underlying carbonate aquifers to determine the origin and distribution of natural gas, and glacial history (Fig. 2). These new results are integrated with previous datasets in the area from Desaulniers et al. (1981), Fritz et al. (1987), Husain et al. (2004), and Weaver (1994).

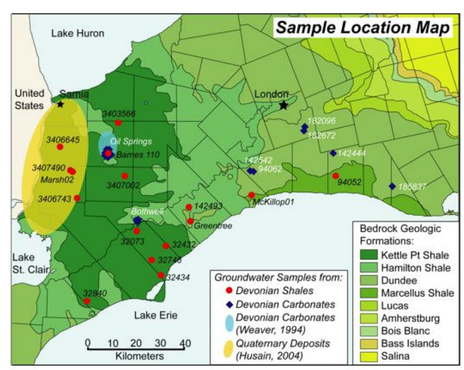

Figure 2. Map of groundwater samples collected as part of this study in southwestern Ontario, in relation to the

bedrock geology and location of previously published data.

2 METHODS

Thirty-four groundwater samples were collected from domestic water supply wells screened in fractured Devonian shales, and from oil production wells completed in underlying Devonian carbonates (Fig. 2). Water samples were analyzed for pH, temperature, dissolved oxygen, conductivity, and alkalinity in the field. Filtered water samples were analyzed for cations and anions by ICP-OES and IC, respectively, at the University of Arizona. Stable isotopes (O,H,C) were analyzed at the University of Calgary. Dissolved gas samples were collected from shale wells in inverted plastic bottles within a bucket of water, and shipped directly to Isotech Laboratories in Champaign-Urbana, Illinois (USA) where they were analyzed for gas composition and stable isotope ratios.

3 EVIDENCE OF PLEISTOCENE RECHARGE

Chloride concentrations in groundwaters in Devonian shales generally increase from 4 to 861 mg/L towards the west (into the Michigan Basin) and to the south towards Lake Erie (into the Appalachian Basin) (Fig. 3). Cl versus Br relations show a broad mixing trend between brines at depth and freshwater in shallow Devonian carbonates and overlying shales (Fig. 4). Where shale and carbonate groundwater samples were collected from the same location, groundwaters in the shales are more dilute than waters in the underlying carbonate aquifers.

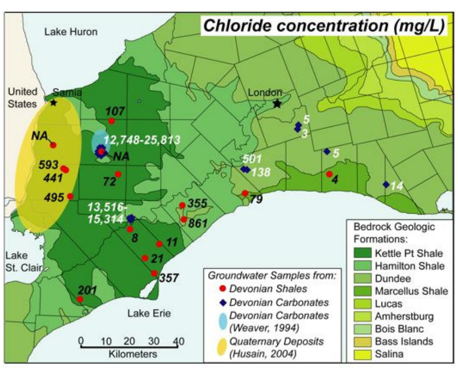

Figure 3. Spatial pattern of chloride concentrations in Devonian shale and carbonate bedrock formations.

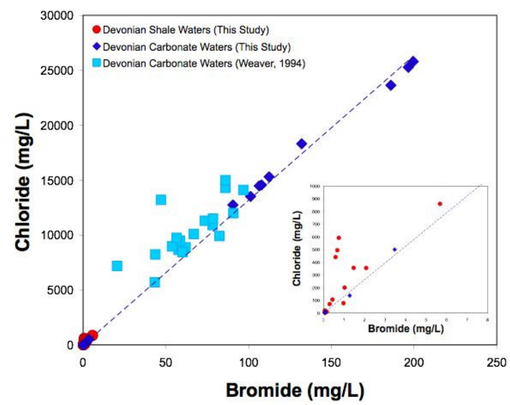

Figure 4. Chloride versus bromide concentrations in Devonian shale and carbonate bedrock formations. The dotted line represents a best-fit linear trend line, and the inset shows a zoomed-in view of samples with <1000 mg/L Cl.

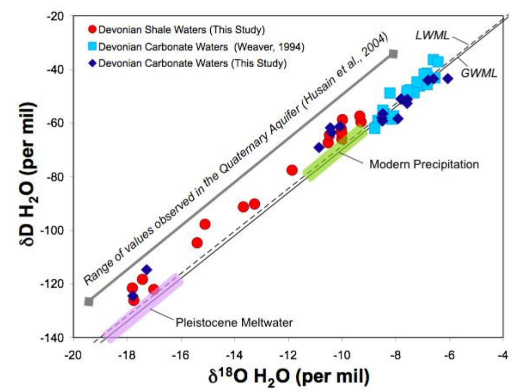

Figure 5. O and H isotope values of groundwaters show mixing of Pleistocene recharge and modern precipitation.

Shale waters have oxygen and hydrogen isotope values that span the range from Pleistocene recharge to modern precipitation (Fig. 5), similar to what has been observed for the overlying Quaternary Aquifer (Husain et al., 2004). The lowest $\delta^{18}O$ values were measured in Devonian shale groundwaters in discharge areas to the south (towards Lake Erie) and to the west, beneath clay-rich confining units (Fig. 6).

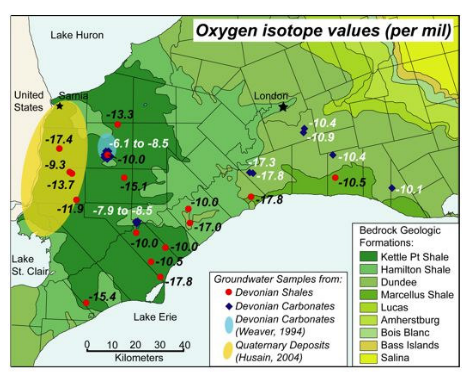

Figure 6. Spatial pattern of $\delta^{18}O$ values of groundwater in Devonian shale and carbonate bedrock formations.

Freshwaters in shallow Devonian carbonate aquifers have $\delta^{18}O$ and δD values consistent with Pleistocene glacial meltwaters retained in overlying glacial till confining units (Desaulniers et al., 1981; Weaver, 1994). Oxygen and hydrogen isotope values of saline waters in the Devonian carbonates are relatively enriched compared to modern precipitation in the study area (Fritz et al., 1987), likely due to mixing with evapo-concentrated brines at depth (Fig. 7).

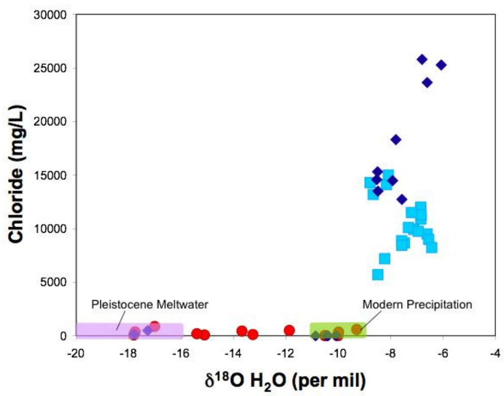

Figure 7. Chloride concentration versus oxygen isotope value of groundwaters in Devonian shale and carbonate formations. Symbols are the same as in Figure 5.

4 LINKS TO MICROBIAL METHANE GENERATION

Brines at depth in Devonian carbonates contain relatively high SO_4 concentrations, likely due to gypsum dissolution (Weaver, 1994) (Fig. 8). These high SO_4 values correspond with relatively negative $\delta^{13}C$ values of dissolved inorganic carbon (DIC), and detectable $H_2S_{(g)}$, suggesting sulfate reduction (Fig. 9). A few Devonian shale waters show similar patterns. These samples are located in recharge areas, as indicated by modern $\delta^{18}O$ values and low Cl concentrations, along the arches region between the Appalachian and Michigan basins.

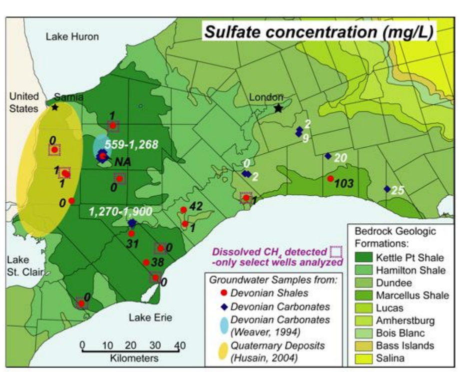

Figure 8. Spatial pattern of sulfate concentrations in Devonian shale and carbonate bedrock formations.

The majority of groundwaters sampled from Devonian shales have relatively positive $\delta^{13}C$-DIC values and no detectable SO_4, indicative of microbial methanogenesis. These waters are primarily located to the south, near Lake Erie (into the Appalachian Basin) and to the west (into the Michigan Basin).

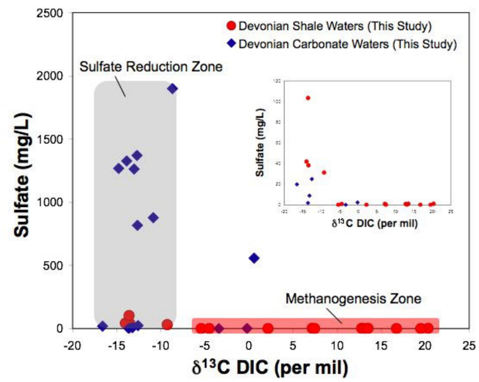

Figure 9. Decreasing SO_4 concentrations with increasing $\delta^{13}C$-DIC values show evidence for microbial methanogenesis in shales. The inset is a zoomed-in view of waters with <120 mg/L SO_4.

Dissolved gases in Devonian shale groundwaters are composed of Ar, N_2, O_2, CO_2, CH_4, and minor amounts of C_2H_6 (<0.02 mole %). Methane concentrations ranged from <0.001 to 56 mg/L. Carbon isotope values of CH_4 (-71.1 to -61.4‰) are typical of microbial methane, while $\delta^{13}C$ values of CO_2 are variable (-22.7 to 3.0‰). Hydrogen isotope values of dissolved CH_4 (-284 to -256‰) and paired water samples show that methane was indeed generated by microbial processes, as the samples plot along the fractionation line for microbial CO_2 reduction (Fig. 10), similar to what has been observed for the Devonian Antrim Shale across the northern Michigan Basin (e.g. Martini et al., 1998). Methanogens extract H from water and organic substrates to produce CH_4; therefore, we can conclude that the isotopically depleted CH_4 was likely generated in-situ with Pleistocene meltwaters.

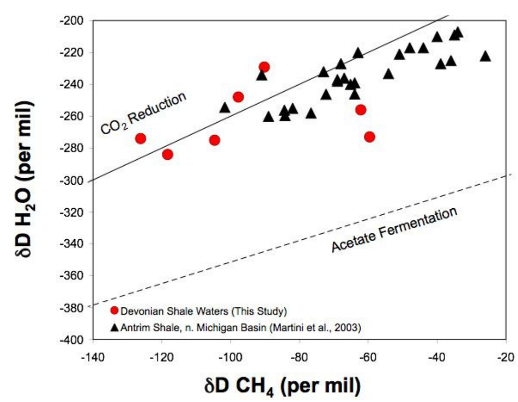

Figure 10. Hydrogen isotope values of paired water and gas samples. Microbial methane is typically generated

via two metabolic pathways, CO_2 reduction and acetate fermentation, which have different H isotope fractionation factors.

5 CONCLUSIONS

Devonian shales contain microbial methane in down-gradient areas where sulfate and oxygen have been consumed. Methane was likely generated since the Late Pleistocene, stimulated by continental glaciation, and has been stored in-situ by adsorption onto shale organic matter. Accounts of high dissolved CH_4 concentrations in shale wells throughout SW Ontario suggest that microbial gas accumulations are likely widespread and maybe an important economic natural gas resource, as has been the case for Devonian shales across the northern margins of the Michigan and Illinois basins.

Devonian carbonate confined aquifers in SW Ontario contain Pleistocene glacial meltwaters that have diluted saline fluids at depth, consistent with previous studies by other researchers. On-going research measuring the stable isotope composition of bedrock aquifers throughout the Province (in collaboration with the Geological Survey of Canada) will help to elucidate further the spatial and depth distribution of these Pleistocene waters, which are an important high-quality drinking water resource.

6 IMPLICATIONS FOR OTHER BASIN SYSTEMS

Subglacial meltwaters have been detected in other sedimentary basins throughout North America that were loaded by continental ice sheets during Pleistocene glaciation, including the northern margin of the Michigan Basin (Martini et al., 1998; McIntosh and Walter, 2005; 2006), Williston Basin (Grasby et al. (2000), Western Canada Sedimentary Basin (Grasby and Chen, 2005; Ferguson et al., 2007), and Illinois Basin (e.g. McIntosh et al., 2002). Several additional sedimentary basins in northern Canada were likely impacted by subglacial recharge, however there are limited to no geochemical data available to access this. Grasby and Chen (2005) point to the lack of extensive esker systems on top of Paleozoic carbonate subcrops, across Canada and the northern United States (Fig. 11) as possible evidence of preferential drainage of subglacial meltwaters into these relatively permeable aquifer systems. Growing evidence for the interaction of continental ice sheets with underlying sedimentary aquifer systems (Person et al., 2007) likely has implications for the growth, evolution, and final retreat of ice that has not always been considered in ice-sheet models.

The generation of shallow microbial gas in shales and coalbeds, in response to the influx of dilute glacial meltwaters, is growing to be a commonly observed trend for basins with sufficient data. This suggests that successful microbial gas plays, such as the Antrim Shale in the Michigan Basin, may have much wider distribution along basin margins. Such shallow gas resources could provide critical local energy resources for remote communities in northern Canada and warrant exploration of organic-rich shales and coalbeds in untested basins.

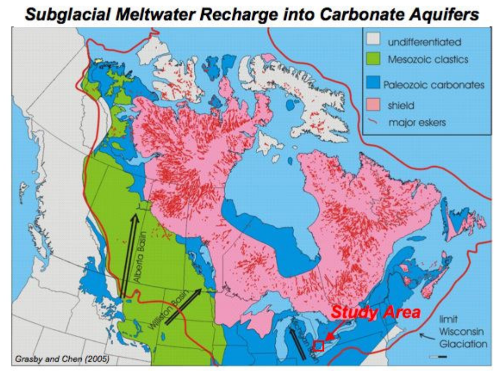

Figure 11. Extent of Paleozoic carbonate aquifers (shown in blue) in North America, modified from Grasby and Chen (2005).

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