



Gas hydrate dissolution rates quantified with laboratory and seafloor experiments

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Abstract

Methane hydrates are stable at high pressure, low temperature, and saturated methane concentrations. However, natural hydrates exist at the seafloor where methane concentrations are well below saturation. Under such conditions, hydrate outcrops should shrink rapidly as they dissolve into the surrounding seawater. However, some natural hydrate outcrops have been observed for years undergoing little to no visible signs of change. Further, hydrate dissolution rates vary greatly among sites where changes have been observed. In this study, we perforated a natural hydrate outcrop on the seafloor of the Gulf of Mexico and measured the expansion of the hole after 30 days. From the rate of volume loss, we calculated a dissolution rate of 15 cm y^{-1} . This rate is nearly an order of magnitude slower than hydrate dissolution rates observed in the Northern Cascadia Margin. We hypothesized that crystal structure influences hydrate dissolution rates and that the variability observed in *in situ* hydrate dissolution is caused by different hydrate structures. To test this hypothesis, we measured methane hydrate (structure I) and propane hydrate (structure II) dissolution rates in a series of laboratory experiments. Hydrates were formed in a pressure vessel and maintained at pressure and temperature conditions conducive to hydrate stability. After formation, the gas source was removed. Dissolution rates were calculated by measuring the increase in the dissolved gas concentration over time. Structure I (methane) hydrate dissolved at an average rate of $5.2 \pm 2.5 \text{ mM CH}_4 \text{ d}^{-1}$. Structure II (propane) hydrate dissolved at an average rate of $0.3 \pm 0.2 \text{ mM C}_3\text{H}_8 \text{ d}^{-1}$. The ratio of these dissolution rates was proportional to the ratio of methane and propane solubilities under the experimental conditions. This suggests that dissolution rates in our experiments were diffusion-controlled and not influenced by differences in the crystal structure. We propose that natural contaminants such as oils or biofilms may have slowed the dissolution rate of the hydrate we observed in the Gulf of Mexico.

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1. INTRODUCTION

Gas hydrates are crystalline structures of hydrogen-bonded water cages that enclose gas molecules (Sloan, 1998). Naturally occurring hydrates are found in Arctic permafrost and ocean sediments where they comprise one of the largest reservoirs of methane (CH_4) on earth (Kvenvolden, 1988). In a 1997 report to the President of the United

States, methane hydrates were acknowledged as a potential energy source and it was suggested that science-based programs be developed to evaluate the production potential of methane hydrates worldwide (Holdren et al., 1997). Because CH_4 is such a powerful greenhouse gas, hydrates may have played a key role in past climate change (Nisbet, 1990; Paull and Dillon, 2001; Kennett et al., 2003; Maslin et al., 2004; O'Hara, 2008). However, the potential role of hydrate destabilization in future climate change is uncertain (Archer, 2007), in part, because we do not fully understand the factors that control natural hydrate stability.

Methane hydrates are known to be stable at high pressure (p), low temperature (T), moderate salinities, and high partial pressure CH_4 . Once formed, hydrates become

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unstable if the temperature increases or pressure decreases beyond a limit known as the hydrate stability zone or HSZ. Hydrates submerged in water will also become unstable if the dissolved methane concentration drops below saturation. Hydrates respond to such changing conditions in either of two ways: dissolution or dissociation (following Zhang and Xu, 2003). Dissociation occurs when the p and/or T conditions are no longer favorable for stable hydrate (regardless of the methane concentration). In this process, hydrate decomposes into gas (e.g., $\text{CH}_{4(g)}$) and liquid water. Dissolution occurs when the hydrate is no longer surrounded by CH_4 saturated water even if the p and T conditions are suitable for stable hydrate. In this process, hydrate decomposes producing liquid water and aqueous $\text{CH}_{4(aq)}$ until either saturation conditions in the surroundings are re-established or all of the hydrate disappears.

While the thermodynamics and kinetics of gas hydrate dissociation have been well studied (Sloan, 1998; Tohidi et al., 2001; Hester and Brewer, 2009), hydrate dissolution has only recently become an active area of research (Sugaya and Mori, 1996; Egorov et al., 1999; Zhang and Xu, 2003; Rehder et al., 2004; Nihous and Masutani, 2006; Bigalke et al., 2009; Hester et al., 2009). Several studies have established that the dissolution rate of artificial methane hydrate is controlled by diffusion (Rehder et al., 2004; Bigalke et al., 2009). Rehder et al. (2004) transferred synthetic CO_2 - and CH_4 -hydrates to the seafloor and then calculated the resulting dissolution rates from changes in the hydrate volume over time. The CH_4 -hydrate dissolved at a rate between 141 and 167 cm/yr. The CO_2 -hydrate dissolved much faster (between 1482 and 1892 cm/yr) than the CH_4 -hydrate, due to the higher solubility of CO_2 in water. Since the ratio of these rates ($\text{CH}_4:\text{CO}_2$) is similar to the ratio of CO_2 and CH_4 solubility concentrations, Rehder et al. (2004) concluded that hydrate dissolution is controlled by diffusion (mass transfer). Even more convincingly, Bigalke et al. (2009) used laboratory experiments to show that methane hydrate dissolution rates were proportional to the stirring rate applied to water in contact with the hydrate. This demonstrated that dissolution of pure sI hydrate is controlled by mass transfer.

The results of studies focusing on natural hydrate dissolution under *in situ* conditions have been less clear. Methane concentrations in ocean bottom water are well below saturation, thus hydrate outcrops exposed to bottom water on the seafloor should shrink rapidly as they dissolve in the surrounding seawater. Massive hydrate outcrops have been studied at numerous seafloor sites in the Gulf of Mexico, the northern Cascadia Margin (Sassen and MacDonald, 1994; MacDonald et al., 2005; Lapham et al., 2010) and in Santa Monica Basin (Paull et al., 2008). While some of these outcrops did exhibit gross changes in morphology (e.g., MacDonald et al., 1994), others were apparently stable with little or no changes in size or morphology over ~ 1 year periods (MacDonald et al., 2005; Vardaro et al., 2005; Chapman, 2009). Few studies have attempted to quantify natural hydrate dissolution rates, but those that do, provide little help reconciling these observations. Dissolution rates of natural hydrates in the northern Cascadia Margin range from 0.03–3.5 cm y^{-1} in one study (Lapham et al., 2010) to 62–104 cm y^{-1} in another (Hester et al., 2009).

To understand the factors that might contribute to such variability, we must first understand the dissolution process. The theoretical model of hydrate dissolution kinetics that has emerged over the last decade (Egorov et al., 1999; Zhang and Xu, 2003; Rehder et al., 2004; Nihous and Masutani, 2006; Bigalke et al., 2009) is summarized in Fig. 1. Under pressure and temperature conditions appropriate for gas hydrate stability, two liquid layers coat the hydrate surface (Zhang and Xu, 2003; Nihous and Masutani, 2006). In the inner “desorption layer”, interface reactions break up the crystal lattice liberating the enclosed gas (e.g., CH_4). The rate at which these bonds break is dependent on the strength of the hydrogen bonds between water molecules that make up the crystal structure (Zhang and Xu, 2003). The outer “diffusional boundary layer” (Fig. 1) only exists when hydrate is surrounded by water that is under-saturated with respect to the enclosed gas (e.g., CH_4). Under such conditions, hydrate will dissolve to re-establish and maintain saturated dissolved gas concentrations. The rate of that step is determined by mass transfer (i.e. diffusion-controlled) (Zhang and Xu, 2003) as observed by Rehder et al. (2004) and Bigalke et al. (2009) for artificial CO_2 and methane hydrates. However, at high bond strengths, the interface reaction rate could be slowed to such a point as to become close to or less than the diffusion rate. In such a case, the rate of dissolution could become influenced (or even controlled) by the interface reaction rate.

Natural hydrate primarily exists as two different structures: structure I (sI) or structure II (sII). Structure II has a higher bond strength than sI (Sloan, 1998) suggesting that the rate of interface reactions within the desorption layer of sII hydrates is slower than the rate of interface reaction for sI hydrates. Under the conditions of Rehder et al. (2004) and Bigalke et al. (2009) experiments, CO_2 and methane both form sI hydrate. The slower dissolution rates reported by Hester et al. (2009) were for thermogenic (likely sII) hydrates. To explain the different dissolution rates obtained in these experiments, we hypothesized that the increased bond strength in sII hydrate may slow the interface reaction enough to impart some interface reaction control on sII hydrate dissolution. Our objective, therefore, was to determine whether crystal structure plays a role in controlling gas hydrate dissolution. We constructed a laboratory hydrate dissolution chamber where only diffusion occurred (no turbulence) and compared the dissolution rates of sI and sII hydrate. We used pure methane gas to form sI hydrate and propane to form sII hydrate. These laboratory experiments help us probe the influence of crystal structure on hydrate dissolution rates. We also contribute to the scarce list of natural hydrate dissolution rates by providing the dissolution rate of a natural structure II hydrate (Sassen et al., 1999) outcrop in the Gulf of Mexico.

2. MATERIALS AND METHODS

2.1. Laboratory experiments

2.1.1. Hydrate dissolution chamber

Laboratory diffusion and gas hydrate dissolution experiments were conducted in a 600 mL (6.3 cm diameter)

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