Equilibrium pressure of gas hydrate enclathrated carbon dioxide isotopologues

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Natural CO_2 hydrate was discovered at the Okinawa Trough, and it is expected that CO_2 hydrate exists in the polar ice caps of the Mars. Isotopic fractionation of CO_2 may provide useful information to understand formation processes of gas hydrate. Luzi *et al.* (2011) revealed that CO_2 $\delta^{13}C$ in hydrate-bound gas is 0.9‰ lower than that of residual gas, suggesting that light CO_2 molecules prefer to be encaged into clathrate cages. We reported at the last JpGU conference (Kimura *et al.*, 2019) that the isotopic difference between GH and residual gases distribute between between 1.2‰ and 1.5‰, agreed fairly well with the previous report. Ozeki *et al.* (2018) reported that the equilibrium pressure of CH_3D is larger than that of CH_4, causes isotopic fractionation in D between GH and residual gases as reported by Hachikubo *et al.* (2007). In this study, we measured the equilibrium pressures of $^{12}CO_2$ and $^{13}CO_2$ hydrates and checked the difference between them. CO_2 hydrate samples were synthesized in small pressure cells (volume: 5 mL). Fine ice powder was put in a pressure cell and introduced guest $^{13}CO_2$ gas. Hydrate crystals were formed by melting the ice powder at the temperature of the quadruple point. We also prepared normal CO_2 (mixture 98.9% $^{12}CO_2$ and 1.1% $^{13}CO_2$) hydrate as a reference, using the same preparation method. These pressure cells were placed in a temperature-controlled liquid bath, and measured their equilibrium pressures from 270 K to 278 K. The equilibrium pressure of $^{13}CO_2$ hydrate was about 0.01 MPa larger than that of normal CO_2 (mainly $^{12}CO_2$) hydrate, and it agreed with the previous results (Luzi *et al.*, 2011; Ozeki *et al.*, 2018).

References

Hachikubo A, Kosaka T, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H (2007) Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases. Geophys Res Lett 34: L21502. doi:10.1029/2007GL030557

Luzi M, Schicks JM, Erzinger J (2011) Carbon isotopic fractionation of synthetic methane and carbon dioxide hydrates. Proc. 7th International Conference on Gas Hydrates (ICGH2011).

Ozeki T, Kikuchi Y, Takeya S, Hachikubo A (2018) Phase equilibrium of isotopologue methane hydrates enclathrated CH_3D and CD_4. J Chem Eng Data 63(6): 2266-2270, doi: 0.1021/acs.jced.8b00203

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