

# Carbon isotope fractionation of CO<sub>2</sub> during the formation of clathrate hydrate

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Hydrogen Isotope fractionation in methane during the formation of clathrate hydrate was reported by Hachikubo *et al.* (2007) that  $\delta D$  of hydrate-bound methane is  $4.8 \pm 0.4\%$  lower than that of residual methane at 274.2K. Although natural methane hydrates distribute widely in the world, natural CO<sub>2</sub> hydrate was only reported at the Okinawa Trough (Sakai *et al.*, 1990). It is also possible that CO<sub>2</sub> hydrate exists in Mars. Isotopic fractionation of guest gas may provide useful information to understand formation processes of gas hydrate. Luzi *et al.* (2011) revealed that CO<sub>2</sub>  $\delta^{13}C$  in hydrate-bound gas is 0.9‰ lower than that of residual gas, suggesting that light CO<sub>2</sub> molecules prefer to be engaged into clathrate cages. In this study, we checked the temperature effect on the isotopic difference between residual and hydrate-bound CO<sub>2</sub>.

Samples of CO<sub>2</sub> hydrate (weight: 0.7 g) were experimentally prepared in a pressure cell (volume: 30 mL), and the temperature was controlled by a liquid bath (258-274 K) and cold rooms (226-254 K). Isotopic compositions of both residual and hydrate-bound CO<sub>2</sub> were measured by an isotope ratio mass spectrometer (IRMS). Samples were formed in the temperature range from 226 K to 274 K. The carbon isotopic differences between hydrate-bound and residual CO<sub>2</sub> distributed between 1.2‰ and 1.5‰, agreed fairly well with the previous report (Luzi *et al.*, 2011). The difference seemed to be large (1.5-2.0‰) at 226 K, indicating that the equilibrium pressure of <sup>13</sup>CO<sub>2</sub> hydrate is slightly larger than that of <sup>12</sup>CO<sub>2</sub> hydrate, and the difference between them becomes large in lower temperature. We will show these equilibrium data for <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> hydrates and compare with the results in stable isotope.

## Reference

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