

Carbon isotope fractionation of carbon monoxide hydrate between gas and hydrate phases

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It is possible that carbon monoxide hydrates exist in the icy bodies of outer planets of the solar system (Zhu *et al.*, 2014). Isotope signatures of carbon monoxide hydrates may provide useful information to understand formation processes of gas hydrate. Kimura *et al.* (2019) reported at the past JpGU conference that the carbon isotopic difference between hydrate-bound and residual gases distributed between 1.2‰ and 1.5‰ in the case of carbon dioxide hydrate, suggesting that the hydrate rather concentrates light molecules ($^{12}\text{CO}_2$). Besides, the equilibrium pressure of $^{13}\text{CO}_2$ hydrate is slightly higher than that of $^{12}\text{CO}_2$ hydrate (Kimura *et al.*, 2020) and agreed with the result of carbon isotopic fractionation. On the contrary, there is no information about carbon monoxide hydrate. In this study, we measured carbon isotopic difference between hydrate-bound and residual gases at the formation of carbon monoxide hydrate.

Samples of carbon monoxide hydrate were synthesized in a pressure cell (volume: 42 mL). Fine ice powder was put in a pressure cell and introduced the guest gas. The temperature was controlled by a liquid bath (253-273 K) and cold rooms (223-243 K) to form hydrate crystals from gas and ice powder. After their formation, isotopic compositions of both hydrate-bound and residual gases were measured by an isotope ratio mass spectrometer (CF-IRMS, DeltaV, Thermo Fisher Scientific).

The results of PXRD pattern showed that the crystallographic structure of carbon monoxide hydrate was the cubic structure I. The carbon isotopic differences between hydrate-bound and residual gas was $0.6 \pm 0.1\text{‰}$ at 223-273 K. In contrast to the result of carbon dioxide hydrate, the hydrate of carbon monoxide concentrated heavier molecules (^{13}CO), indicating that the equilibrium pressure of ^{13}CO hydrate is lower than ^{12}CO hydrate.

References

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