Variation of carbon isotopic composition with formation of clathrate hydrate

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In interstellar molecular clouds, various molecules such as H_2O, CO, CO_2, CH_3OH, H_2CO, and NH_3 are condensed onto dust grains. Water exists as amorphous ice on the dust grains and is transformed into various structures depending on thermal conditions and compositions of coexisting molecules. From the results using transmission electron microscopy and Fourier transformed infrared (IR) spectroscopy, it was found that the vapor deposited amorphous ice including CH_3OH and CO_2 is transformed into clathrate hydrate at around 120 K [1]. This suggests that the cometary ice exists as clathrate hydrate. Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guest molecules. From infrared astronomical observation, it was found that the $^{12}C/^{13}C$ isotopic ratio of comets is larger than that of interstellar matter [2]. To investigate the effect of clathrate hydrate formation on $^{12}C/^{13}C$ isotopic ratio, IR spectra of vapor deposited amorphous ice including $^{12}CO_2$ and $^{13}CO_2$ were measured. Using the spectra, the variation process of $^{12}CO_2/^{13}CO_2$ ratio during warming was analyzed.

Amorphous ice including $^{12}CO_2$ and $^{13}CO_2$ was prepared with vapor deposition of mixture of $^{12}CO_2$, $^{13}CO_2$ gases and distilled and degassed water on a substrate of oxygen-free copper at 43 K. In the gas mixture, the $^{12}C/^{13}C$ isotopic ratios were 4–92, and $(^{12}CO_2 + ^{13}CO_2)/ H_2O$ ratio was 1. The total pressure in the vacuum chamber was kept at about 5.0×10^{-5} Pa during the deposition. After the deposition of amorphous ice, the substrate was warmed to 180 K at a rate of 1–4 K/min. The IR spectra were measured using a spectrometer (Shimadzu IRPrestage-21) at 2 K intervals during warming. To analyze the sublimation behaviors, the temperature programed desorption (TPD) curves were also measured using quadrupole mass spectrometer (Pfeiffer QME220) during warming.

The results show that the wave number of the O–H stretching modes of H_2O, $^{12}C{=}O$ asymmetric stretching mode of $^{12}CO_2$, and $^{13}C{=}O$ asymmetric stretching modes of $^{13}CO_2$ during the warming significantly change at 100 ± 10 K. The wave number of newly appeared peak at this temperature was close to that of $^{12}C{=}O$ asymmetric stretching mode of $^{12}CO_2$ in clathrate hydrate. Furthermore, a gas release was also observed at this temperature from the TPD curves. These results indicates the formation of CO_2 clathrate hydrate at 100 ± 10 K. From the analyses of integrated intensities of $^{12}CO_2$ and $^{13}CO_2$ peaks, it was found that the $^{12}CO_2/^{13}CO_2$ ratio increases at around 100 K. These results suggest that the formation of clathrate hydrate from amorphous ice with warming can be a cause of ^{12}C condensation. Furthermore, it was found that the changing rate of $^{12}CO_2/^{13}CO_2$ with formation of clathrate hydrate depends on initial $^{12}C/^{13}C$ rate in amorphous ice. The present results have important implications for water states and their role in materials' evolution in the universe.

References

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