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

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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 δD) 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 δD 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

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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 Philp, 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 δD 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‰ in CH_4 were associated with biogenic methanogenesis. Together, $\delta^{13}C$ and δD 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 cellulosic 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 subsidence 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

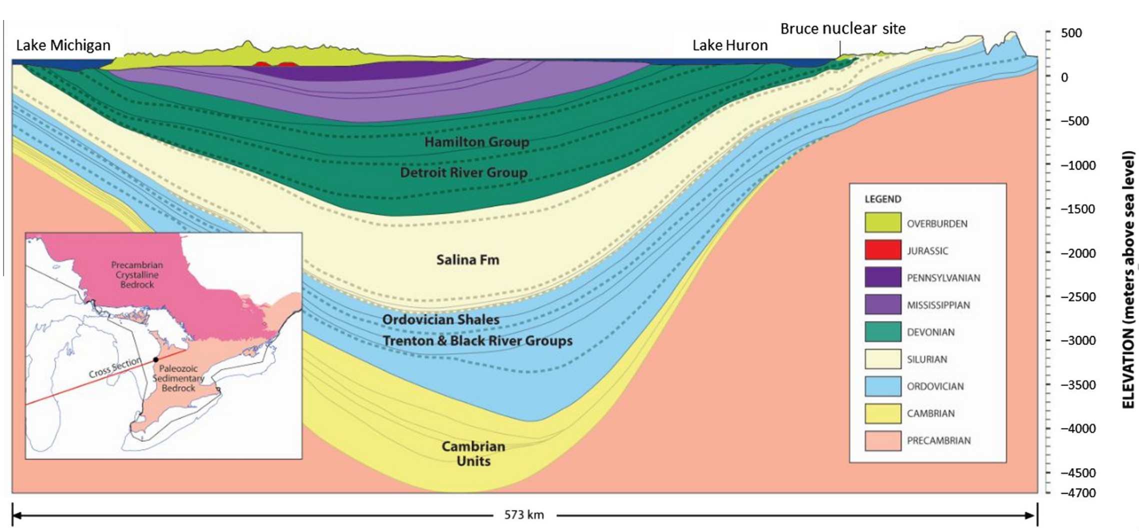

Fig. 1. Michigan Basin bedrock stratigraphy and location of the Bruce site, Municipality of Kincardine, Ontario (Intera Engineering Ltd., 2011). Vertical exaggeration 45×.