Paleozoic-aged microbial methane in an Ordovician shale and carbonate aquiclude of the Michigan Basin, southwestern Ontario

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Abstract

Interest in the origin and migrational history of methane in low permeability shales reaches beyond that of resource potential to include the evaluation of such formations as geological barriers for the purposes of isolating surface environments from the impacts of deep exploitation and the deep disposal of waste. Here, we present detailed isotope and geochemical profiles of porewaters and methane from an Ordovician shale and carbonate aquiclude on the eastern flank of the Michigan Basin, where a deep geological repository for low and intermediate level nuclear waste is proposed. The solute concentrations and stable isotopes of water (\(\delta^{18}O\) and \(\delta^D\)) indicate that this aquiclude hosts saline brine (39% TDS), originating as evaporated seawater. Methane concentrations are <4 mmol/g in the shale section, with negative \(\delta^{13}C\) and \(\delta^D\) signatures that are consistent with archaeal methanogenesis and are accompanied by a well defined positive excursion in \(\delta^{13}C\) of CO\(_2\). Below the aquiclude, porewaters contain lower concentrations of methane with a thermocatalytic signature, consistent with regional methane elsewhere in the Michigan Basin. No evidence for archaea was identified by microcosm experiments or through PCR rRNA analysis, suggesting that the microbial methane present in these sediments is not the result of recent microbial activity. Based on these results and considering that archaeal activity has not been observed in such hypersaline brines with low water activities (<0.75), it is concluded that the methane likely formed prior to the infiltration of hypersaline Silurian seawater. The methane has since remained in place, making it, perhaps, the oldest documented occurrence of biogenic methane. This is consistent with helium isotope data, which also suggests authigenic production and accumulation in this aquiclude since the Paleozoic.

1. Introduction

1.1. Aquitards and natural gas

Methane in low permeability sedimentary formations in the Michigan Basin has attracted interest beyond the generation and migrational history of natural gas resources in the region (Barker and Pollock, 1984; Sherwood Lollar et al., 1994; McIntosh et al., 2002; Martini et al., 2003, 2008). Such studies have relied on samples from producing oil and gas wells, but few have examined gases in the porewaters within the low permeability confining formations. Such samples can provide insights into the properties of these low permeability formations as barriers to fluid and contaminant migration in the context of CO\(_2\) sequestration, shale gas exploitation and the performance of deep geological repositories for radioactive waste.

While natural gas in sedimentary basins is most commonly generated by thermocatalytic degradation of sedimentary organic carbon during burial and heating, growing evidence suggests that biogenic processes are important for self-sourced gas reserves (Rowe and Muehlenbachs, 1999; Curtis, 2002; Martini et al., 2003; Faiz and Hendry, 2006; Pang et al., 2006). Salinity constraints appear to preclude microbial methanogenesis at depth in most sedimentary basins, and, as a result, formations with self-sourced biogenic gas tend to host lower salinity formation waters (McIntosh et al., 2002; Waldron et al., 2007). North American intracratonic sedimentary basins are dominated by Paleozoic formations hosting high salinity brines (Clayton et al., 1966; Hitchon and Friedman, 1969; Kharaka and Hanor, 2004) that are...
considered to have originated through infiltration from evaporitic seas, often with associated dolomitization reactions (Bottomley et al., 2005). The high salinity in these formations, which almost uniformly host thermocatalytic methane (Rodriguez and Philip, 2010), represents a constraint on methanogenic microbial activity (Lai and Gunsalus, 1992; Gomec et al., 2005; Oren, 2011).

Attribution of a microbial source to methane in the subsurface is made on the basis of its $\delta^{13}C$ and $\delta D$ characteristics. Dubrova and Nesmelova (1968) and Galimov (1969) provided the earliest distinction of geogenic methane from biogenic methane based on the depletion in $^{13}C$ values; values less than about $-60^\circ$ in CH$_4$ were associated with biogenic methanogenesis. Together, $\delta^{13}C$ and $\delta D$ are used to distinguish sources of methane, as well as biogenic pathways of methanogenesis (Barker and Fritz, 1981; Klass, 1984; Whiticar et al., 1986; Aravena and Wassenaar, 1993). Biogenic methane is typically associated with low salinity conditions where anaerobic degradation of kerogen and cellulose carbon sources generate lower molecular weight fatty acids, including acetate, together with CO$_2$ and H$_2$ (Klass, 1984). Where marine conditions exist, the associated supply of sulfate provides sulfate reducing bacteria with a competitive advantage over acetoclastic archaea in consuming acetate and hydrogen substrates (Oremland and Polcin, 1982; Whiticar, 1999), although methanogenesis can proceed with other substrates (e.g., methanol). This has been observed not only in marine sediments (Sowers, 2009), but also in organic rich anaerobic freshwater environments (Aravena et al., 2004; Mohammadzadeh and Clark, 2008).

The origin and history of methane in tight formations provide insights regarding the characteristics of the formations themselves with respect to their permeability to fluid migration and their potential effectiveness as barriers for waste isolation. Much can be learned from the concentrations and isotope characteristics of methane in low permeability horizons, although, until now, studies have been limited to sampling oil and gas wells rather than the low permeability rocks themselves. Here, we document the occurrence of biogenic methane in the hypersaline porewater of an Ordovician shale and carbonate aquiclude on the eastern flank of the Michigan Basin in southern Ontario, which is found immediately above thermogenic methane in limestones underlying the aquiclude. Biomolecular testing shows no evidence for methanogenic activity. Geochemical characterization of the porewaters within the shale and carbonate aquiclude formations, together with methane, carbon dioxide and microbiology data, are used to constrain the origin and timing of methane generation.

### 1.2. Site background

Ontario Power Generation (OPG) proposes to build a deep geologic repository (DGR) for low- and intermediate-level radioactive waste at the Bruce nuclear site, in the Municipality of Kincardine, Ontario, Canada, on the eastern flank of the Michigan Basin (Fig. 1). The proposed DGR would be constructed as an engineered facility at a depth of 680 m below ground surface (mbgs) in argillaceous limestone of the Ordovician Cobourg Formation (Fig. 2).

One component of site characterization activities was the extraction and analysis of porewaters and gases from high quality, 75 mm diameter core recovered during the drilling of six boreholes (DGR1–DGR6) to various depths, up to a maximum of ~860 mbgs (Intera Engineering Ltd., 2011). Of particular interest was the methane sampled through a 240 m thick sequence of Ordovician shales and carbonates between approximately 450 mbgs and 690 mbgs. Hydraulic testing shows this zone to be an aquiclude, with measured hydraulic conductivities ($K_h$) between $10^{-15}$ and $10^{-13}$ m/s and effective diffusion coefficients ($D_e$) among the lowest reported for sedimentary rocks, on the order of $10^{-12}$ m/s (Intera Engineering Ltd., 2011; NWMO, 2011).

Formation of the intracratonic Michigan Basin began with Late Precambrian rifting and crustal extension (Van Schmus, 1992). Marine transgression and subidence led to the accumulation of over 4.5 km of sandstones, carbonates and shales through Cambrian to Jurassic time (Dorr and Eschman, 1970; Catacosinos et al., 1991). Subsequent exhumation and erosion has left an approximately 860 m thick Paleozoic section at the Bruce site, beginning with a thin basal Cambrian sandstone overlying the granitic gneiss of the Precambrian shield. The Ordovician stratigraphy comprises lithographic supratidal limestones of the Black River Group, grading upward into the Trenton Group argillaceous shelf limestones. Continued deepening led to the deposition of some 200 m of shale during the Late Ordovician Taconic Orogeny. Restricted circulation and deepening during the Silurian to Devonian Acadian Orogeny resulted in the deposition of over 200 m of interbedded shales, carbonates and evaporites. Carboniferous sediments may have added another 1000 m of burial to the section, prior to erosion (Obermajer et al., 1999).

The hydrogeological conditions at the Bruce site have been studied as part of associated work on site and are summarized here based on Intera (2011) and NWMO (2011). Groundwater circulation is largely restricted to the variably karstic Devonian carbonate units and the Silurian Bass Islands Formation dolostone, to depth of...
approximately 170 mbgs (meters below ground surface). These groundwaters are comprised of Holocene to modern aged meteoric waters, with an increasing component of glacial meltwater with depth. Low permeability conditions exist through a section of more than 450 m, extending from the lower Silurian dolostone through to the base of the Ordovician shales and limestones. This section is bound by two thin confined aquifers: (1) the Middle Silurian Guelph Formation, which yields brine (370 g/l TDS) from a 5 m interval (375–380 mbgs); and (2) the 15 m thick basal Cambrian sandstone at 844–859 mbgs, which yields brine with 225 g/l TDS. Hydraulic head in the basal Cambrian aquifer is > 100 m above hydrostatic conditions. This overpressured condition dissipates upward through the overlying Black River Group limestones with anomalous underpressured conditions, as much as 300 m below hydrostatic, existing within the Trenton Group limestones and overlying Ordovician shales.

2. Methods

Twenty centimeter long samples of high quality, 75 mm diameter core were preserved on-site during drilling by double sealing the samples in a nitrogen flushed polyethylene–nylon bag and an aluminium–polyethylene–nylon sleeve. The samples were shipped to the University of Ottawa in coolers and stored at approximately 4 °C prior to analysis.

The geochemical and isotopic composition of pore fluids and gases in these low permeability rocks was determined by vacuum distillation, modified specifically for the very low permeability and low water content conditions characteristic of the formations at the site (Clark et al., 2013). Cores used for vacuum distillation were brought to room temperature and 5–10 mm of the outer core removed. For each analysis, approximately 100 g of rock was crushed and sieved (2–4 mm), and ~45 g was loaded into a 50 ml Erlenmeyer flask. The sample containers were evacuated and frozen, followed by heating under vacuum at a temperature of 150 °C for 6 h. On-line trapping in a septum-fitted extainer at −200 °C allowed for collection of H₂O for the determination of gravimetric water content, as well as δ¹⁸O and δD by CO₂ and H₂ equilibration, followed by isotope ratio mass spectrometry (IRMS) with an analytical reproducibility of ±0.15‰ and ±1.5‰, respectively. CO₂ was also trapped with H₂O and analyzed for both δ¹³C and concentration by IRMS, with analytical uncertainties of 0.5‰. Porewater solutes were then leached over a period of 60 d from the dry rock and analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) for metals and by liquid chromatography (LC) for anions. The leaching period was established on the basis of initial tests to monitor leaching over time until stable concentrations were reached. Recovered solute mass was then normalized to the mass of recovered water to yield in situ molal concentrations in the porewaters.

Methane was allowed to outgas over a two week period from core samples broken into 1–4 cm diameter pieces. The samples were encapsulated in gas tight Isoljar® containers with septum-fitted lids. The Isoljar® headspace was air filled and a subsequent correction was made for the (minor) contribution from 1.8 ppmv methane in the air. Outgassing experiment results (not shown) showed the shale and limestone materials to have stabilized at a constant methane concentration after a 4 day period. Concentration and isotope analyses were made on a continuous flow isotope ratio mass spectrometer. The sample inlet to the mass spectrometer is equipped with both combustion (δ¹³CCH₄; ±0.5‰) and pyrolysis (δDCH₄; ±2‰) gas chromatographs. Calibrated laboratory standards, together with peak areas, allowed direct determination of concentration to within ±5%.

Organic carbon in the DGR formations was analyzed by standard loss on ignition. Oxygen and hydrogen indices were determined by Rock-Eval pyrolysis (Jackson, 2009) of 100 mg samples of ground (< 250 μm) core at 300 °C (in oven) for volatilization of organic distillates, giving a gas chromatographic peak, S₁ (GC-FID). The oven was then ramped to 600 °C to crack and elute the S₂ (kerogen) peak (GC-FID), which defines the hydrogen index,
HI = 100 S2/TOC. A third GC peak (TCD) from CO2 at 300–390 °C defines the organic index, OI, as $S_2$/TOC. The instrument was calibrated with a sample of Eagle Ford shale, run every 10 samples to check instrument status.

Biomolecular testing was carried out on core samples (collected and stored as indicated above) using polymerized chain reaction (PCR) to amplify any bacterial and/or archaeal DNA that could be extracted from the rock. This was carried out on flame brushed, powdered and thoroughly washed (tris–HCl, sodium phosphate, EDTA, and E GTA solution) rock samples (10 g) collected from the core centres, to avoid biological and chemical contaminants associated with the surface or drilling fluids, as the samples were not drilled or collected aseptically. DNA was extracted (MO Bio Laboratories PowerMax Soil DNA Isolation Kit # 12988–10) and amplified by PCR (Invitrogen Platinum Taq DNA polymerase; # 10966) using archaeal (A571F: 5'-GCV TAA AGS RIC CTG AGC-3' and UA1204R: 5'-TTM GGG GCA TRC IKA CCT-3') and bacterial (27F: 5'-AGA GTT TGA TCM TGG CTC AG-3' and 907R: 5'-GCC TCA ATT CMT TTR AGT TT-3') primers. PCR products were loaded onto 1% agarose gel with ethidium bromide staining and separated by electrophoresis at 80 V for 50 min. All steps of the rock preparation and DNA extraction procedure were performed in a laminar flow hood. The hood and equipment were sterilized using 70% ethanol, 1% bleach and UV decontamination. Aerosol resistant filter tips were used throughout the DNA extraction procedure.

Methanogenic activity was tested by inoculation of a medium optimized for culturing archaea. Rock materials were surface sterilized by immersing in 2% glutaraldehyde for 12 h, then rinsed three times in sterile water and immersed in 70% ethanol for 2 h at room temperature, rinsed three times with sterile water and immersed in 70% ethanol for 2 h at room temperature and then flame sterilized (Cano and Boruki, 1995). A 5 g chip of shale from the core centre (DGR-4-595.38) was disaggregated to inoculate a 25 ml aliquot of growth medium II based on Hungate (1969) and Romesser et al., 1979 in 162 ml serum bottles with 80:20 H2:CO2 headspace (6 replicates plus 2 negative and 2 positive controls using sewage treatment system sludge). The inoculated medium was then incubated at 30 °C in a dark anaerobic chamber. Growth of methanogens was tested over an eight week period by weekly measurement of headspace gas for methane by gas chromatography GC and isotope ratio mass spectrometry.

3. Results and discussion

3.1. Porewater geochemistry and isotopes

The ~200 m Ordovician shale section is characterized by volumetric water loss porosities of about 7.0% (5.5–8.5%) while the underlying Trenton Group limestones have considerably lower water loss porosity values of ~1.6 (0.5% ± 5.0%). Throughout the Ordovician shale and carbonate aquiclude, porewater has high salinity, with Cl− (5780 ± 392 mmol/kg; Fig. 2) enriched to greater than 15 × that of seawater (546 mmol/kg), indicating that this large difference in salinity and depletion in 18O is typical of basin brines of evaporative origin (Clayton et al., 1966). From the base of the Ordovician shales through to the deeper Black River Group carbonates, both salinity and 18O in the porewaters begin a downward trend to a more dilute (Cl = 3300 mmol/kg) and 18O depleted (δ18O = −8.6‰) brine found at 785 mbgs. In the lower part of the Gull River Formation, at the base of the Ordovician carbonates, the trend toward a decrease in salinity and depletion in 18O is reversed, with Cl− and δ18O increasing down section through the Shadow Lake and Cambrian formations at the base of the Paleozoic section (Fig. 2).

3.2. Organic carbon and methane

The organic carbon component of these rocks (Fig. 3) was characterized by measurement of the hydrogen index (hydrogen production by pyrolysis of kerogen) and oxygen index (CO2 released by pyrolysis of kerogen) (Jackson, 2009; Fig. 4). The high oxygen index of the Georgian Bay and Queenston formations signify a type III kerogen characterized by lower hydrocarbon generation potential. These rocks also have total organic carbon (TOC) contents below 0.5%. The organic rich Blue Mountain and Collingwood shales, where the highest concentrations of methane occur, are characterized as being a type II kerogen with high hydrogen index and higher hydrocarbon generation potential. These rocks also have TOC concentrations greater than 0.5%, and approaching 2.5% in a very thin section (~1 m thickness) at the base of the Blue Mountain Formation.

Methane concentrations in the Ordovician section are shown in Fig. 3, normalized both to mass of rock (mmol/g rock) and to mass of porewater (mmol/kg water). Two principal intervals are observed: (1) comparatively high methane concentrations in the lower Ordovician shales and the Cobourg Formation, identified above as hosting hypersaline porewaters; and (2) low methane concentrations in the underlying Sherman Fall to Gull River formations, characterized by decreasing salinity. The lowest methane concentrations are found in the Silurian section.

Within the upper interval, methane concentrations increase down section from values < 1 mmol/g in the low TOC Queenston and Georgian Bay formations (~450–608 mbgs) to up to 4 mmol/g in the more organic rich Blue Mountain shales (~608–650 mbgs), and up to 8 mmol/g in the Cobourg limestone (~650–690 mbgs; Fig. 3). Through the Queenston to the Cobourg, methane correlates strongly with the organic carbon content ($R^2 = 0.87$; Fig. 5), and this is particularly so for the Blue Mountain and Cobourg formations, which have the highest methane and organic carbon contents. This good correlation suggests that methane is self-sourced within this section characterized by high hydrogen index, type II kerogen (Jackson, 2009). Methane concentrations are lower in the Georgian Bay and Queenston shale formations, which have a lower hydrogen index and less organic carbon. Methane concentrations are low and show no correlation with organic carbon in the deeper Ordovician limestones (Sherman Fall to Gull River; $R^2 = 0.18$; Fig. 5), though organic carbon contents can reach values above 1%.

The distinction between the upper (Queenston to Cobourg) and the lower (Sherman Fall to Gull River) methane intervals is clearly observed in the δ13C and δD composition of methane (Fig. 6). Methane in the upper interval shows significant depletions in both isotopes relative to the deeper methane interval. Moreover, the interface in the isotope profiles between these two intervals is remarkably narrow, suggesting a lack of significant methane diffusion between the two intervals. Methane above this interface is characterized by values as low as δ13CC8H18 = −53.7‰ and δD8H2 = −360.4‰ (average −50.0‰ and −323‰, respectively), while values are uniformly more enriched below the interface (see Fig. 6). Plotted on a co-isotope graph, methane from the upper interval in the aquiclude (Queenston, Georgian Bay and Blue Mountain shales and Cobourg limestone) plots within the region defined by Schoell (1988) as biogenic (Fig. 7) via an acetate fermentation (acetoclastic) metabolic pathway (Klass, 1984; Whiticar, 1999):
CH$_3$COOH $\rightarrow$ CH$_4$ + CO$_2$.

In contrast, the isotopically enriched methane from the Sherman Fall to Gull River section below this apparent interface plots within the field for thermogenic methane (Schoell, 1988). A biogenic origin for methane in the upper zone would account for methane production within the formations characterized by elevated concentrations of oil-generating type II kerogen (i.e., Blue Mountain and Collingwood shales), and is also consistent with the observed correlation between methane and organic carbon content (Fig. 5), further supporting in situ methane generation. The lack of correlation with organic carbon content in the deeper, thermogenic methane section is consistent with a regional source, as observed in hydrocarbon wells of southwestern Ontario (Sherwood Lollar et al., 1994).
Measurements of $\delta^{13}C$ in the associated CO$_2$ provide supporting evidence for biogenic methanogenesis. Throughout most of the Ordovician section, $\delta^{13}C$CO$_2$ closely follows a baseline value of $-4.9 \pm 1.8$‰. Over a 70 m interval, where the most isotopically depleted methane occurs within the Ordovician shales, the $\delta^{13}C$CO$_2$ profile exhibits a 15‰ positive excursion to values greater than $+10$‰. In contrast with evidence for acetoclastic methanogenesis seen in Fig. 7, the sharp positive excursion in $^{13}C$ enriched CO$_2$ is consistent with archaeal methanogenesis via CO$_2$ reduction (Klass, 1984; Whiticar, 1999):

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O.$$

Considered in a plot distinguishing acetoclastic from CO$_2$ reduction on the basis of $^{13}C$ fractionation (Whiticar, 1999; Fig. 7), it is apparent that acetoclastic methanogenesis has dominated through much of the shale section, with a zone in the lower Georgian Bay and upper Blue Mountain shales that trends toward CO$_2$ reduction as a dominant pathway (see Fig. 8).

Authigenic, microbial methane in the Ordovician shales and the Cobourg Formation is supported by helium data, which suggests that helium has been accumulating in this section for more than 260 Ma (Clark et al., 2013). Fig. 9 presents the profile of helium isotopes, which features a shift at the same depth as that observed for the isotopes of methane. The helium $^{3}He$ value of 0.02 measured in the Ordovician shales matches with that calculated from $^{3}He$ and $^{4}He$ production rates. As observed for methane, helium in this section appears to be authigenic and preserved since the Paleozoic. Helium isotope values below the Cobourg Formation shift toward values measured in the deeper basin and, similar to the
interpretation of the methane isotopic data, the deeper helium is presumed to be mainly derived from a regional source in the Michigan Basin (Clark et al., 2013). The section of authigenic helium and biogenic methane is characterized by halite mineralization, as observed by X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis of core (Fig. 9). This halite mineralization is believed to have occluded porosity and limited diffusive loss of helium and methane.

3.3. Constraints on archaeal methanogenesis

Microbial methane production via CO₂ reduction on a substrate of H₂, or by fermentation of acetate, is less favorable in the presence of sulfate due to the energetic advantage gained by sulfate reducing bacteria (SRB). The presence of framboidal pyrite in these sediments (see Fig. 10) suggests that sulfur was sequestered in the system as pyrite, and so reduced the competition for substrate, allowing methanogenic archaea to flourish for a time.
While metabolic products from SRB and methanogens are found in these strata, the existing porewater salinities are not conducive to, or favorable for, microbial activity. Though SRB are known to tolerate elevated salinities, van Lith et al. (2002), Kulp et al. (2007) and Oren (2011) show SRB activity to terminate above total salinities of about 130 g/l (2200 mM Cl\(^{-}\)). Methanogenic archaea show similar halotolerances. CO\(_2\) reduction has not been observed in the natural environment at NaCl salinities above 90 g/l (1500 mM Cl\(^{-}\)). Oren (2011), Gomec et al. (2005) and Waldron et al. (2007) found acetotrophic methanogenesis in the Devonian Antrim Shale of the Michigan Basin to be limited to salinities of < 130 g/l.

In addition to salinity, the pore throat diameter of these shales, which is less than 0.02 μm (measured by Hg porosimetry; Jackson, 2009), presents a second constraint on the viability of archaeal cells. While dormant cells may reduce to some 0.2–0.4 μm (Fredrickson et al., 1997), activity and available nutrient supply at the measured pore throat diameters is unlikely. Nonetheless, attempts were made to resolve whether or not this could be a product of recent activity using microcosms inoculated with core from the biogenic methane interval and by DNA extraction by polymerase chain reaction (PCR) (see Methods above). Methane production in the microcosms was limited to only the positive controls; methanogens could not be cultivated from the cores. While not conclusive, the results support the hypothesis that the microbial methane in these cores is not recent. PCR results produced very faint traces of bacterial DNA, including heterotrophic, lithotrophic, acidophilic, radiotolerant, and sulfate reducing species, but none for archaea. As survival of non-viable DNA in the geosphere may be several hundred thousand years (Willerslev et al., 2004), an absence of archaean DNA supports the interpretation that the methane is not the result of recent microbial activity. This suggests that the biogenic methane is ancient, likely related to diagenetic archaeal activity during the Ordovician, when salinity conditions were more conducive to microbial viability.

The geochemical evidence from the halite profiles (Cl\(^{-}\) and Br\(^{-}\); Fig. 2) show the hypersaline porewaters in the Ordovician shales to be of evaporated seawater origin, enriched 38-fold in Br\(^{-}\), and likely of Silurian age. Subsequent mineralization by this halite-saturated brine then occluded porosity and substantially reduced permeability. Halite is observed with the greatest frequency throughout the aquiclude from the top of the Ordovician shales to the base of the Cobourg Formation (Fig. 9). It is hypothesized that halite precipitation would have occurred during infiltration of the Silurian brine into the shales by a combination of Ca\(^{2+}\) exchange onto Na-clays and ion filtration during compaction (refer to Bredehoef et al., 1963; Kharaka and Berry, 1973; Hart and Whitworth, 2005). Methanogenic activity is interpreted to have been terminated by the development of hypersaline conditions and the biogenic methane preserved in these rocks since the Paleozoic.

4. Conclusions

The establishment of the stable isotope and halide profiles through the Ordovician section are considered to have originated as early Paleozoic seawater of normal salinity present in the Ordovician to Cambrian stratigraphy and the Precambrian basement. The early, low salinity porewaters in the kerogen enriched shales of the Blue Mountain Formation could have hosted a range of sulfate reducing, kerogen fermenting and methanogenic communities. Influx of high salinity brine originating as evaporated seawater during Silurian time would have generated hypersaline conditions in the Ordovician shales and led to the termination of archaeal methanogenesis. Precipitation of halite in pores and fractures within the Ordovician shales and the Cobourg Formation would have reduced the effective porosity of the formations as well, likely driven by ion exchange during solute migration and ion filtration associated with dewatering during consolidation.

The mineralization of the Ordovician shales and the Cobourg Formation with halite may have established the observed aqueous conditions and the preservation of archaean methane and CO\(_2\), as well as authigenic helium, making this possibly the oldest documented occurrence of biogenic methane.

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