



# CO<sub>2</sub> hydrate formation and dissociation rates: Application to Mars



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## ABSTRACT

CO<sub>2</sub> clathrate hydrate is a crystalline material composed of water cages around a CO<sub>2</sub> molecule. CO<sub>2</sub> gas hydrates are naturally occurring on Earth and are a likely phase on Mars as well as other cold planetary bodies. CO<sub>2</sub> hydrates have minor effects on terrestrial atmospheric composition, but may be a major reservoir for greenhouse gases on Mars. In this study, CO<sub>2</sub> hydrate formation and dissociation rates were measured experimentally on ultrapure and CO<sub>2</sub> infused water ice (ice containing previously trapped CO<sub>2</sub> gas bubbles). Overall, increasing pressure and temperature increased CO<sub>2</sub> consumption rates, indicating enhanced hydrate formation rates. CO<sub>2</sub> consumption and release rates both increased significantly in infused ice experiments as did the overall amount of CO<sub>2</sub> consumed. CO<sub>2</sub> bubbles formed during freezing of the infused ice likely provided more surface area for hydrate nucleation, increasing the rate of formation. Higher dissociation rates in infused ice experiments compared to ultrapure ice may be due to the higher concentration of hydrate originally formed in the bubble-filled samples. These results suggest that CO<sub>2</sub> hydrate formation in natural, gas-rich ice occurs significantly faster than previously assumed. In addition, formation rates would be maximized and dissociation rates minimized at Mars equatorial conditions, perhaps leading to long-term storage of atmospheric CO<sub>2</sub> in localized clathrate reservoirs.

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## 1. Introduction

### 1.1. CO<sub>2</sub> hydrate

Gas clathrate hydrates are made up of water ice cages around a 'guest' gas molecule and form in areas with low temperatures and/or elevated pressures (Sloan, 1998; Koh, 2002; Kuhs et al., 2006; Hester and Brewer, 2009). In addition to forming in permafrost and seafloor deposits on Earth (Koh, 2002; Hester and Brewer, 2009), CO<sub>2</sub> hydrate is a stable phase under Mars conditions and may be present in ice caps and/or permafrost (Miller and Smythe, 1970; Chastain and Chevrier, 2007; Thomas et al., 2009; Chassefière et al., 2013). Based on polar temperature estimates from data gathered by the Mariner 6 and 7 spacecraft, Miller and Smythe (1970) proposed that CO<sub>2</sub> hydrate may be a stable phase in these regions. In addition to polar ice, permafrost extends into the mid-latitudes on Mars and localized pockets may be preserved near the equator. Feldman et al. (2004) calculated water equivalent hydrogen levels in the near surface ranging from a minimum of 2% to a maximum of 100% at the poles based on neutron data from the Mars Odyssey spacecraft. This permafrost is another potential hydrate reservoir (Chastain and Chevrier, 2007; Thomas et al., 2009; Chassefière

et al., 2013). The top of the hydrate stability field (HSF) is within the top 15 m of the martian surface at the equator and reaches the surface at the poles (Chastain and Chevrier, 2007; Clifford et al., 2010; Root and Elwood Madden, 2012). This stability field extends to a depth of 3–5 km at the equator and 8–13 km at the poles, leading to the possibility of large CO<sub>2</sub> hydrate reservoirs if sufficient gas and water are available (Chastain and Chevrier, 2007; Thomas et al., 2009; Clifford et al., 2010; Root and Elwood Madden, 2012).

Therefore, hydrate formation and dissociation may affect atmospheric concentrations of greenhouse gases, such as CH<sub>4</sub> and CO<sub>2</sub> on both Earth (i.e. Dickens et al., 1997; Hunter et al., 2013) and Mars (i.e. Atreya et al., 2007; Root and Elwood Madden, 2012; Mousis et al., 2013). CO<sub>2</sub> hydrates may also sequester CO<sub>2</sub> on Mars, providing a major hidden reservoir of gases required for warm wet conditions early in Mars history (Brain and Jakosky, 1998; Hoffman, 2000; Longhi, 2006; Chassefière et al., 2013). For liquid water on the martian surface to have been stable the atmosphere would have needed to be much thicker than its present value of 0.006 MPa. The 'missing' atmospheric gas could have been lost to space through impact atmospheric erosion and pick-up ion sputtering or be sequestered in the martian polar caps or regolith (Brain and Jakosky, 1998). Within the regolith, CO<sub>2</sub> may be stored in a pure solid or liquid state or as a hydrate phase (Longhi, 2006).

Understanding how hydrate decomposes can aid in modeling of the release of CO<sub>2</sub> from permafrost and polar caps in response to

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seasonal temperature fluctuations, seismic events, landslides, pore water salinity changes, impacts and changes in obliquity (Mienert et al., 2005; Liu and Flemings, 2006; Chastain and Chevrier, 2007; Elwood Madden et al., 2009; Root and Elwood Madden, 2012). These models can then be used to interpret past and future climate conditions on both Mars and Earth. While the thermodynamics of CO<sub>2</sub> hydrate are fairly well constrained (Fuller et al., 2006; Svandal et al., 2006; Tegze et al., 2006; Sloan and Koh, 2008), the kinetics of CO<sub>2</sub> hydrate formation and dissociation below the freezing point of water has received significantly less study. This has led to a lack of quantitative kinetic data required for meaningful models of CO<sub>2</sub> release and sequestration. Most clathrate kinetic studies have focused on methane hydrate due its prevalence and energy implications on Earth, leading to a relative lack of CO<sub>2</sub> hydrate kinetic data.

### 1.2. Gas hydrate formation and dissociation

Hydrate formation at low temperature (below the freezing point of water) has been studied through a variety of experiments, including simple batch reaction gas consumption experiments, *in situ* neutron and X-ray diffraction, and scanning electron microscopy (Kawamura et al., 2002; Wang et al., 2002; Kuhs et al., 2006; Gainey and Elwood Madden, 2012; Falenty et al., 2013). These studies suggest that bulk hydrate formation occurs in two stages. Initially, gas reacts with ice at the surface of the particle; during this stage a hydrate shell forms rapidly and the rate of formation is controlled by the amount of ice surface area. For the second stage of hydrate formation, gas and/or water must diffuse through the clathrate shell to form more hydrate, which is a much slower process (Kawamura et al., 2002; Wang et al., 2002; Kuhs et al., 2006; Gainey and Elwood Madden, 2012; Falenty et al., 2013).

While the two stage model of hydrate formation from ice is generally accepted, other factors affecting clathration are not as clearly understood. For instance, there is a so-called “memory effect” in gas hydrate formation in liquid water. Water that has been previously frozen or has previously formed hydrate and then thawed will form hydrate more readily a second time (Takeya et al., 2000b; Ohmura et al., 2003), increasing the subsequent rate of formation. Takeya et al. (2000b) studied CO<sub>2</sub> hydrate nucleation rates in CO<sub>2</sub> saturated liquid water. They found that nucleation rates increased by a full order of magnitude using water from melted ice compared to water which had not been previously frozen. Nucleation rates also increased with the amount of O<sub>2</sub> dissolved in the water. The workers attributed the increase in nucleation rate to the presence of metastable polyhedral water cages surrounding O<sub>2</sub> molecules formed as ice melts. These polyhedra may serve as nucleation sites upon refreezing (Takeya et al., 2000b). These memory effects can be controlled using kinetic inhibitors, such as Poly(N-Vinylpyrrolidone) and Poly(N-Formylpyrrolidone) (Pic et al., 2001).

Like the formation process, hydrate dissociation below the freezing point of water also occurs in two stages. Based on methane hydrate dissociation experiments, methane hydrate initially dissociates at the hydrate-atmosphere boundary. Overtime, an ice shell forms and further dissociation is controlled by the diffusion of gas through the ice shell (Gainey and Elwood Madden, 2012). Other studies have suggested similar mechanisms for hydrate dissociation (Stern et al., 2003; Kuhs et al., 2004; Falenty and Kuhs, 2009). These studies also noted an anomalous self-preservation regime for gas hydrate; over temperatures from 240 to 273 K long-term hydrate dissociation rates are slower than expected, indicating that some process is inhibiting gas diffusion. Circone et al. (2003) compared dissociation behavior of CO<sub>2</sub> hydrate to CH<sub>4</sub> hydrate during isobaric temperature ramping and isothermal depressurization experiments. CO<sub>2</sub> hydrate released only 3% of its gas at 240 K (22 K above the hydrate phase boundary at

0.1 MPa) in contrast to the >95% gas release by CH<sub>4</sub> hydrate at 193 K and 0.1 MPa, within 25 K of its phase boundary. Only 20% of the CO<sub>2</sub> was released by 270 K and the system temperature was buffered at 271 K until hydrate dissociation was complete (Circone et al., 2003).

Through *in situ* neutron diffraction, Kuhs et al. (2004) determined that annealing of fractures in the secondary ice formed during the initial dissociation stage forms an efficient barrier to diffusion over this temperature range. The initial ice microstructure formed upon initial freezing also factors into the self-preservation, due to changes in the permeability of the ice. From 240 to 273 K, the ice formed upon initial dissociation has a hexagonal crystal structure, which packs together more efficiently than the cubic ice that forms at lower temperatures (Falenty and Kuhs, 2009).

These microscale formation and dissociation processes may be even more important in natural heterogeneous systems where ice is not a pure phase, but likely contains preexisting volatiles as bubbles or dissolved constituents. On Earth volatiles are commonly found in gas bubbles in polar ice and permafrost (Miller, 1969; Shoji and Langway, 1982; Dallimore and Collett, 1995; Lipenkov, 2000; Kipfstuhl et al., 2001; Calmels and Allard, 2004). In polar ice, where ice is formed through the densification of snow pack and/or frost, gas bubbles get trapped and can form up to 10% of the firn volume (Lipenkov, 2000). Bubbles are also present in permafrost deposits where they form as gas is exsolved from ground water as it freezes. In permafrost, the gas bubble concentration is 2% on average (Calmels and Allard, 2004). Bubbles can also be found in lake ice where they again form from exsolved gas (Jeffries et al., 1994). These processes have likely taken place on Mars as well. Since water ice on Mars can be found within ice caps at the poles and in a planet wide permafrost layer, gas bubbles are likely to be present. If the gas trapped within the ice has an atmospheric origin, gas bubbles on Mars would be filled primarily with CO<sub>2</sub> (Owen et al., 1977).

This study establishes a comprehensive dataset of CO<sub>2</sub> hydrate formation and dissociation rates on ultrapure water ice over a range of temperatures (245–260 K) and pressures (0.6–1.4 MPa). Once this database was established, a second dataset of CO<sub>2</sub> hydrate formation and dissociation rates on CO<sub>2</sub> infused ice was determined. These datasets were then compared to assess the effect of initial volatile content within the ice on CO<sub>2</sub> hydrate formation/dissociation rates. In natural systems, ice likely contains volatiles prior to clathration. These volatiles will vary depending on the atmospheric composition. On Earth, ice contains mostly nitrogen and oxygen while on Mars the primary volatile will be carbon dioxide. We hypothesize that these volatiles could affect hydrate formation and dissociation in ice cores on Earth, ice caps on Mars, and frozen lakes or oceans preserved as permafrost on both.

## 2. Methods

Two experimental systems were used in this study (Fig. 1). The single hydrate reactor (1HR) consists of a 300 mL gas reserve tank connected to a 500 mL reactor with ice. The reserve and reactor each contained a thermocouple and a pressure transducer. The second set up, the triple hydrate reactor (3HR), consists of three smaller reactors (150 mL each) and a gas reserve (300 mL). Like the 1HR set up, each reactor and the reserve contained a thermocouple and a pressure transducer. Volume and surface area data for both experimental systems are summarized in Table 2.

### 2.1. Formation/dissociation

Hydrate formation experiments were performed after the methods used by Gainey and Elwood Madden (2012). For hydrate

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