



# Effect of marine environmental factors on the phase equilibrium of CO<sub>2</sub> hydrate



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## ABSTRACT

We monitored the stability of CO<sub>2</sub> hydrate by investigating its three-phase (L<sub>w</sub>-H-V) equilibrium at different marine environmental conditions in the range of 273.3–280 K and 17–30 bar. The phase equilibrium of CO<sub>2</sub> hydrate in synthetic seawater (aqueous solution with 3.5% NaCl and 0.1 M NaHCO<sub>3</sub>) was observed in higher pressure and lower temperature region of phase diagram ( $\Delta P$ :  $5.063 \pm 0.019$  bar,  $\Delta T$ :  $-1.950 \pm 0.019$  K), compared to that in deionized water (DIW) control. Effect of soil minerals (illite and pyrite) and organic matters (glycine and humic acid) on CO<sub>2</sub> hydrate phase equilibrium was not significant in both DIW and synthetic seawater. The phase equilibrium of CO<sub>2</sub> hydrate in Ulleung basin (UB) sediment suspension was very similar to that of the synthetic seawater control ( $\Delta P$ :  $0.115 \pm 7.969 \times 10^{-4}$  bar,  $\Delta T$ :  $-0.038 \pm 8.466 \times 10^{-5}$  K); however, in the absence of organic fraction in UB sample by baking the sediment, its phase equilibrium shifted to the unstable upper left region ( $\Delta P$ :  $0.360 \pm 0.043$  bar,  $\Delta T$ :  $-0.215 \pm 8.442 \times 10^{-4}$  K). The results can provide fundamental knowledge to predict the stability of sequestered CO<sub>2</sub> and estimate CO<sub>2</sub> leakage from the sites in seabed sediment environments as a part of significant criteria to implement successful offshore CO<sub>2</sub> storage.

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## 1. Introduction

The concentration of anthropogenic CO<sub>2</sub> level in atmosphere has dramatically increased since the burning of fossil fuels. This has been reported to significantly affect severe environmental disasters such as global warming and climate change (Houghton et al., 2001). As one of promising tactics to cut down the massive anthropogenic CO<sub>2</sub>, geological CO<sub>2</sub> sequestration technology has been focused as a short- to mid-term solution because the fossil fuels will be still used as a dominant energy resource in the near future (White et al., 2003; Chu, 2009).

Diverse storage options for geological CO<sub>2</sub> sequestration which can store enormous amount of CO<sub>2</sub> in terrestrial and marine areas, have been suggested, i.e., CO<sub>2</sub> storage in depleted oil and gas reservoirs, coal beds, saline aquifers, and seabed sediments (or subsea sediments) (Blunt et al., 1993; Bergman and Winter, 1995; White et al., 2005; Tohidi et al., 2010). Among the several options for the geological CO<sub>2</sub> sequestration, recently, offshore CO<sub>2</sub> storage in seabed sediments has attracted an attention because it can

guarantee quite an extensive CO<sub>2</sub> storage capacity corresponding to the exponentially increased amount of global CO<sub>2</sub> emission (Bachu, 2003; Lee et al., 2013) and avoid potential risks of terrestrial one such as buoyant CO<sub>2</sub> leakage due to the subsurface temperature profile of terrestrial storage site (House et al., 2006).

Injected CO<sub>2</sub> in seabed sediments (>3000 m of ocean depth) below the hydrate formation zone (HFZ) can remain as stable liquid phase due to its higher density than overlying pore fluid and CO<sub>2</sub> hydrate layer formed in the vicinity of HFZ may provide a secondary shield that can effectively reduce the risk of CO<sub>2</sub> leakage (House et al., 2006; Tohidi et al., 2010; Sun et al., 2013). Another potential promising technology for the offshore CO<sub>2</sub> storage is to inject CO<sub>2</sub> into a stable natural gas hydrate (e.g., CH<sub>4</sub> hydrate) deposit as a form of CO<sub>2</sub> hydrate and simultaneously acquire the potential alternative energy resource by swapping CH<sub>4</sub> molecules in its hydrate structure by CO<sub>2</sub> (Ota et al., 2005; Park et al., 2006; Shin et al., 2008). In South Korea, a huge reservoir of CH<sub>4</sub> hydrate has been explored in Ulleung basin (UB) of East Sea, and this area has been regarded as proper site to store 50 billion tons of CO<sub>2</sub> so that researchers of the country expect to implement such sequestration technologies at the area in the near future (Ryu et al., 2009; Yun et al., 2011).

CO<sub>2</sub> hydrate is an ice-like crystalline compound composed of hydrogen-bonded 'cages' with water molecules and CO<sub>2</sub> as a 'guest

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molecule' inside its cavity (Sloan, 2003). This special structure can be formed and maintained under low temperature and high pressure environment which happens to occur at seabed sediment as well as continental margins and permafrost regions (Sloan, 2003; Sloan and Koh, 2008). CO<sub>2</sub> hydrate stability zone (HSZ) has been estimated by considering CO<sub>2</sub> hydrate phase equilibrium conditions with temperature and pressure gradients under seabed sediment environments (House et al., 2006; Tohidi et al., 2010). CO<sub>2</sub> hydrate phase equilibrium directly related to the shielding capacity and stability of stored CO<sub>2</sub> has been known to be significant along with the CO<sub>2</sub> hydrate formation kinetic which can predict how fast CO<sub>2</sub> can be trapped in hydrate structure when CO<sub>2</sub> is injected to the sediment environments (Lamorenna and Lee, 2008; Lee et al., 2013).

It has been revealed that one of the critical environmental factors affecting the CO<sub>2</sub> hydrate phase equilibrium is a salt concentration of sea water that shifts the phase equilibrium condition to the higher pressure and the lower temperature (Dholabhai et al., 1993; Englezos and Hall, 1994). Pore and particle size distributions in seabed sediments are also appeared to significantly alter the equilibrium pressure condition for the formation of CO<sub>2</sub> hydrate because they change the capillarity (Smith et al., 2002; Prasad et al., 2012). Few studies, however, have dealt with the effect and role of complex constituents in natural sediments on the CO<sub>2</sub> hydrate phase equilibrium to date. The effect of significant marine environmental factors on the phase equilibrium of CO<sub>2</sub> hydrate should be clearly understood before the implementation of offshore CO<sub>2</sub> storage technology to achieve successful CO<sub>2</sub> sequestration and its safe storage in natural seabed sediment environments.

In this paper, we investigated the effect of representative marine environmental factors commonly found in the seabed sediment (electrolytes, soil minerals, and organic matters) on the stability of CO<sub>2</sub> hydrate by monitoring its three-phase (L<sub>W</sub>-H-V) equilibrium change quantitatively. We additionally reported the phase equilibrium of CO<sub>2</sub> hydrate in UB sediment suspensions using a real core sample obtained from the gas hydrate deposit in UB where CH<sub>4</sub> hydrate has been naturally formed and safely contained for a long time to provide fundamental knowledge for evaluating the possibility of long-term stable CO<sub>2</sub> storage in this area.

## 2. Methodology

### 2.1. Chemicals and sample preparation

Hydrate forming gas was a commercial 99.9% compressed CO<sub>2</sub> (Sam-O Gas Co., Korea). Ultrapure deionized water (DIW) was used to prepare solutions and suspensions in this research. An exact amount (0.1 M) of NaHCO<sub>3</sub> (99.7–100.3%, Sigma–Aldrich) was dissolved in NaCl solution (3.5%, w/w), prepared by dissolving an exact amount of NaCl (99.5%, Junsei, Japan) in the DIW. This solution was used as synthetic seawater because its salinity (3.5%) and pH range (8.0–8.5) were very similar with real seawater. Illite (Youngdong, South Korea) and pyrite (Ward's Science, USA), main silicate and non-silicate soil mineral constituents of UB sediment were used as representative soil minerals (Lamorenna et al., 2011; Lee et al., 2013). Soil mineral suspensions were prepared by adding 1.0 g of soil mineral samples to 10 mL of DIW or synthetic seawater in 24 mL clear vials. The suspensions were completely mixed at 200 rpm until pH of the suspensions reached constant values. Commercial humic acid (technical grade, Sigma–Aldrich, USA) and glycine (99.0%, Duksan Chemical Co., Korea) were used as representative humic and protein-like organic matters. Exact amounts of humic acid and glycine were added to 10 mL of DIW or synthetic seawater to obtain 1000 ppm of organic matter suspensions, respectively. Seabed sediment sample was taken from a piston core sample from Ulleung basin (UB) in the East Sea of Korea (36°35.9005' N and

130°55.5507' E) at the depth of 2055 m and freeze-dried for 48 h before preparing UB sediment suspensions. To examine an effect of organic composition of UB sediment on the phase equilibrium of CO<sub>2</sub> hydrate, the sediment sample was baked in a muffle furnace at 823 K for 2 h to remove its organic fractions (Lee et al., 2013) and surface area of UB and baked UB sediments were measured by nitrogen adsorption/desorption isotherms obtained by an automatic adsorption instrument (ASAP 2000, Micromeritics) at 77 K. Both UB and baked UB samples were used to prepare UB and baked UB sediment suspensions with synthetic seawater. Organic fractions from alkaline extraction of 1.0 g UB sediment were freeze-dried and added to baked UB sediment suspension to prepare synthetic UB sediment suspension (Lamorenna et al., 2011). The experimental results were compared to those obtained from the UB sediment suspension.

### 2.2. Experimental setup and procedure

Detailed schematic diagram of experimental setup is demonstrated in Fig. S1 in Supplementary data. A 304 stainless steel pressure vessel with volume of 50 cm<sup>3</sup> was used for the phase equilibrium experiments. Tempered glass window at one side can allow visual observation of the hydrate formation and dissociation. A pressure transducer and a resistance temperature detector (RTD) sensor were installed to monitor pressure and temperature in the vessel. The pressure transducer and RTD sensor were connected to a data acquisition unit (Agilent 34970A), recording the data at a response time of 20 s. CO<sub>2</sub> hydrate three-phase (L<sub>W</sub>-H-V) equilibrium was monitored during the hydrate dissociation rather than formation because hydrate formation period requires higher pressure than its equilibrium state to induce hydrate nucleation during the formation period. Reproducible measurements of equilibrium conditions can be continued during sufficiently slow hydrate dissociation (Gayet et al., 2005). Prepared solution or suspension (~10 mL) was transported to the vessel. It was tightly sealed and placed in a circulating bath at ~278 K. The solution or suspension was completely mixed in the vessel by a PTFE-coated magnetic bar with external magnetic stirrer (Handa and Stupin, 1992). The vessel was purged by CO<sub>2</sub> (1–2 bar) and vacuumed by a vacuum pump (Rocker 300, Rocker Scientific Co., Taiwan) five times to remove air in its head-space and aqueous phase. CO<sub>2</sub> gas was then injected to the vessel in 2 min and its pressure nearly reached an expected equilibrium pressure at a certain setting temperature. For 30 min, a low flow rate of CO<sub>2</sub> was continuously supplied so that a constant pressure can be maintained. The pressure became stable even after stopping the CO<sub>2</sub> supply, indicating that the hydrate formation system was fully saturated with CO<sub>2</sub>. Temperature of circulating bath was set to decrease to ~269 K. The mixing in the vessel stopped during the temperature change and restarted after reaching a constant temperature. A sudden restart of the mixing easily induced the formation of CO<sub>2</sub> hydrate (Englezos and Hall, 1994). After 3–5 h of hydrate formation, temperature increased to ~278 K to dissociate the CO<sub>2</sub> hydrate. By repeating this formation/dissociation cycle twice before measurement of dissociation pressure, we removed the hysteresis effect known to cause a critical experimental error (Englezos and Hall, 1994; Seo et al., 2005). The measurement started during the dissociation of CO<sub>2</sub> hydrate at third cycle by increasing the temperature by a step of 0.5 K in the range of 273.3–280 K. Once hydrate dissociation occurred, vessel pressure started to increase and the temperature was maintained unchanged until the pressure reached an equilibrium point. To assure the stability of vessel pressure, the vessel stood in the circulating bath for 100 min even after reaching the equilibrium pressure. The dissociation pressure was recorded and the temperature increased again to obtain a new equilibrium point. This procedure was continued until the hydrate was fully dissociated. The same experimental

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