Observing methane hydrate dissolution rates under sediment cover

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Abstract

Dissolution rates of naturally occurring hydrates vary by orders of magnitude across studies suggesting that environmental factors may influence hydrate dissolution. To determine the role that sediment cover plays in hydrate dissolution, we used a mini-pore fluid array sampler (mPFA) to continuously collect sediment porewater adjacent to a hydrate outcrop and maintain it at *in situ* pressure for later analysis. This allowed us to measure *in situ* dissolved hydrocarbon concentrations in the porewater over time without sample loss due to degassing. We deployed the mPFA at a hydrate outcrop at Barkley Canyon in the Cascadia Margin for nine months. This novel approach yielded concentration data that was used to determine the steady-state dissolution rate of the hydrate outcrop and test predictions of the diffusion-control model for dissolution in the field. In the lab, we conducted a series of experiments with artificial hydrate to directly compare dissolution rates between exposed and sediment-covered hydrate. The dissolution rate of the natural hydrate outcrop covered with sediment was 0.06 cm y^{-1} . The laboratory experiments of sediment-covered hydrate yielded dissolution rates of $0.6 \pm 0.5 \text{ cm y}^{-1}$ ($n = 5$). In both laboratory and field observations, the dissolution rate of hydrates exposed directly to bulk water ($3.9 \pm 1.7 \text{ cm y}^{-1}$ and 3.5 cm y^{-1} respectively) were at least an order of magnitude faster than the dissolution rate of sediment covered hydrate. These results are consistent with expectations of diffusion-control and support this model of hydrate dissolution. In nature, sediment may account for the persistence of hydrate in otherwise methane-depleted environments by increasing the diffusive boundary layer and slowing the rate of molecular diffusion via porosity/tortuosity effects. We provide a number of “Lessons Learned” for improving the instrument design and for consideration during future studies.

Keywords: Methane, Hydrates, Dissolution, Stability, Pacific Ocean, Barkley Canyon

Introduction

Gas hydrates are crystalline solids consisting of guest molecules enclosed within water cages (Sloan, 1998). Natural hydrates form when potential hydrate guests (such as hydrocarbons or CO₂) come into contact with water under conditions of high pressure and low temperature. Such conditions are found in Arctic permafrost and continental slopes deeper than 350 m water depth. Large quantities of gas can be stored within these structures. For example, natural methane hydrates have been estimated by some to contain more carbon than all conventional fossil fuel sources combined (Kvenvolden, 2000). Because methane is both a potent greenhouse gas and an important energy source, hydrates are of considerable interest to scientists and industry alike. In particular, questions relating to the stability of hydrates are becoming more important as interest in methane recovery and concern about the release of methane into overlying ocean (and eventually the atmosphere) increase.

Four primary factors control hydrate stability: pressure (P), temperature (T), salinity, and the concentration of the guest in the surrounding environment. When hydrate is exposed to P/T regimes outside of the hydrate stability zone (HSZ), regardless of the ambient gas concentration, the hydrate decomposes by *dissociation*, a relatively fast process resulting in the release of gaseous phase guest molecules (e.g. CH_{4(g)}). However, if the P/T regime is within the HSZ, but the concentration of the guest molecule in the surroundings falls below saturation, the hydrate will decompose by *dissolution* resulting in the release of dissolved gas (e.g. CH_{4(aq)}; Zhang and Xu, 2003). While hydrate dissociation has been the topic of numerous kinetic studies (reviewed in Sloan, 1998), hydrate dissolution is a comparatively unexplored process. A handful of studies have explored hydrate dissolution in the field and through laboratory experiments (e.g. Egorov et al. 1999, Brewer et al. 2002; Rehder et al. 2004; Bigalke et al. 2009; Hester et al. 2009; Lapham et al. 2010, 2012, 2014), however, field results have been highly variable, occasionally contradictory, and remain difficult to reconcile with controlled laboratory findings.

Rehder et al. (2004) produced artificial hydrate in the lab and then transferred that hydrate to a field site where P/T conditions were within the stability zone for hydrate. They found that the dissolution rates of pure methane hydrate (~150 cm y⁻¹) and pure CO₂-hydrate (~1600 cm y⁻¹)

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4 exposed directly to seawater under hydrate-favorable P/T conditions were approximately
5 proportional to their respective solubilities, supporting a diffusion-controlled dissolution
6 mechanism. In controlled laboratory tests, Bigalke et al. (2009) measured hydrate dissolution
7 under various stirring rates (96-119 cm y⁻¹) and concluded that the dissolution of hydrate
8 exposed directly to methane-undersaturated water was a diffusion-governed process. Similarly,
9 Lapham et al. (2014) recently demonstrated that the dissolution rates of pure methane hydrate
10 (3.9 cm y⁻¹) and pure propane hydrates (0.5 cm y⁻¹) exposed directly to methane-undersaturated
11 water under controlled laboratory conditions were proportional to their hydrocarbon solubilities,
12 thereby supporting Bigalke et al.'s (2009) conclusion of a diffusion-controlled mechanism for
13 hydrate dissolution.
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16 Results from *in situ* observations of natural hydrate formations, however, do not so clearly
17 support a diffusion-control mechanism for dissolution. In Cascadia Margin, dissolution rates
18 from 0.03 cm y⁻¹ to over 100 cm y⁻¹ have been measured in various studies; while in the Gulf of
19 Mexico observations range from very little to no discernible changes over time (MacDonald et
20 al. 2005) up to 15 cm y⁻¹ (Lapham et al. (2014). Lapham et al. (2010), using various
21 measurements, report dissolution rates in Cascadia Margin ranging from 3.5 to 0.03 cm y⁻¹, these
22 rates are one to three orders of magnitude slower than would be expected from diffusion-
23 controlled dissolution based on measurements of methane concentrations at the site. In short, the
24 dissolution rates of hydrate formations observed in nature span orders of magnitude and are
25 sometimes slower than predictions based solely on methane diffusion.
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28 Two mechanisms have been proposed to account for the apparent stability and high
29 variability in dissolution rates observed for natural hydrate outcrops. Apparent stability may be
30 explained if dissolution of hydrate from an exposed surface is approximately balanced by
31 formation of additional hydrate from below as gas migrating upwards through the sediment
32 enters the hydrate stability zone such that there is no net change in the size of the hydrate over
33 time (Egorov et al. 1999), what Lapham et al. (2010) referred to as the “push-up pop” model. In
34 addition, natural hydrate outcrops may be ‘shielded’ by some kind of covering consisting of
35 biofilms or sediment, which increases the thickness of the diffusive boundary layer thereby
36 slowing hydrate dissolution (Egorov et al. 1999; Lapham et al. 2010; Lapham et al. 2014).
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4 In order to explore this second mechanism (shielding) and the geochemical controls on
5 natural hydrate stability, we deployed a newly designed mini Pore Fluid Array (mPFA) to collect
6 porewater samples from within a few centimeters of a sediment-covered natural hydrate surface
7 (see Lapham et al. 2013 and Lapham et al. 2008 for an earlier prototype). These osmotic-
8 samplers continuously draw pore fluids over time and are capable of storing many months of
9 porewater samples at *in situ* pressures (Jannasch et al. 2004). This allows us to generate a time
10 series of geochemical parameters in sediments to explore dynamic controls on hydrate stability.
11 Most importantly, because the samples are stored at *in situ* pressures, these samplers allow us to
12 measure *in situ* dissolved gas concentrations without the complication of sample loss due to
13 degassing.
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15 Because of the potential for sulfate and DIC to co-vary with methane in marine
16 sediments, samples from the osmotic-samplers were also analyzed for sulfate concentrations and
17 DIC concentrations and stable isotopes. In seawater sediments along coastal margins such as
18 occur at the Barkley Canyon site, sulfate and DIC concentrations reflect the balance between
19 diffusion of overlying seawater (which has a sulfate concentration = 28 mM and DIC
20 concentration = 2.2 mM) into the sediments and any microbial cycling of these elements. Sulfate
21 concentrations could be influenced by organoclastic sulfate reduction or by anaerobic oxidation
22 (AOM) of methane in which sulfate reduction is coupled to methane oxidation. Either of these
23 processes would result in sulfate concentrations less than ambient seawater concentrations (28
24 mM) and elevated DIC, but anaerobic oxidation of methane (AOM) would further result in
25 decreased methane concentrations. Thus if microbial cycling of sulfate is occurring at the site,
26 we would expect sulfate and DIC concentrations to be inversely correlated. Conversely, if the
27 geochemistry is being driven by mixing with bottomwater (either through advection or by
28 seeping in through cracks in the sediment ('seawater infiltration')), the sulfate concentrations
29 should increase while DIC concentrations decrease. However because bottomwater has very low
30 methane concentrations (1.4×10^{-3} mM, Lapham et al. 2013), seawater infiltration should also
31 lower the total hydrocarbon concentration. Thus, sulfate and DIC could provide valuable clues
32 to understanding the controls on methane concentrations in these sediments.
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4 We present here the first continuous time series of *in situ* dissolved hydrocarbon,
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6 chloride and dissolved inorganic carbon (DIC) concentrations measured from marine sediment
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8 porewater in contact with a hydrate surface. We also conducted laboratory experiments to
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10 directly test the influence of sediment cover on hydrate dissolution rates.

11 12 13 **Materials and Methods**

14 15 *In-situ hydrate dissolution field measurements*

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17 A mini Pore Fluid Array system (mPFA, Lapham et al. 2008, Lapham et al. 2013), which
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19 incorporated four OsmoSamplers (Jannasch et al. 2004) to collect and store porewater samples
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21 from sediments, was deployed at a hydrate outcrop in Barkley Canyon, Northern Cascadia
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23 Margin (Figure 1) from August 2009 through May 2010. The sampling system included a 21 cm
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25 long probe tip on a lead that allowed the sampling ports to be precisely placed by the
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27 OceanNetworks Canada remotely operated vehicle (ROV) ROPOS into sediments of interest.
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29 The sampling ports were positioned at 1 cm and 3 cm from the end of the probe tip with the
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31 intent of providing a measure of geochemical gradients next to the hydrate surface. Water depth
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33 at the field site was 860 m with an average temperature of 4°C, conditions favorable for hydrate
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35 stability. Outcropping hydrate has been observed at this site previously (Pohlman et al. 2005)

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37 The mPFA was deployed atop a hydrate scarp projecting from the seafloor. The sampler
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39 probe tip was placed by ROV in the sediment drape overlying the hydrate outcrop such that
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41 porewater sample depths were collected at 1 cm and 3 cm away from the hydrate surface (Figure
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43 2). These depths were assured by pressing the probe tip into the sediments until it met
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45 significant resistance at the hydrate surface. The total sediment thickness overlying the hydrate
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47 was estimated from the depth that the probe shaft (of known length) penetrated the sediments
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49 before encountering the hard hydrate surface. A temperature logger (Antares© recording
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51 thermistor) was affixed to the outside of the pump box to monitor bottom water temperatures
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53 over the course of the deployment. The loggers came pre-calibrated by Antares. Temperature
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55 measurements were recorded every 9 seconds for the duration of the deployment with a precision
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4 To retrieve the package, an ROV arm pushed a lever that in turn closed a high pressure
5 valve to isolate the samples at *in situ* pressures until analysis. The sampler package was then
6 brought to the ship via the submersible and placed in the walk-in cooler to await return to dock.
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8 Dockside, the sampler package was visually checked for leaks before sample coils were crimped
9 (maintaining their *in situ* pressure within the copper coil), removed from the valve, and shipped
10 back to Florida State University for analysis. An identical sampler package was used
11 concurrently at a gas seep site (Lapham et al. 2013). Methane saturated water (up to 85 mM)
12 was recovered in that instrument indicating that the mPFA is capable of recovering *in situ*
13 methane concentrations and that methane is not lost from the coils during transport or storage, at
14 least on the order of 3-4 months (Lapham et al. 2013).
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17 Temperature loggers were removed from the sampler package, the data was downloaded to a
18 PC and plotted as daily average temperatures (Figure 3a). Upon arrival at the lab, the fluid-filled
19 coils were sectioned (due to analytical constraints on sample volume, sampling resolution was
20 approximately 4 days) and the porewater contents removed via gas-tight connections to
21 evacuated, sealed vials. Helium was added to each sample to bring the vials to ambient
22 atmospheric pressure then an additional 10 mL of helium was added to overpressure the vials for
23 analysis. This helium headspace was allowed to equilibrate with the water sample while shaking
24 for at least 2 minutes. Hydrocarbon (methane, ethane and propane) concentrations were
25 determined by headspace analysis on a Shimadzu (GC-2014) gas chromatograph with a flame
26 ionization detector equipped with a 27.5 m Poroplot Q capillary column set at 30°C with a 250
27 μ L sample loop. Reported *in situ* methane, ethane, and propane concentrations in millimolar
28 (mM) were corrected for the helium dilution and Bunsen solubility. Isotope ratios ($\delta^{13}\text{C}$) of
29 methane and isotope ratios ($\delta^{13}\text{C}$) and concentrations of dissolved inorganic carbon (DIC) were
30 determined via a continuous flow Hewlett-Packard 5890 GC equipped with a 6 m Poroplot Q
31 column (held at 35°C) coupled to a Thermo Delta V isotope ratio mass spectrometer following
32 acidification of the samples with 100 μ L of 40% phosphoric acid. Isotope results are reported as:
33 $\delta^{13}\text{C} = 1000 \cdot (R_{\text{sample}}/R_{\text{standard}} - 1)$, where R is the ratio of the heavy to light isotope. Each sample
34 was run twice and the mean of those results was reported. Analytical error on the isotope
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analysis was 0.6‰. Chloride and sulfate concentrations were determined via standard procedures of ion chromatography on a Dionex ICS-1000, the analytical error was 4%.

Laboratory hydrate dissolution measurements

In laboratory experiments we examined the effect of sediment cover on hydrate dissolution. Hydrate was formed in a high pressure chamber (previously described in Lapham et al. 2014, 2012) using pure methane as the source gas in contact with a solution of 380 ppm sodium dodecyl sulfate (SDS) in water to facilitate the formation of the hydrate (Zhong and Rogers, 2000). The chilled (2°C), empty chamber (total volume = 600 mL) was filled with 300 mL of the 380 ppm SDS solution and then the total pressure was brought to 55 bar by introducing methane gas (Figure 4a). Hydrate initiation typically occurred within 1-12 hours as indicated by a drop in pressure and concomitant temperature increase. Once hydrate formation had ceased, as indicated by a slowing in the pressure drop, hydrate was allowed to anneal for 24-48 hours at 2°C. After this time, the pressure in the chamber was released as rapidly as possible via the headspace vent to a final pressure of 1.9 bar. Once the chamber had reached atmospheric pressure, the lid was removed, any excess water was decanted and the hydrate was pressed to the bottom of the chamber. A 1 cm layer of 300 µm silica sand was added on top of the hydrate and cold (2°C) distilled water (no SDS) was added. The chamber was then closed and brought back to 50 bar pressure through the addition of N₂ gas. This procedure was conducted as rapidly as possible to minimize hydrate dissociation during sand addition. Typically the entire procedure from the initial pressure venting to resealing the chamber and repressurizing with N₂ required about 15-25 minutes, the bulk of which was the initial depressurization of the chamber to atmospheric pressure.

Water samples were collected from the chamber via a Valco valve which allowed the chamber to maintain pressure while dispensing a fixed amount of the water (250 µL per sample) which was collected via gas-tight fittings in a syringe. Helium was added to the syringe to bring the total volume to 10 mL and the water was equilibrated with the helium. Methane concentrations were analyzed using a Shimadzu gas chromatograph (GC-2014) as was done for the field samples.

Calculating hydrocarbon solubility in contact with sII mixed gas hydrate at our field site

Hydrocarbon solubility in equilibrium with hydrate at the conditions for Barkley Canyon was calculated using the method of Velaga (2014) for mixed gas hydrates in equilibrium with a liquid phase (only). This method uses an iterative approach to solve for the total hydrocarbon saturation concentration starting from an initial guess and the measured dissolved gas hydrocarbon composition at our site (*i.e.* $C_1 = 88\%$, $C_2 = 10\%$, $C_3 = 2\%$). From that initial guess, the cage occupancies of the hydrate (θ_{ij}) are calculated from the guest gas fugacity (the critical pressure for the hydrocarbon mixture was calculated according to the method of Grieves and Thodos (1963) and the respective Langmuir constants calculated by Anderson et al. (2005) and corrected for temperature (T) by $C_{ji}(T) = C_{0ji}e^{(m_{ji}/kT)}$, where m_{ji} and C_{0ji} for each hydrocarbon (*i*)-cage (*j*) combination are provided by Velaga (2014) and k = Boltzmann constant. From these cage occupancies and the relative proportion of large and small cages in sII hydrate provided by Holder et al. (1980), the total hydrate gas composition was estimated. The result of these calculations was a hydrate composition of 60.7% methane, 10.2% ethane, and 29.1% propane.

Velaga's (2014) solubility calculations are based on the van der Waals and Platteeuw (1958) thermodynamic model where the difference in chemical potential between the unfilled and fully-filled hydrate lattice ($\Delta\mu_w^{\beta-H}$) must equal the chemical potential difference between the unfilled lattice and the liquid phase ($\Delta\mu_w^{\beta-L}$). The equation for calculating $\Delta\mu_w^{\beta-H}$ from the fractional cage occupancies is given in Velaga (2014). The equations and parameters necessary for calculating $\Delta\mu_w^{\beta-L}$ are also given in Velaga (2014), where ΔH_w^0 and $\Delta\mu_w^0$ for the hydrocarbon mixture is assumed to be a linear combination of the corresponding parameters for methane, ethane, and propane. If the calculated $\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-L}$ then the initial hydrocarbon concentration guess was correct, otherwise the guess is improved until $\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-L}$ is true within some acceptable margin of error (in this study the iterations stopped when $|\Delta\mu_w^{\beta-H} - \Delta\mu_w^{\beta-L}| < 0.1 \text{ J mol}^{-1}$). Velaga (2014) also suggests a salinity correction based on their finding that hydrate in equilibrium with liquid only (*i.e.* no vapor phase) forms at a lower total pressure suggesting that the equilibrium solubility of hydrocarbons in seawater in equilibrium with

hydrate is lower than the solubility concentration in freshwater. Velaga (2014) suggests using the activity coefficients derived from the Setschenow (1889) equation: $\ln(\gamma_i) = \sum k_s m_j$ where k_s is the salting (Setschenow) coefficient and m_i is the molality of the solution. The seawater salting coefficients for methane and ethane were approximated by a linear combination of the salting coefficients of the six major seawater ions given in Velaga (2014). Fewer specific salting coefficients are available for propane, so k_s for propane was estimated from a linear combination of the available salting coefficients for propane supplemented by the salting coefficients for ethane for the six major ions used for estimating ethane and methane k_s . From these calculations we determined the total porewater hydrocarbon solubility concentration of 28.6 mM in equilibrium with a mixed gas hydrate. As a comparison, at the same T and P conditions as our site, Velaga (2014) calculated a total hydrocarbon solubility concentration of ~24 mM for a mixture of 87.5% methane, 8.1% ethane, and 4.4% propane in seawater.

Hydrocarbon flux and hydrate dissolution calculations of natural mixed gas hydrate

Assuming that molecular diffusion controls the flux of methane through sediment layers covering the hydrate at the Barkley Canyon site (Egorov et al. 1999), we calculated the steady-state flux through the diffusive sublayer according to Fick's First Law (equation 1):

$$J = -\phi \times D_s \times \frac{\partial C}{\partial x} \times \frac{3.2 \times 10^7 s}{y} \times \frac{L}{0.001 m^3} \times \frac{m^3}{100^3 cm^3} \quad (1)$$

Where sediment porosity, $\phi = 0.9$ (estimated based on measurements made by these authors at other seep sites). $\frac{\partial C}{\partial x}$ is the hydrocarbon concentration gradient across the sediment layer assuming saturated conditions at the hydrate surface (28.6mM) and near zero concentrations (1.4×10^{-3} mM, Lapham et al. 2013) at 1 mm above the sediment surface (Egorov et al. 1999). D_s , the diffusion coefficient for the hydrocarbons was assumed to be a linear combination of the T, P, and tortuosity-corrected diffusion coefficients for methane, ethane, and propane given in table 1. Diffusion coefficients were corrected for tortuosity corrections using the assumed porosity of 0.9 following the methods of Iverson and Jørgensen (1993). Ethane and propane diffusion coefficients were calculated from the diffusion coefficient for methane using the relation given by Witherspoon and Saraf (1965).

From the above methane fluxes we can estimate a steady-state dissolution rate (DR) in cm y^{-1} following the equation given by Lapham et al. (2010):

$$DR = J \times \frac{22.4 L_{\text{guest}}}{n_{\text{guest}}} \times \left(\frac{m^3 \text{hydrate}}{0.8 \times 160 m^3 \text{guest}} \right) \quad (2)$$

Where n_{guest} is the number of moles of the guest gas and the hydrate is assumed to be 80% filled.

Hydrate dissolution calculations of laboratory single guest hydrate

The concentration gradient in our laboratory experiments was assumed to be linear and controlled by the molecular diffusion of the methane through the sand layer. This is justified since the flux at the port suspended 7 cm above the hydrate in the bulk water had to equal the flux at the sediment water interface (and the flux at the hydrate surface). The change in methane with respect to time (mM y^{-1}) was calculated by fitting a linear regression to the methane concentrations measured at each time point for each experiment. The flux in each experiment was then calculated by multiplying the change in concentration with respect to time by the volume of the chamber divided by its surface area. The dissolution rate in cm y^{-1} for each experiment was then calculated as in equation 2.

The porosity of the sand ($\theta = 0.5$) was determined gravimetrically by wetting a known volume of sand with distilled water. The diffusion coefficient for methane through the sand (Table 1) was corrected for tortuosity using the method of Iversen and Jørgensen (1993).

Results

In-situ hydrate dissolution field measurements

The sampler package was deployed from August 2009 until May 2010. During deployment of the box and again during the retrieval process, photographs were taken of the mPFA and the surrounding hydrate (Figure 5). Several differences were noted during the retrieval. When deployed, the probe was inserted into the sediments such that the sampling ports were oriented at 1 cm and 3 cm (respectively) from the hydrate surface (depicted in Figure 2). Upon retrieval we noticed that the probe came out of the sediments at some point during the

deployment and landed behind the pump box, close to the outcropping hydrate (Figure 5). The implications of this for our data are presented in the Discussion.

Upon visual inspection following retrieval, the mPFA appeared in good conditions showing no visible signs of leaking or other indications of sample loss. Once in the lab, the valve box was disassembled and all sample-bearing lines were confirmed to be intact. Average pumping rates for each coil were calculated as the distance to the distilled water front (converted to mL of sample) divided by the total number of days deployed and averaged 0.5 mL d^{-1} (± 0.02 , one standard deviation here and throughout) for both pumps which allowed us to calculate dates for individual subsamples. Overall the temperature varied from 3.6 to 4.3°C during the sampling period (Figure 3a). There was a rapid temperature increase of 0.5°C between 21 Nov 2009 and 13 Dec 2009 followed by a similarly rapid decrease of approximately 1°C between 01 Mar 2010 and 15 Mar 2010. The sharp rise at the end of the record indicates the increase during retrieval to ambient air temperature. Chloride concentrations remained fairly constant over the time series and while the variability in the 1cm port was slightly greater than that at the 3cm port, neither was significantly different from bottomwater measured at a nearby site ($525 \pm 15 \text{ mM}$ in Lapham et al. 2013) (Figure 3b).

Total hydrocarbon concentrations ($C_1 + C_2 + C_3$) varied greatly and with a distinct pattern over the time series. On average methane made up 88% ($\pm 11\%$) of the total dissolved hydrocarbons, ethane made up 10%, and the balance was propane. Total hydrocarbon concentrations were low ($<10 \text{ mM}$) early in the deployment period became elevated during the late fall to a maximum of 25 mM. The hydrocarbon concentration remained relatively high and stable for 106 days and then total hydrocarbon concentrations decreased again to $<2 \text{ mM}$ in the spring (Figure 6 upper panel). In general, the total hydrocarbon concentrations in the port 3 cm above the hydrate were slightly lower than the total hydrocarbon concentrations measured at the 1 cm port and the concentrations in the 3cm port were much more variable than measurements at the 1cm port between 09 Oct 2009 and 01 Jan 2010. From 09 Oct 2009 through 23 Jan 2010, methane isotopes were similar at 1 cm and 3 cm (Figure 6 lower panel) and fairly constant at about -50‰ ($\pm 3\text{‰}$). At 23 Jan 2010 there was a 4‰ drop in methane isotope values over 1 sampling period (4 d) corresponding to the drop in DIC (dissolved inorganic carbon)

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4 concentrations. From 4 Feb 2010 through the end of the record, methane isotopes became
5 increasingly enriched in ^{13}C .
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8 DIC isotopes mirrored the methane isotopes (Figure 6, lower panel) becoming slightly
9 enriched over time from -10‰ to a maximum of 0‰ on 4 Feb 2010. Following the maximum,
10 DIC became increasingly more depleted again towards the end of the deployment to a minimum
11 value of -12.8‰ on 18 May 2010. There were no apparent trends between the 1cm and 3cm
12 ports in the isotope data.
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17 Sulfate concentrations started out low relative to overlying seawater early in the
18 deployment (~10 mM, Figure 6 upper panel) and increased over time eventually reaching
19 approximately 28 mM (equivalent to bottom water) around December 2009 (red line in Figure
20 6). DIC concentrations were highly variable. In the early part of the record the DIC
21 concentration in both ports was 10-15 mM (Figure 6 upper panel). After 09 Oct 2009 (purple
22 line in Figure 6), DIC concentrations decreased until 23 Jan 2010 (red arrow in Figure 6) when
23 DIC concentrations dropped to 2 mM over 4 days and then slightly increased again over the
24 remainder of the deployment to just above average seawater concentrations (3.2 mM; Figure 6
25 upper panel).
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35 *Hydrocarbon flux and hydrate dissolution calculations*

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37 The steady-state hydrocarbon flux at the buried natural hydrate in Barkley Canyon was
38 estimated to be $0.3 \text{ mmol cm}^{-2} \text{ y}^{-1}$. This flux corresponded to an average hydrate dissolution rate
39 of 0.06 cm y^{-1} .
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44 *Laboratory hydrate dissolution measurements*

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46 Five methane hydrate dissolution experiments with added sand layer were conducted in
47 the hydrate dissolution chamber. Experiments lasted from 100 to 500 hours and were ended
48 when methane concentrations ceased to increase (see Lapham et al. 2014).
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51 Methane concentrations from the chamber were plotted against time (Figure 4b) and were
52 found to increase linearly. Regression analysis revealed that the rate of methane concentration
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4 increase in the experiments ranged from 0.01 to 0.04 mM d⁻¹; however, none of the experiments
5 reached theoretical saturation (57 mM following Duan and Mao (2006) model).
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8 The average flux in the laboratory experiments of pure methane hydrate buried in a 1 cm
9 sand layer was 3.3 ± 1.3 mmol CH₄ cm⁻² y⁻¹ (n = 5, value reported as averages $\pm$ standard
10 deviation of multiple experiments here and throughout) which corresponded to a hydrate
11 dissolution rate of 0.6 ± 0.5 cm y⁻¹.
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15 16 17 **Discussion**

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19 These data are the first time-series record of *in situ* hydrocarbon concentrations from
20 sediment porewater adjacent to a hydrate surface. Our results demonstrate that the conditions at
21 this hydrate scarp are dynamic in terms of both physical changes that take place to the overall
22 morphology of the hydrate as well as the chemical conditions measured in the porewater over the
23 course of the instrument deployment. We observed changes in the sediment cover as well as an
24 increase in bacterial mat coverage across the site as inferred from an increase in the white
25 reflective substance at the seafloor (Figure 5) and, perhaps most strikingly and unfortunate for
26 our experiment, the complete dislodging of the probe tip from its original position during the
27 deployment.
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35 We also observed changes around the base of the pump box (Figure 5). The bottom left
36 edge of the box (middle right photograph of Figure 5) shows accumulation of material. This
37 could be due to sediment and or hydrate falling from the above scarp and landing about the edge
38 of the box, perhaps accounting for the dislodging of the probe tip. Alternatively, the pump box
39 may have been slowly sinking under its own weight into the sediments on which it was resting.
40 Finally, the overall size and shape of the hydrate mounds appears to have changed over the
41 course of the deployment. These physical changes to the gross morphology of the hydrate
42 outcrop likely influence likely correspond to geochemical changes in the environment which, in
43 turn, likely influenced hydrate stability contributing to the dynamic nature of this natural setting.
44 The implications of these changes are considered throughout this discussion.
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53 We assume that the hydrate in these surface expressions are dissolving, however, it is
54 also conceivable that while the hydrate mound was dissolving at the top surface, hydrate may
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4 also have been accumulating at other surfaces where hydrocarbon concentrations were sufficient
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6 to support hydrate growth resulting in changes of the overall hydrate morphology during the
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8 course of our measurements. While our data do not allow us to account for the influence of
9
10 hydrate growth during the instrument deployment, we suggest that formation of new hydrate
11
12 most likely occurred from deep within the sediments underneath the hydrate mound with the
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14 result that the overall mound with its sediment cover would be pushed upwards towards the
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16 water-column.

17 We further suggest that it is unlikely that significant net hydrate growth was occurring at
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19 the top surface where surrounding hydrocarbon concentrations were at or below saturation
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21 throughout our deployment and where there was actually evidence of hydrate dissolution.
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23 Because the probe tip was designed to measure localized porewater concentrations we suggest
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25 that the net changes in overall morphology of the hydrate mound did not significantly contribute
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27 to the rates of hydrate dissolution measured within centimeters of the hydrate surface. However,
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29 it will need to be remembered during the following discussion of our results that these effects
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31 were not directly testable in our study.

32 Given the hydrocarbon mixture measured in the porewater, we infer that the hydrate at
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34 this site was most likely sII. This is in line with previous findings at this and nearby sites (Hester
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36 et al. 2009; Pohlman et al. 2005). Despite technical challenges encountered during the
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38 deployment, the hydrocarbon concentrations measured between 09 October 2009 and 29
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40 December 2009 are the highest ever reported in contact with hydrate and are consistent with
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42 expectations from diffusion-controlled dissolution. We have provided an estimate of the rate of
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44 steady-state hydrate dissolution at this site based on our calculations of the hydrocarbon
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46 saturation adjacent to the hydrate surface. To our knowledge, this is the first *in situ* time-record
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48 of the dissolution of a buried massive hydrate in the data-poor field of hydrate dissolution
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50 studies. Further, our laboratory experiments demonstrate that sediment cover significantly
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52 influences hydrate dissolution rates, presumably by slowing the diffusion of guest molecules
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54 from the hydrate surface, thereby prolonging the stability of hydrate in otherwise hydrocarbon-
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56 poor environments.
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Evidence for Diffusion-controlled Dissolution at Barkley Canyon Hydrate

The diffusive boundary layer for the hydrate is assumed to be approximately the thickness of the sediment cover (15 cm). According to hydrate stability theory, the total hydrocarbon concentration at the hydrate surface (what we'll refer to as the proximal edge of the diffusive boundary layer) should be 28.6 mM as calculated according to the mixed gas hydrate model proposed by Velaga (2014). At the distal edge of the diffusive boundary (i.e. the sediment-water interface), the total hydrocarbon concentration is maintained at 1.4×10^{-3} mM (average seawater methane concentration measured by Lapham et al. 2013) by turbulence, currents and other non-diffusive effects. At a diffusion-controlled steady-state, the concentration gradient across the diffusive boundary layer should assume a linear profile (Egorov et al. 1999). The change in concentration with respect to distance from the hydrate surface (i.e. the slope of that gradient) at our field site can therefore be calculated as $(28.6 \text{ mM} - 1.3 \times 10^{-3} \text{ mM})/15 \text{ cm} = 1.9 \text{ mM cm}^{-1}$. Thus at 1 cm from the hydrate surface we expect the total hydrocarbon concentration to be 26.7 mM and at 3 cm from the hydrate surface the total hydrocarbon concentration should be 22.9 mM. In section B of Figure 6 (09 October 2009 through 29 December 2009), the total hydrocarbon concentrations average 22.3 ± 1.2 mM at 1 cm from the hydrate surface and 19.1 ± 1.2 mM at 3cm from the hydrate surface. Considering the cumulative analytical error in the hydrocarbon concentrations, the error in the sediment thickness estimation, and the potential error of the saturation calculation (which we cannot fully quantify at this time), the measured hydrocarbon concentrations in the porewater in contact with a hydrate surface during the time period in section B are consistent with expectations for steady-state diffusion.

The trend in sulfate and DIC concentrations in time section B of figure 6 are more challenging to interpret. Sulfate concentrations increase from approximately 11 mM to near seawater (28 mM), while DIC concentrations decrease from approximately 11 mM to ~ 3 mM. Alone, these trends indicate the possibility that overlying seawater is mixing with porewater during sampling until pure bottom seawater is being sampled at the end of time section B when the sulfate concentrations reach expected seawater values. However, because of the low concentrations of hydrocarbons in seawater, we would expect that seawater mixing would similarly lower the total measured hydrocarbon concentrations. In our data, however,

hydrocarbon concentrations remained elevated well above expected bottomwater values throughout time section B and are in fact consistent with diffusion-controlled dissolution from the hydrate surface. To explain these contradictory findings, one possible explanation is that the placement of the sampling box on the seafloor altered the benthic boundary layer at the site resulting in sediment erosion around the probe. Thus while the probe tip remained adjacent to the hydrate surface, the sediment water interface became increasingly close to the sampling ports as the sediment surface eroded away. This would result in increasing sulfate concentrations and decreasing DIC concentrations, as observed. This scenario further explains how hydrocarbon concentrations remain elevated as the probe would have remained in place adjacent to the hydrate surface (i.e. the hydrocarbon source). Although we would expect that erosion of the sediment on the hydrate surface would have decreased the thickness of the diffusive boundary layer and therefore led to an increase in the dissolution rate of the hydrate which would in turn have led to an increase in the hydrocarbon concentrations we measured, we did not observe this in our data. Perhaps the variability observed in the hydrocarbon data in the port 3 cm from the hydrate surface reflects some attempt of the system to adjust to the changes in sediment thickness (i.e. changes to the thickness of the diffusive boundary layer).

Another possibility to explain the increase in sulfate concentrations and concomitant decrease in DIC concentrations while methane concentrations remain near saturation, is that some perturbation to the system (perhaps our introduction of the sampling probe) caused sulfate production to commence during the time period in section B. Sulfate production, in which DIC is consumed to regenerate oxidized sulfur from sulfides, could explain the increase in sulfate concentrations that was inversely correlated with DIC concentrations, while allowing total hydrocarbon concentrations to remain relatively stable. The increased coverage of bacterial mat across the site as inferred from a comparison of the deployment and retrieval photographs (Figure 5) suggests that microbial cycling may be influencing the changes in the geochemical profiles over the course of the deployment. DIC $\delta^{13}\text{C}$ values become more positive during this time interval consistent with CO_2 uptake by sulfide oxidizing microbes. Alternatively equilibration of DIC with overlying waters could also drive the observed isotope change. Testing this hypothesis would require H_2S measurements or measurement of sulfur stable

isotopes, neither of which was within the original scope of this study. We plan to include these measurements on future deployments of this system to hydrate outcrops and recommend consideration of these measurements to others considering similar work at hydrate outcrop locations.

Geochemical features not consistent with diffusion-controlled dissolution

In time section A (representing the first 45 d of the deployment) the concentrations of all the measured constituents in Figure 6 (total hydrocarbons, sulfate, and DIC) generally increased following a nearly linear pattern. The rise in hydrocarbon concentrations over time is not consistent with steady-state diffusion, nor is it consistent with either AOM or mixing with bottomwater of low hydrocarbon content. We, therefore, interpret this increase in the early part of the record as a sampling artifact representing the equilibration time of the instrumentation package.

In time section C (representing 01 Jan 2010 through the end of the deployment) we see an apparently exponential decline in hydrocarbon concentrations, a single-point decrease in DIC concentrations and a similarly rapid decline in methane isotopes, particularly at the 1 cm port, followed by an increase in both these parameters, while sulfate concentrations are maintained near seawater values. The decrease in DIC concentrations and methane isotopes, indicated by the red arrows in the top and bottom panels of figure 6 (respectively), suggests a sudden perturbation to the system. Curiously, following the rapid drop indicated by the red arrow, the DIC concentrations slowly increase again to a final concentration of 3.3mM at the end of the deployment. These changes are also coincident with an increase in the $\delta^{13}\text{C}$ of the methane of approximately 8‰ and a decrease in the $\delta^{13}\text{C}$ of the DIC of approximately 8‰ over the remainder of the deployment. Cumulatively, these results suggest a possibility that methane oxidation could have occurred over time section C. We would expect that if anaerobic oxidation was occurring, the sulfate concentrations would also decline during this time section, which was not the case. Thus the geochemical results are not wholly consistent with AOM but would be consistent with aerobic oxidation.

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4 The conditions under which aerobic methane oxidation could produce the observed
5 trends in the geochemical parameters we measured are somewhat difficult to envision. The
6 proliferation of microbial (likely Beggiatoa) mats during the instrument deployment, as inferred
7 from the increase in white reflective surfaces in the site photographs, suggest that the aerobic
8 layer in the sediments must be very shallow indeed, perhaps on the order of millimeters. Thus, it
9 is not likely that aerobic methane oxidation could occur in the sediments where the probe was
10 initially placed. If the probe was pulled out of the sediments, however, and exposed to
11 bottomwater, sufficient oxygen would be available to fuel aerobic methane oxidation. However,
12 for this to be a plausible explanation, we would further have to explain why the hydrocarbon
13 concentrations do not immediately drop to near zero values if and when the probe tip was pulled
14 out of the sediments and exposed to low hydrocarbon water. There should be a rapid drop in
15 methane concentrations all the way to 1.3×10^{-3} mM on the order of 1-2 sampling points as the
16 probe sucked in bottomwater, contrary to the slow decline over months that we observed. This
17 may be further evidence of an instrument equilibration time or may lend further support to the
18 original suggestion of aerobic methane oxidation.
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33 *Lessons learned from the field experiments*

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35 When considered as a whole, a combination of sampling artifact, physical disturbance,
36 sediment erosion, and natural dynamic variability at the hydrate mound all play a role in
37 producing the complex geochemical time-series we observed. In the following paragraphs we
38 present a discussion of the lessons learned from this deployment to improve future designs and
39 aid further studies in the field of *in situ* dissolution studies.
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45 The movement of the probe tip during the deployment created significant challenges to
46 the interpretation of the data. Incorporation of a seafloor camera or other periodic observations
47 of the probe tip orientation would be helpful to determine if and when significant events such as
48 the probe tip falling out occurred during the time record. Further, the fact that we cannot infer
49 from the geochemical profiles when the probe tip came out of the sediments suggest that there
50 may be an equilibration time within the OsmoSampler copper tubing. The chloride apparently
51 equilibrates rapidly as inferred from the high chloride concentrations at the beginning of the
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record, however the equilibration times of methane and some of the other constituents are less well known. Without the equilibration rates and given the shape of the observed profiles, it has been difficult to infer when the probe tip fell out of the sediments. Thus rigorous testing of equilibration times should be determined for all desired geochemical parameters in future.

Future iterations of the sampling package should incorporate a more streamlined design so that the tether connection between the probe tip and the pump box (black line in Figure 2) is not drifting in the currents where enough force may be exerted to pull the probe tip out of the sediments. This force could have played a role in dislodging the probe tip during our deployment.

There is some evidence for microbial activity controlling these geochemical profiles in complex ways. However, despite the measurement of sulfate and DIC concentrations as well as DIC and methane stable isotopes we were not able to unequivocally determine whether and to what extent microbial processes may have been influencing the profiles. Inclusion of O₂ and H₂S concentrations and sulfate stable isotope measurements should be considered for future work in these complex systems to fully understand the role that microbial cycling has in shaping the geochemical profiles.

Contrary to what we expected, the concentration difference between the 1 cm and 3 cm ports was not consistent. This result precluded us from calculating fluxes over time as we had originally intended. While this could suggest that the system is not at diffusion-controlled steady-state, we must also consider the possibility that our instrument was not practically capable of collecting samples at the depth resolution we had anticipated. We calculated a theoretical depth sampling resolution starting from the total sample volume at each time point of 2mL. Then by assuming that the sampling ports draw from an approximately hemispherical area surrounding each port (bisected by the port shaft itself):

$$0.5 * \frac{4}{3} \pi r^3 = 2 \text{ mL} \quad (3)$$

we calculated that the “sphere of influence” or depth sampling resolution should be approximately 2 cm (1 cm radius for each port). However, this calculation does not take into account sediment porosity or water diffusion through the sediment. Based on our data (i.e. the lack of a consistent concentration difference between the 1 cm and 3 cm ports), this ideal

theoretical resolution may not have been met. Further work quantifying the actual depth resolution of the sampling equipment as well as design changes to improve the depth sampling resolution will be implemented in future efforts.

Laboratory Contributions to Understanding Hydrate Dissolution

Our previous experiments measuring pure methane hydrate with no sediment layer found that the average hydrate dissolution rate of pure methane hydrate exposed directly to water with no sediment in our experimental setup was $3.9 \pm 1.7 \text{ cm y}^{-1}$ (Lapham et al. 2014). Thus, addition of a 1 cm sand layer to the hydrate in our laboratory experiments reduced the dissolution rate to $0.6 \pm 0.5 \text{ cm y}^{-1}$. However, this lower dissolution rate cannot be explained by changes to the thickness of the diffusive boundary. In our experimental chambers there is no turbulence, current, or other disturbance and molecular diffusion is assumed to dominate from the hydrate surface to the top of the water phase (see Figure 4a). Therefore, assuming that the water depth is held constant, addition of a sand layer to the top of the hydrate should not influence the thickness of the diffusive boundary layer in our experiments. The observed reduction in dissolution rates was due (at least in part) to the effects of tortuosity and porosity on the rate of molecular diffusion of methane through the sediment.

The combined effects of porosity and tortuosity induced by the sand layer on the dissolution rate should be proportional to the porosity squared. In the next several steps we will show this is true for our experiments. From the equation for flux (equation 1 in Materials and Methods), we know that in addition to the concentration gradient the flux is dependent on the diffusion coefficient of the methane and the porosity of the sediments. For the sand experiments, the tortuosity correction of the diffusion coefficient supplied by Ullman and Aller (1982) tells us that the corrected diffusion coefficient (D_s):

$$D_s = \frac{D_o}{\phi * (\frac{1}{\phi^2})} = \phi D_o \quad (4)$$

Where D_o is the diffusion coefficient in bulk water. Thus the combined effects of tortuosity and porosity on the flux are $\phi * \phi D_o = \phi^2 D_o$. For a sand with porosity = 0.5, this results in a 75% reduction in the expected dissolution rate in our lab experiments. We suggest that this result

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4 agrees quite well within the experimental error of our experiments. Thus, in addition to
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6 increasing the thickness of the diffusive boundary layer, our experiments show that sediments
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8 also influence hydrate dissolution via porosity and tortuosity in non-trivial ways necessitating the
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10 consideration of these parameters when modeling the stability of hydrates in natural systems.
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12 13 **Conclusions** 14

15 Despite the difficulties in interpreting all of the geochemical data, what sets this dataset
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17 apart is that, for the first time, we have measured *in situ* hydrocarbon concentrations within
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19 centimeters of a natural hydrate surface. This has never been done before. Further, we have
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21 shown for the first time that in proximity to the hydrate, the porewater concentrations of
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23 hydrocarbons are consistent with the predictions of the diffusion-control model of hydrate
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25 dissolution. Concurrent laboratory experiments demonstrated that in addition to possible
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27 chemical controls and boundary layer thickness effects, the addition of sediment slows hydrate
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29 dissolution via sediment porosity and tortuosity effects. The cumulative results of the dissolution
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31 rates calculated from seafloor measurements and laboratory experiments support the hypothesis
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33 that sediments or other surface coatings could “shield” hydrate against dissolution and thereby
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35 prolong their existence in the methane-poor environment of the seafloor. This conclusion alone
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37 makes this dataset unique and moves our understanding of hydrate dissolution forward by
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39 providing empirical evidence in support of the model for a natural hydrate system. However,
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41 because many unexplained patterns remain in this geochemical dataset, we put forward a set of
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43 “lessons learned” that should inform future research efforts attempting to collect time-records of
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45 in situ dissolution rates.

46 Photographic observations of the natural hydrate in the field chronicled extensive
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48 changes to the hydrate shape and amount of sediment cover and while we were not able to rule
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50 out sampling artifacts due to limitations in the instrument design, porewater analyses also
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52 suggest changes in the geochemistry adjacent to the hydrate surface. If these changes are real
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54 and not an artifact of the instrument, these results would suggest that the geochemical
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56 environment surrounding natural hydrate outcrops is highly dynamic and that dissolution rates
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58 may be constantly changing in response to chemical and physical environmental controls. These
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dynamic conditions may contribute to the large variability in dissolution rates observed across field studies.

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Table 1: Physical parameters used in flux calculations. P is the pressure given in bars, T is the average temperature given in °C, $\emptyset$ is the porosity, ${}^x D_S$ is the pressure, temperature, and tortuosity-corrected diffusion coefficient for the hydrocarbon x through the sediment layer given in $\text{cm}^2 \text{s}^{-1}$.

System	P(bar)	T(°C)	$\emptyset$	${}^{CH_4} D_S$	${}^{CH_3CH_3} D_S$	${}^{CH_3CH_2CH_3} D_S$
Barkley Canyon	87.5	3.9	0.9	6.944×10^{-6}	5.623×10^{-6}	4.553×10^{-6}
Lab Experiments	50	2.0	0.5	4.420×10^{-6}	NA	NA

Figure 1: Map of the Barkley Canyon study site. The first panel (a) shows the Barkley Canyon hydrate site in relation to Vancouver Island, Canada off the Pacific Coast of North America. The shaded area represents known or inferred (from seismic data) hydrate occurrences. The second panel (b) shows the bathymetry at the hydrate site (mPFA location marked with a black dot).

Figure(s)

Figure(s)

Figure 2: Schematic of the sampling package showing the probe tip buried in the sediments relative to the hydrate surface during the initial deployment. Arrows highlight the 1 cm and 3 cm inlet ports where sample is drawn into the sampler package. Blue color is bottom seawater.

Figure 3: Temperature and chloride measurements during the sampler deployment. a) Temperature profile approximately 18 cm above the seafloor recorded with a temperature logger attached to the sampler package. The sharp spike in temperature at the last point indicates sampler retrieval and reflects the increase to ambient shipboard temperatures. b) Chloride concentrations in the sediment porewater over time.

Figure 4: Results of experimental hydrate dissolution. The left side of the figure shows a cartoon schematic of the hydrate chamber where dissolution laboratory experiments were conducted. The right side panel (a) presents the results of those dissolution experiments. Results from all five experiments are plotted on this graph. The dashed line at the top of the graph represents theoretical saturation based on Duan and Mao's (2006) model for water in contact with a hydrate surface.

Figure 5: mPFA deployment and retrieval pictures. The top center photograph depicts the site prior to deployment of the instrument package. The left middle photograph shows the instrument package just after deployment and the inset shows the position of the probe tip in the sediment overlying the hydrate. The right middle photograph shows the conditions of the site and the position of the probe at retrieval. The red box outlines the top of the probe at retrieval and shows that the probe moved during the deployment.

Figure 6: Geochemical profiles measured during the deployment. The top panel presents the total hydrocarbon ($C_1 + C_2 + C_3$), DIC, and sulfate concentrations measured at 1cm and 3cm from the hydrate surface. The lower panel presents the stable isotopes ($\delta^{13}C$) of the methane and DIC at the same depths. Section A is the time period from deployment until 09 Oct 2009 bounded on the right by the purple vertical line in both graphs. Section B represents the time period from 09 Oct 2009 through 29 Dec 2009, which is bounded on the right by the red vertical line. Section C represents the time period from 29 Dec 2009 through the conclusion of the deployment. The geochemical changes observed during each of these time periods are described in the text. The red arrow highlights 23 Jan 2010 where there was a sharp drop in DIC concentrations and methane $\delta^{13}C$, the possible causes of which are discussed in the text.