



Observing methane hydrate dissolution rates under sediment cover



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ABSTRACT

Dissolution rates of naturally occurring gas 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 on the Cascadia Margin for nine months. This novel approach yielded concentration data that were 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) was 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.

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1. 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 CO_2) 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. $\text{CH}_{4(g)}$). 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. $\text{CH}_{4(aq)}$; 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

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rates of pure methane hydrate ($\sim 150 \text{ cm y}^{-1}$) and pure CO_2 -hydrate ($\sim 1600 \text{ cm y}^{-1}$) exposed directly to seawater under hydrate-favorable P/T conditions were approximately proportional to their respective solubilities, supporting a diffusion-controlled dissolution mechanism. In controlled laboratory tests, Bigalke et al. (2009) measured hydrate dissolution under various stirring rates ($96\text{--}119 \text{ cm y}^{-1}$) and concluded that the dissolution of hydrate exposed directly to methane-undersaturated water was a diffusion-governed process. Similarly, Lapham et al. (2014) recently demonstrated that the dissolution rates of pure methane hydrate (3.9 cm y^{-1}) and pure propane hydrates (0.5 cm y^{-1}) exposed directly to methane-undersaturated water under controlled laboratory conditions were proportional to their hydrocarbon solubilities, thereby supporting Bigalke et al.'s (2009) conclusion of a diffusion-controlled mechanism for hydrate dissolution.

Results from in situ observations of natural hydrate formations, however, do not equally support a diffusion-control mechanism for dissolution. Along the Cascadia Margin, dissolution rates from 0.03 cm y^{-1} to over 100 cm y^{-1} have been measured in various studies; while in the Gulf of Mexico observations range from very little to no discernible changes over time (MacDonald et al., 2005) up to 15 cm y^{-1} (Lapham et al., 2014). Lapham et al. (2010), using various measurements, report dissolution rates in Cascadia Margin ranging from 3.5 to 0.03 cm y^{-1} , these rates are one to three orders of magnitude slower than would be expected from diffusion-controlled dissolution based on measurements of methane concentrations at the site. In short, the dissolution rates of hydrate formations observed in nature span orders of magnitude and are sometimes slower than predictions based solely on methane diffusion.

Two mechanisms have been proposed to account for the apparent stability and high variability in dissolution rates observed for natural hydrate outcrops. Apparent stability may be explained if dissolution of hydrate from an exposed surface is approximately balanced by formation of additional hydrate from below as gas migrating upwards through the sediment enters the hydrate stability zone such that there is no net change in the size of the hydrate over time (Egorov et al., 1999), what Lapham et al. (2010) referred to as the “push-up pop” model. In addition, natural hydrate outcrops may be ‘shielded’ by some kind of covering consisting of biofilms or sediment, which increases the thickness of the diffusive boundary layer thereby slowing hydrate dissolution (Egorov et al., 1999; Lapham et al., 2010, 2014).

In order to explore this second mechanism (shielding) and the geochemical controls on natural hydrate stability, we deployed a newly designed mini Pore Fluid Array (mPFA) to collect porewater samples from within a few centimeters of a sediment-covered natural hydrate surface (see Lapham et al., 2013, 2008 for an earlier prototype). These osmotic-samplers continuously draw pore fluids over time and are capable of storing many months of porewater samples at in situ pressures (Jannasch et al., 2004). This allows us to generate a time series of geochemical parameters in sediments to explore dynamic controls on hydrate stability. Most importantly, because the samples are stored at in situ pressures, these samplers allow us to measure in situ dissolved gas concentrations without the complication of sample loss due to degassing.

Because of the potential for sulfate and DIC to co-vary with methane in marine sediments, samples from the osmotic-samplers were also analyzed for sulfate concentrations and DIC concentrations and stable isotopes. In seawater sediments along coastal margins such as occur at the Barkley Canyon site, sulfate and DIC concentrations reflect the balance between diffusion of overlying seawater (which has a sulfate concentration = 28 mM and DIC concentration = 2.2 mM) into the sediments and any microbial cycling of these elements. Sulfate concentrations could be influenced by organoclastic sulfate reduction or by anaerobic oxidation (AOM) of methane in which sulfate reduction is coupled to methane oxidation. Either of these processes would result in sulfate concentrations less than ambient seawater concentrations (28 mM) and elevated DIC, but anaerobic oxidation of methane (AOM)

would further result in decreased methane concentrations. Thus if microbial cycling of sulfate is occurring at the site, we would expect sulfate concentrations to decrease and DIC concentrations to decrease. Conversely, if the geochemistry is being driven by mixing with bottom water (either through advection or by seeping in through cracks in the sediment (‘seawater infiltration’)), the sulfate concentrations should increase while DIC concentrations decrease. However because bottom water has very low methane concentrations ($1.4 \times 10^{-3} \text{ mM}$, Lapham et al., 2013), seawater infiltration should also lower the total hydrocarbon concentration. Thus, sulfate and DIC could provide valuable clues to understanding the controls on methane concentrations in these sediments.

We present here the first continuous time series of in situ dissolved hydrocarbon, chloride and dissolved inorganic carbon (DIC) concentrations measured from marine sediment porewater in contact with a hydrate surface. We also conducted laboratory experiments to directly test the influence of sediment cover on hydrate dissolution rates.

2. Materials and methods

2.1. In-situ hydrate dissolution field measurements

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

The mPFA was deployed atop a hydrate scarp projecting from the seafloor. The sampler probe tip was placed by ROV in the sediment drape overlying the hydrate outcrop such that porewater sample depths were collected at 1 cm and 3 cm away from the hydrate surface (Fig. 2). These depths were assured by pressing the probe tip into the sediments until it met significant resistance at the hydrate surface. The total sediment thickness overlying the hydrate was estimated from the depth that the probe shaft (of known length) penetrated the sediments before encountering the hard hydrate surface. A temperature logger (Antares® recording thermistor) was affixed to the outside of the pump box to monitor bottom water temperatures over the course of the deployment. The loggers came pre-calibrated by Antares. Temperature measurements were recorded every 9 s for the duration of the deployment with a precision of $0.01 \text{ }^\circ\text{C}$.

To retrieve the package, an ROV arm pushed a lever that in turn closed a high pressure valve to isolate the samples at in situ pressures until analysis. The sampler package was then brought to the ship via the submersible and placed in the walk-in cooler to await return to dock. Dockside, the sampler package was visually checked for leaks before sample coils were crimped (maintaining their in situ pressure within the copper coil), removed from the valve, and shipped back to Florida State University for analysis. An identical sampler package was used concurrently at a gas seep site (Lapham et al., 2013). Methane saturated water (up to 85 mM) was recovered in that instrument indicating that the mPFA is capable of recovering in situ methane concentrations and that methane is not lost from the coils during transport or storage, at least on the order of 3–4 months (Lapham et al., 2013).

Temperature loggers were removed from the sampler package, the data was downloaded to a PC and plotted as daily average temperatures (Fig. 3a). Upon arrival at the lab, the fluid-filled coils were sectioned

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