Flux of methane release and carbon dioxide sequestration at Winterhouse Canyon, Gros Morne, Newfoundland, Canada; a site of continental serpentinization

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Title: Flux of methane release and carbon dioxide sequestration at Winterhouse Canyon, Gros Morne, Newfoundland, Canada; a site of continental serpentinization

Authors: Liam S. Morrissey\textsuperscript{1} and Penny L. Morrill\textsuperscript{1}\textasteriskcentered

\textsuperscript{1}Department of Earth Sciences, Memorial University, St. John’s, NL A1B 3X5, Canada

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*Corresponding Author

Memorial University of Newfoundland

Department of Earth Sciences

300 Prince Philip Dr., St. John’s, NL, Canada, A1B 3X5

Phone: (709) 864-6729

Fax: (709) 864-2589

Email: pmorrill@mun.ca
Abstract

We measured CO$_2$, CH$_4$, and N$_2$O gas fluxes from a pool of ultra-basic water discharging from serpentinized rock in Winterhouse Canyon, Gros Morne, Newfoundland. The flux of CH$_4$ released and CO$_2$ sequestered were calculated to be $4.6 \times 10^{-7}$ mol/m$^2$min and $1.9 \times 10^{-5}$ mol/m$^2$min, respectively, whereas N$_2$O concentrations showed little change. The net radiative forcing due to the changing concentrations of CO$_2$ and CH$_4$ during the sampling period was -0.21, suggesting that the ultra-basic pool in WHC has a net cooling effect on the atmosphere. Similarly, the net global warming potential over a time horizon of 100 years was -7, also suggesting a small cooling of the atmosphere. Overall this study was the first to consider the impact of CO$_2$ sequestration and CH$_4$ emissions from an ultra-basic pool above serpentinized rock and demonstrated the need for more research on the net global impacts of serpentinization.

Key words: Serpentinization, Greenhouse Gas, Flux, Chemical Enhancement
Introduction

Serpentinization: a source for CH₄ and a sink for CO₂

Serpentinization involves the hydration of ultramafic rock to produce serpentine, ultra-basic groundwater, and hydrogen gas (H₂). The produced H₂ may then react with inorganic carbon to produce CH₄ (McCollom and Seewald 2006; Taran et al. 2007; Holm et al., 2015). However, while sites of serpentinization often lead to abiogenic CH₄ production, these sites can also feature thermogenic and/or microbial CH₄ (Brazelton et al. 2006; Kelley et al. 2005; Morrill et al. 2013; Szponar et al. 2013). For example, microbial CH₄ has been proposed for samples in the Precambrian shield (Canada) (Sherwood Lollar et al. 1993), the Lost City Vents (Mid Atlantic Ocean) (Kelley et al. 2005) and at the Cedars (United States) (Morrill et al. 2013; Kohl et al. 2016). In addition, if sedimentary organic matter is present beneath the serpentinizing ultramafic body then thermogenic CH₄ is also a possibility. Regardless of the source, CH₄ can be transported with the groundwater and become discharged at the surface where it volatilizes, or, in some cases bubbles out of the spring, acting as a CH₄ source to the atmosphere.

In addition to producing CH₄, the characteristically high pH of serpentinizing systems creates conditions where atmospheric CO₂ can dissolve in the spring water and, through a series of inorganic carbon speciation reactions (Equation 1a and b), can react with the dissolved calcium ions in the spring water to form solid carbonates.

\[
\begin{align*}
(1a) & \quad \text{CO}_2(g) & \rightarrow & \text{CO}_2(aq) & \rightarrow & \text{H}_2\text{CO}_3(aq) & \rightarrow & \text{HCO}_3^-(aq) & \rightarrow & \text{CO}_3^{2-}(aq) \\
(1b) & \quad \text{CO}_3^{2-}(aq) + \text{CO}_2^{2+}(aq) + \text{Ca}^{2+}(aq) & \rightarrow & \text{Ca}_2\text{CO}_3(s)
\end{align*}
\]
In addition, research has also shown the potential for utilizing these types of systems to reduce global CO$_2$ levels (Kelemen and Matter 2008). For example, adding 1 wt% CO$_2$ to the Semail ophiolite in Oman would consume approximately 25% of atmospheric CO$_2$ (Kelemen and Matter 2008). However, although these methods show the promising potential of enhanced CO$_2$ sequestration, they only consider the sequestered gas, and not the gases that may be released to the atmosphere. Therefore there still exists a knowledge gap with respect to natural fluxes of both the CO$_2$ sequestered and the CH$_4$ released for sites of serpentinization. Additionally, to our knowledge, the greenhouse, N$_2$O has not been measured at sites of serpentinization.

**Gas flux**

A common method used to determine the diffusive gas flux between surface waters and atmosphere assumes that the gas transfer is a function of the concentration gradient between the two phases and the gas exchange coefficient at a given temperature via the following equation (Raymond and Cole 2001):

\[
\text{flux} = \alpha k (C_{gasw} - C_{sat})
\]

where $k$ is the gas transfer velocity (m/s); $\alpha$ is the coefficient of chemical enhancement (dimensionless); $C_{gasw}$ is the aqueous concentration of the dissolved gas in the surface water (mol/L); and $C_{sat}$ is the equilibrium aqueous gas concentration (mol/L).

Chemical enhancement occurs when a gas is reactive with the water molecules or hydroxide ions in the surface boundary, and therefore it is a function of temperature, pH
and ionic strength (Wanninkhof 1992; Wanninkhof and Knox 1996). Therefore, in ultra-basic pools fed by waters discharging from serpentinizing systems like the site in question, chemical enhancement is relevant for a molecule such as CO$_2$ which participates in hydrolysis reactions, and less relevant for molecules that do not participate in hydrolysis such as CH$_4$ and N$_2$O. The chemical enhancement for CH$_4$ would be set to a value of 1 by convention (Wanninkhof and Knox 1996). Moreover, while research has been conducted on the CO$_2$ chemical enhancement factors in oceans and lakes, to our knowledge a CO$_2$ chemical enhancement factor for high pH pools of water discharging from serpentinized rock has yet to be determined.

In addition to the above method, gas flux between the aqueous fluid and the atmosphere can also be measured directly by monitoring gas concentrations in a closed floating chamber. Using this method, a chamber is placed over a water body and gases are sampled from the chamber’s headspace at specific time intervals. Based on the ideal gas law, the gas flux is calculated using the initial and final gas concentrations (Equation 3). Therefore, this empirical method could be used to determine unknown parameters in the theoretical Equation 2.

\[
 Flux = \frac{V (P_2 - P_1)}{RTA(t_2 - t_1)}
\]

where V is the volume of the chamber (m$^3$); R is the ideal gas constant (m$^3$ Pa/K mol); T is the air temperature (K); A is the surface area of chamber opening (m$^2$); P$_1$ and P$_2$ are
gas partial pressures at two different sampling times (Pa); $t_1$ and $t_2$ are times at which the samples were taken (min).

This second method assumes a linear relationship between time and gas concentrations. This assumption can be validated with intermittent gas sampling between $t_1$ and $t_2$. The possible deployment duration for the closed floating chamber depends on the time it takes for the gas in question to equilibrate between the water and the headspace in the closed chamber. Equilibration times of 20-40 minutes for CO$_2$, and up to 24 hours for CH$_4$ have been reported (Podgrajsek et al. 2014).

**Gas flux at sites of serpentinization**

Current research on gas flux at sites of serpentinization has been limited to measuring the flux of CH$_4$ and CO$_2$ released from the Chimera gas seep, a system of gas vents from the Tekirova ophiolites in Turkey (Etiope et al. 2011b). This site featured subsurface CO$_2$ venting to the surface and the atmosphere. Fluxes were measured using a closed-chamber system using a linear regression of gas concentration in the chamber (Etiope et al. 2011b). The study tested 27 locations with diffuse CH$_4$ seepage and fluxes were calculated to be on the order of $4.3 \times 10^{-3}$ to $4.3 \times 10^{-2}$ mol/(m$^2$·minute). In comparison, CO$_2$ fluxes ranged from $1.6 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mol/(m$^2$·minute) (Etiope et al. 2011b). While this study provided an approximate value for CH$_4$ and CO$_2$ fluxes at a site of serpentinization, the gas vents studied only released CO$_2$ and did not show any sequestration. Therefore, these results cannot be used to estimate the rates of CO$_2$ sequestration at an ultra-basic pool of water discharging from serpentinized rock.
Materials and methods

Field site description

To determine the impact of greenhouse gas fluxes from a site of serpentinization, CH$_4$, CO$_2$, and N$_2$O gases were sampled above a small reservoir of water that pooled at the discharge point of an ultra-basic spring in Winterhouse Canyon of the Tablelands, a Paleozoic ophiolite complex in the Gros Morne area of western Newfoundland, Canada. The Tablelands is mainly composed of peridotite rocks from an ophiolite complex that was formed approximately 485 ma ago during the closure of the Iapetus Ocean (Elthon 1991). Previous studies at this site have shown that the subsurface, groundwater reacts with ultramafic rock, in a process known as serpentinization, which produces several active, highly reducing (~ -609 mV) and ultra-basic (pH 10-12) groundwater springs discharging at the surface (Szponar et al. 2013). These springs can be identified by the white carbonate that precipitates around them. These carbonates were likely recently deposited as atmospheric CO$_2$ dissolved into pooled water and precipitated due to the high pH of the system (Equation 1). Therefore, these ultra-basic pools are potentially sinks of atmospheric CO$_2$.

This study focused on one of these springs, WHC2, situated in the valley of Winterhouse Canyon. WHC2 is a pool of ultra-basic water that is approximately 40 cm deep and 126 cm wide and is exposed to the atmosphere. Geochemical parameters of the spring water have been studied previously and the water has been shown to have characteristically high pH values along with elevated dissolved concentrations of CH$_4$ ranging from 2.5x10$^{-6}$ mol/L to 2.4x10$^{-5}$ mol/L (Szponar et al. 2013). Overall, there are two ultra-basic groundwater discharge points (WHC2a and WHC2b) at the bottom of the
WHC2 pool that are characterized by a relatively higher pH and lower Eh values compared to the rest of the pool water. WHC2 is surrounded by calcium carbonate deposits (see Figure 1) consisting of calcite (90%) and aragonite (10%), indicating potential carbon sequestration (Szponar et al. 2013).

Field sampling

Gas samples for flux calculations were collected using a closed floating chamber (Figure 1). An 18.9 L (5-gallon) container was turned upside down and submerged 14 cm into the WHC2 pool. A weighted styrofoam platform was used to support the chamber over the water during the experiment. The chamber had been previously modified to allow 0.5 m long HDPE tubing to connect through an opening in the top of the inverted bucket, which was secured using a gas-tight O-ring seal. A two way luer lock valve was fitted to the other end of the tubing for sampling purposes. During headspace sampling, the needle of a 60 mL syringe was pushed through a rubber septum on the end of the two-way luer lock valve. 60 mL of headspace gas was then slowly drawn into the syringe and, once filled, the valve was closed and the needle was removed from the septa. The 60 mL gas sample was transferred to a 45 mL evacuated bottle sealed using a blue butyl septa. This procedure was repeated such that each sample 45 ml bottle received 120 mL of gas.

This study focused on headspace sampling during the initial 3 hours for CO$_2$ and the final 5 hours for CH$_4$, knowing that CO$_2$ in the pool typically equilibrates with the atmosphere within a few hours, whereas CH$_4$ equilibration can take over 24 hours (Podgrajsek et al. 2014). In addition, N$_2$O concentrations in the headspace were measured during the duration of the experiment to determine if there was any change over the 24
hours. Headspace samples were taken from the closed floating chamber at 0 minutes, 10 minutes, 25 minutes, 1 hour, 2 hours and 11 minutes (131 minutes), 3 hours and 45 minutes (225 minutes), 13 hours and 39 minutes (819 minutes), 15 hours and 35 minutes (935 minutes), 18 hours and 5 minutes (1085 minutes) and 20 hours and 7 minutes (1207 minutes). All samples were stored in a cooler and were analyzed within 8 weeks of sampling. Concentration values for duplicate samples deviated up to 5% for CO$_2$ and 8.6% for CH$_4$.

The pH, conductivity, and temperature of the water were taken in-situ prior to, and directly after, the 24 hour flux experiment. Conductivity and pH were measured using an Oakton 10 series (Eutech Instruments) handheld pH meter and temperature was measured with a hand-held alcohol thermometer.

Water samples were taken for dissolved CO$_2$ and CH$_4$ concentration analyses prior to, and directly after, the 24 hour flux experiment. Dissolved CO$_2$ and CH$_4$ were extracted from the water using a modified gas stripping method (Rudd et al. 1974). In short, this method involved stripping the dissolved gases from the water by vigorously shaking a 60 mL sealed syringe containing 25 mL of He gas and 25 mL of water sample for 5 minutes. After stripping the gas, two syringes with 25 mL of the gas phase each were injected into a 40 mL Wheaton vial that was prefilled with degassed nanopure water and sealed with a conditioned blue butyl septa. Holding the Wheaton vial upside down, the gas sample was pushed into the bottle and the degassed nanopure water left the vial through an exit needle.
Analytical methods

**CH$_4$ and CO$_2$ concentrations**

CH$_4$ and CO$_2$ concentrations were measured using a SRI 8610 gas chromatograph with a flame ionization detector (GC-FID). A Carboxen 1010 fused silica capillary column with a helium carrier gas and a temperature program of 40°C hold 6 minutes, ramp 15°C/minute to 120°C, hold 5 minutes, was used to separate the specific gases. After column separation a methanizer converted the CO$_2$ to CH$_4$ so that it could be analyzed using the FID. The standard error based multiple injections of standards was always less than or equal to 5%.

Daily calibration curves were created for CH$_4$ and CO$_2$. The CH$_4$ calibration curves were made by injecting varying volumes (3-30 μl) of a Restek 34522 standard containing 100 ppm of CH$_4$ using a 50-microliter gas tight locking Hamilton syringe. Similarly, the CO$_2$ calibration curves were made by injecting varying volumes (7 – 15 μl) of a Restek 34512-PI gas standard containing 5% CO$_2$ using a 25 μl gas tight locking Hamilton syringe. The lower detection limit for the GC-FID for CO$_2$ was a concentration of 4.7x10$^{-5}$ mol/L and the lower limit for CH$_4$ was a concentration of 3.3x10$^{-7}$ mol/L.

**N$_2$O concentrations**

N$_2$O concentrations in the headspace were measured using a gas chromatograph with an electron capture detector (ECD). A HayeSep D column with a helium carrier gas and a temperature program of 80°C hold 7 minutes, ramp 15°C/minute to 150°C, hold 5 minutes, was used to separate the specific gases. The standard error based multiple
injections of the N$_2$O standard was always less than or equal to 5%. Daily calibration curves were created for N$_2$O by injecting varying volumes (0.3-1 mL) of a standard containing 2.1 ppm by volume of N$_2$O using a 1 ml gas tight locking Hamilton syringe. Standard error through multiple 1 mL injections was determined to be +/- 10% and the detection limit was 2.2 x 10$^{-8}$ mol/L.

**Flux calculations**

To calculate the fluxes using the closed floating chamber method Equation 3 was applied i.e., the difference between gas concentrations in the headspace at two separate time points. This method requires non-equilibrium conditions between the gas and liquid phases in the chamber. For this method to be accurate there must be a linear relationship of gas concentration with respect to time. This linearity was tested in our experiments using the concentration data collected at intermediate time points. The error associated with the duplicate concentration measurements taken at each time point was propagated through the flux calculation and are reported in parentheses following each reported flux.

**Results**

**Geochemical characterization**

The temperature, pH, dissolved gas concentrations, and conductivity were measured at the WHC-2 spring at the beginning (Sept 1, 2015) and end of the sampling (Sept 2, 2015) period (Table 1). Air and water temperatures for the beginning and end of the experiment were within 1.5% of each other while pH and dissolved methane concentration values were within 5%. However, dissolved carbon dioxide concentrations
in the pool dropped 60% from the initial measurement to the final measurement after sampling.

**CH₄ flux**

CH₄ concentrations in the flux chamber increased over time during the 24 hr experiment (Figure 2A). Initially CH₄ concentrations were below our detection limits (<3.3 x 10⁻⁷ mol/L), and the CH₄ concentrations remained that way for the first 2 hours and 12 minutes (132 minutes). Once detected, CH₄ concentrations continued to increase over time to a final concentration of 2.7 x 10⁻⁶ (± 4.9x10⁻⁸, 1σ, n=2) mol/L. Changes in CH₄ concentrations measured between 2 hours and 12 minutes (132 minutes) to 20 hours and 7 minutes (1207 minutes) were well described by a linear approximation (r² = 0.96). Therefore the CH₄ concentrations at these two times points were used in Equation 3 to calculate a CH₄ release of 4.6 x 10⁻⁷ mol/m²min (± 0.4 x 10⁻⁷ mol/m²min) out of the WHC2 ultra-basic pool.

**CO₂ flux**

Conversely, CO₂ concentrations in the flux chamber decreased over time during the 24 hr experiment (Figure 2B). At the beginning of the experiment there was 8.9 x 10⁻⁵ mol/L (± 3.1x10⁻⁶, 1σ, n=2) of CO₂ in the chamber. During the first phase of sampling (i.e., 0 minutes to 3 hours and 46 minutes (226 minutes) the CO₂ concentrations declined to a value of 5.62x10⁻⁵ mol/L (± 1.3x10⁻⁶, 1σ, n=2) of CO₂. During the second phase of sampling (i.e., 13 hours and 40 minutes (820 minutes) to 20 hours and 7 minutes (1207 minutes) CO₂ concentrations were below our detection limits (i.e., <4.7x10⁻⁵ mol/L). Changes in CO₂ concentrations measured between 12 minutes, and 3 hours and 46 minutes (226 minutes) were well described by a linear approximation (r² = 0.91).
CO₂ concentrations at these time points were then used in Equation 3 to calculate a CO₂ sequestration of $1.9 \times 10^{-5}$ mol/m²·min ($\pm 0.1 \times 10^{-7}$ mol/m²·min) into the WHC2 ultra-basic pool. Therefore, CO₂ was being sequestered 41 times faster than CH₄ being released.

**N₂O flux**

N₂O concentrations in the gas phase in the chamber remained within our analytical error during the 24 hr experiment (Figure 2C). The average concentration of N₂O was of $3.2 \times 10^{-8}$ (± $2.6 \times 10^{-9}$, 1σ, n=10) mol/L. Therefore, the flux of N₂O in the chamber over the 24 hr experiment was negligible for the WHC2 ultra-basic pool.

**Discussion**

**CO₂ coefficient of chemical enhancement**

In this study we calculated CO₂, CH₄ and N₂O gas fluxes into and out of ultra-basic serpentinization-associated groundwater discharging and pooling in Winterhouse Canyon of Gros Morne National Park, NL, Canada. These gas fluxes were calculated using Equation 3 and gas concentrations determined from samples collected over a 24 hour period. However, as mentioned previously, this is not the only method used for calculating flux. A less labor-intensive method for estimating flux could have been used if the site-specific parameters such as the gas transfer velocity (k), the coefficient of chemical enhancement ($\alpha$), and initial gas concentration differences between the measured value and the theoretical concentration at equilibrium with the overlying atmosphere were known. While the $\alpha$ for CH₄ is, by convention, set to 1 because it does not participate in hydrolysis reactions (Wanninkhof and Knox 1996), the $\alpha$ for CO₂ for serpentinizing systems is unknown. However, we can use the information gained in this
study to determine the unknown parameters in Equation 2, potentially allowing for future studies of this site and other similar sites of serpentinization to avoid the labor intensive methods described above.

The \( k_{\text{CH}_4} \) can be calculated for our study system using Equation 2 by substituting the measured \( \text{CH}_4 \) flux \( (4.6 \times 10^{-7} \text{ mol/ m}^2 \text{ min}) \) and setting \( \alpha_{\text{CH}_4} \) to 1. Once the \( k \) value is known within a system for a specific gas and temperature it can be calculated for any other gas based on the ratios of the Schmidt numbers via the following equation (Jähne et al. 1987):

\[
(4) \quad k_{\text{CO}_2} = k_{\text{CH}_4} \left( \frac{S_{\text{CO}_2}}{S_{\text{CH}_4}} \right)^n
\]

where \( S_{\text{CO}_2} \) and \( S_{\text{CH}_4} \) are the Schmidt numbers 783 and 798 for \( \text{CO}_2 \) and \( \text{CH}_4 \), respectively. The variable \( n \) ranges from \(-2/3\) for a smooth water surface and \(1/2\) for a turbulent surface and was set to \(-2/3\) because the surface was smooth (Jähne et al. 1987).

\( C_{\text{sat}} \) values for \( \text{CH}_4 \) and \( \text{CO}_2 \) \( (1.3 \times 10^{-5} \text{ mol/m}^3 \) and \( 1.0 \times 10^{-1} \text{ mol/m}^3 \) respectively) were calculated using Henry’s law (applicable for ideal gas mixtures and dilute solutions) (MacIntyre et al. 1995; Raymond and Cole 2001):

\[
(5) \quad C_{\text{sat}} = C_g RTK_h
\]
Where $C_g$ is the initial concentration of gas in the atmosphere (taken as the initial concentration in the headspace of the closed chamber) ($3.3 \times 10^{-7}$ mol/L and $8.9 \times 10^{-5}$ mol/L for CH$_4$ and CO$_2$ respectively); R is the universal gas constant ($m^3$ Pa/k mol); T is temperature (285 K and 291 K during the beginning and end of the sampling for CO$_2$ and CH$_4$ respectively); and $K_h$ is a temperature-dependent Henry’s constant ($1.6 \times 10^{-5}$ mol/m$^3$ Pa and $0.0005$ mol/m$^3$ Pa for CH$_4$ and CO$_2$ respectively at 283K) (Sander 2015).

To solve for $\alpha$ in Equation 2, the measured dissolved gas concentrations from the beginning of the experiment was used for $C_{\text{gasw}}$ (Table 1).

We calculated an $\alpha$ for CO$_2$ of 22.7 by substituting our CO$_2$ flux ($-1.9 \times 10^{-5}$ mol*m$^{-2}$*min$^{-1}$), $k_{\text{CO}_2}$ ($7.9 \times 10^{-6}$ m/min), $CO_{2\text{gasw}}$ ($3.2 \times 10^{-8}$ mol/L), $CO_{2\text{sat}}$ ($1.0 \times 10^{-4}$ mol/L) values into Equation 2. To our knowledge, there are no other studies that report CO$_2$ enhancement factors in waters associated with sites of serpentinization. In the absence of site-specific $\alpha$ values, high pH lakes may be considered the closest analogues to our system. For example, CO$_2$ enhancement factors at a high pH lake were between 3.5 to 7.5 for a pH range of 9.45 to 9.75 (Bade and Cole 2006). Similarly, CO$_2$ chemical enhancement factors at both the Mono Lake (pH 9.8) and Big Soda Lake (pH 9.5) were 4.9 and 27.5 respectively for CO$_2$ invasion into water (Wanninkhof and Knox 1996). Therefore, our calculated $\alpha_{\text{CO}_2}$ falls within the range of high pH lakes. If pH were the only factor affecting the chemical enhancement of CO$_2$, then we would have expected the chemical enhancement calculated from data collected at WHC2, a water body with a pH of >12, to be higher than the chemical enhancement of CO$_2$ from the lower pH lakes.
mentioned above. Factors such as temperature and ionic strength also clearly affect the chemical enhancement at WHC2.

**Natural global warming potential**

In this study we observed that CO$_2$ is sequestered from the atmosphere 41 times faster than CH$_4$ gas is emitted to the atmosphere at the WHC2 ultra-basic pool in the Tablelands. However, the direct climate-change effect of this exchange cannot be determined using fluxes alone since CH$_4$ is a more powerful greenhouse gas than CO$_2$ and the gases have different atmospheric residence times. The Intergovernmental Panel on Climate Change (IPCC) uses radiative forcing to calculate the effect of a change in gas concentration on the overall energy balance (in W/m$^2$) between incoming solar radiation and the energy re-radiated back into space (IPCC 2013), such that the radiative forcing caused by CO$_2$ sequestration can be directly compared to the radiative forcing of CH$_4$ being emitted at the surface of the WHC2 ultra-basic pool. To determine the current effect this has on the atmosphere the radiative forcing can be used to calculate a gas’ effect on the overall energy balance. Using Equations 6a and 6b for CO$_2$ and CH$_4$ respectively the net radiative forcing (RF) of this site was calculated. The gas concentrations at 2 hours and 12 minutes (132 minutes), and 3 hours and 46 minutes (226 minutes) were used in Equations 6a and 6b because they are the only times in the linear range where neither CO$_2$ nor CH$_4$ were below detection. In addition, the measured N$_2$O concentration in the headspace was used in the following equation:

(6a) \[ RF_{CO2} = \alpha \ln \left( \frac{C}{C_0} \right) \]
(6b) \[ RF_{\text{CH}_4} = \alpha (\sqrt{M} - \sqrt{M_0}) - (f(M, N_0) - f(M_0, N_0)) \]

Where \( RF_{\text{CO}_2} \) and \( RF_{\text{CH}_4} \) are radiative forcing values for \( \text{CO}_2 \) and \( \text{CH}_4 \) respectively, \( \alpha \) is 5.35 and 0.036 for \( \text{CO}_2 \) and \( \text{CH}_4 \) respectively, \( M \) is \( \text{CH}_4 \) in ppb (taken at 3 hours and 46 minutes), \( N \) is \( \text{N}_2\text{O} \) in ppb (taken at 3 hours and 46 minutes), and \( f(M, N) = 0.47 \ln[1 + 2.01 \times 10^{-5} (MN) + 5.31 \times 10^{-15} M(MN)^{0.75}], \), and the subscript 0 refers to unperturbed molar fraction of the species (taken at 2 hours and 12 minutes) (Myhre et al. 1998).

The RF associated with the \( \text{CO}_2 \) sequestered between 2 hours and 12 minutes (132 minutes) to 3 hours and 46 minutes (226 minutes) for \( \text{CO}_2 \) was -0.22. This negative value indicated an overall atmospheric cooling effect from the \( \text{CO}_2 \) removal from the atmosphere. In contrast the RF for the \( \text{CH}_4 \) releases at the same time was +0.01. This positive value indicated a warming effect from the \( \text{CH}_4 \) addition to the atmosphere alone. However, the net RF due to the changing concentrations of \( \text{CO}_2 \) and \( \text{CH}_4 \) was -0.21. Therefore, the negative net RF value calculated at this site of serpentinization suggests that the ultra-basic pool in WHC has a net cooling effect on the atmosphere.

While radiative forcing provides a prediction of the immediate impact of changing GHG concentration it does not consider the different residence times of the gases in the atmosphere. In addition to radiative forcing, the IPCC also uses the global warming potential (GWP) to make future predictions about the impacts of different greenhouse gases. GWP is a relative measure of the heat that a greenhouse gas traps in the atmosphere over a specific time horizon as compared to the amount of heat trapped...
by an equivalent mass of CO₂. The GWP is calculated as a ratio of the time-integrated radiative forcing from the instantaneous release of 1 kg of a trace substance relative to the release of a 1 kg reference gas where CO₂ has a GWP of 1 (IPCC 2001). This relative value is a function of the residence time of the gas in question, such that GWP changes with time. For example, CH₄ has a GWP value of 86 over a time horizon of 20 years and a decreased GWP value of 34 over a time horizon of 100 years (Gillett and Matthews 2010).

To determine the overall long-term effect of this site the GWPs of the gases must be converted to a CO₂ equivalent for various time horizons. The conversion of GWP to CO₂ equivalence is simply a 1:1 ratio because a gas’s GWP is relative to that of CO₂. Over a 20-year time horizon the GWP of methane is 86 (CO₂ equivalence of 86) but the site is removing 41 times more CO₂ than methane (CO₂ equivalence of -41). Therefore, the CO₂ equivalence can be added to get a net CO₂ equivalence of 45 over 20 years, referring to a net global warming potential of 46 and a heating of the atmosphere. In contrast, over a 100 year time horizon the GWP of methane is 34 (CO₂ equivalence of 34) but the site is removing 41 times more CO₂ than methane (CO₂ equivalence of -41). Therefore, over 100 years the site has a net CO₂ equivalence of -7, referring to a global warming potential of -7, and a cooling of the atmosphere, congruent with the RF prediction.

While these results show the immediate and long-term impact of this specific ultra-basic pool, this is a small site that likely makes a relatively insignificant environmental impact. However, within the Tablelands alone there are several other
ultra-basic pools where carbonates have been observed and that are potentially taking in CO$_2$ and releasing CH$_4$. In addition, carbonate has been found near sites of runoff without pooling, indicating potential sequestration in the absence of ultra-basic pools. Moreover, sites of serpentinization like the Tablelands can be found all over the world. However, fluxes for each site must be considered on a case-by-case basis. For example, the Cedars, a site of serpentinization in Sanoma, California, features bubbling gases from ultra-basic springs, likely indicating higher CH$_4$ concentrations and flux than measured at Winterhouse Canyon (Morrill et al. 2013). With this in mind, some of these sites, specifically the Oman ophiolite, have been proposed for enhanced carbon capture storage that would involve injecting CO$_2$ to enhance carbon sequestration (Kelemen and Matter 2008). However, a recent study has also shown that under certain conditions CO$_2$ can be converted to CH$_4$ microbially at the Cedars (Kohl et al. 2016). Therefore, before we focus on ways to modify these systems to enhance CO$_2$ sequestration we must first gain a better understanding of the natural baseline of the sites and their impacts on the environment as a whole. This study is the first to consider the impact of green house gases (CO$_2$, CH$_4$, N$_2$O) coming into and out of an ultra-basic pool above serpentinized rock and highlighted the need for more research on the net impact of serpentinization globally.

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Morrissey, and Chevron Canada Rising Star Scholarship awarded to L. Morrissey.

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References


Figure Captions:

Figure 1: Closed floating chamber deployed in Winter House Canyon Spring 2 (WHC2). The chamber was supported with styrofoam. Gases collect in the headspace of the chamber and were sampled over a 24 hour period from the top of the chamber. The white rock surrounding the pool is carbonate.

Figure 2: Time series data of gas concentrations sampled from the closed chamber floating over an ultra-basic pool created by a groundwater springs associated with serpentinization in the Tablelands, NL: (A) methane, (B) carbon dioxide, and (C) N$_2$O. For (C) the dashed lines indicate the analytical error associated with the GC-ECD analysis. Error bars on all plots indicate standard deviation of the mean plotted point based on sample duplicates.
Table 1. Sampling conditions for Winterhouse Canyon Spring (WHC-2b)

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<tr>
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<th>Sep 1 2015</th>
<th>Sep 2 2015</th>
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<tr>
<td><strong>Field Air</strong></td>
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<tr>
<td>Temperature (K)</td>
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<td>291</td>
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<tr>
<td><strong>Field Water</strong></td>
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<td></td>
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<tr>
<td>Temperature (K)</td>
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<td><strong>Lab Air</strong></td>
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<td>pH</td>
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<td><strong>Conductivity (ms)</strong></td>
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<td><strong>CO$_2$ in Water</strong></td>
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<td>1.9E-08</td>
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<td>Conc. (mol/L)</td>
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<tr>
<td><strong>CH$_4$ in Water</strong></td>
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<td>Conc. (mol/L)</td>
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<td></td>
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<tr>
<td><strong>Average wind</strong></td>
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<td></td>
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<tr>
<td>*Speed (km/hr)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Taken as an average of the hourly reported data from "TheWeatherNetwork" for the 24-hour period at the Rocky Harbor Weather Station.
(http://climate.weather.gc.ca/climate_data/hourly_data_e.html?StationID=6938&timeframe=1&Year=2015&Month=9&cmdB1=Go&Day=2)
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