

Variation of carbon isotopic composition with formation of CO₂ clathrate hydrate

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In interstellar molecular clouds, various molecules such as H₂O, CO, CO₂, CH₃OH, H₂CO, and NH₃ 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 spectroscopy, it was found that the vapor deposited amorphous ice including CH₃OH and CO₂ 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 (IR) astronomical observation, it was found that the ¹²C/¹³C isotope ratio of comets is larger than that of interstellar matter [2]. To investigate the effect of clathrate hydrate formation on ¹²C/¹³C isotopic ratio, IR spectra of vapor deposited amorphous ice including ¹²CO₂ and ¹³CO₂ were measured. Using the spectra, the variation process of ¹²CO₂/¹³CO₂ ratio during warming was analyzed.

Amorphous ice including ¹²CO₂ and ¹³CO₂ was prepared with vapor deposition of mixture of ¹²CO₂, ¹³CO₂ gases and distilled and degassed water on a substrate of oxygen-free copper at 42 K. In the gas mixture, the ¹²C/¹³C isotopic ratio was 92, and (¹²CO₂ + ¹³CO₂)/H₂O was 1.4. The total pressure in the vacuum chamber was kept at about 3.5 × 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 programmed desorption (TPD) curves were also measured using quadrupole mass spectrometer (Pfeiffer QME220) during warming.

From the analyses of the wave numbers of the O–H stretching modes of H₂O, ¹²C=O asymmetric stretching mode of ¹²CO₂, and ¹³C=O asymmetric stretching modes of ¹³CO₂ during the warming, remarkable changes were found at around 100 K. From the TPD curve, furthermore, a remarkable gas release was observed at this temperature. Because of the closed wave number of the ¹²C=O asymmetric stretching mode at 100 K with that of CO₂ clathrate hydrate [3], the formation of CO₂ clathrate hydrate at 100 K was confirmed. It was found that the ¹²CO₂/¹³CO₂ 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 ¹²C condensation.

References

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