Nitrogen isotopic fractionation of ammonia accompanied with adsorption-desorption process on montmorillonite and saponite

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Solar system objects show wide variation in the nitrogen isotopic composition. The $\delta^{15}N$ value (‰, normalized as vs. Air) ranges from -400‰ in the solar wind [1] and Jovian atmosphere [2] to around +1500‰ of comets, chondrites, and interplanetary dust particles (IDPs)[3, 4]. These pristine solar system materials also show occasional extreme ^{15}N-enrichment up to +5000‰ [5, 6]. This $\delta^{15}N$ variation in the solar system objects is considered to have been inherited from the cold interstellar environments [7]. However, only a few models can explain the interstellar chemistry to enhance ^{15}N-enrichments, such as photodissociation of nitrogen molecules and subsequent formation of ammonia [8], and conceivable isotopic fractionation processes have not well understood.

In the study, we conducted simple adsorption-desorption experiments using ammonia gas and two clay minerals (montmorillonite and saponite). From the results, we propose the adsorption-desorption process of ammonia on grain surface of interstellar dusts as a potential mechanism for ^{15}N-enrichmentin interstellar environments. Ammonia is a simple nitrogen-containing molecule and one of major nitrogen carriers in the molecular clouds. It is a highly reactive chemical and regarded as a precursor for other complex nitrogen-containing molecules. Thus, adsorption of ammonia could be a first step for grain surface chemistry to form more complex organic molecules. The adsorption-desorption experiments were performed to examine the possibility of nitrogen isotopic fractionation of ammonia by adsorption and desorption on the clay minerals. Each clay mineral sample, with controlled amount of water (0, 5, 10, 20 wt.% vs. dry cry minerals), was sealed into the glass serum bottles with ammonia gas (+27‰, SI Science). The glass vial was rested for a week under room temperature (25℃) to reach a stable state before analysis. After the initial analysis was completed, the glass vial was vacuumed for 1 to 8 hours to examine the results under vacuumed environment. The nitrogen isotopic composition of the adsorbed ammonia at each step of the experiments was determined by nanoEA/IRMS technique [9].

The results showed that adsorbed ammonia generally had larger $\delta^{15}N$ value than the initial ammonia gas. The degree of isotopic fractionation from the initial ammonia were +2.4~+40.3‰ for montmorillonite and -1.6~44.4‰ for saponite as $\Delta^{15}N$ value. There was also a negative correlation observed between the adsorbed ratio (wt. %) and the $\delta^{15}N$ value. When the glass vial was vacuumed for only 1 hour, the $\delta^{15}N$ of the remaining ammonia increased (+64.1‰ for montmorillonite and +60.1‰ for saponite as $\Delta^{15}N$ value). However, when the glass vial was vacuumed more than 1 hour, selective removal of $^{15}NH_3$ was observed. The water content of the sample was not an influential factor throughout the experiments. The results suggest that adsorption and desorption of ammonia on clay minerals causes significant nitrogen isotopic fractionation ($\Delta^{15}N$=−1.6~+64.1‰) and could be a potential mechanism for ^{15}N-enrichment in interstellar environments.

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Keywords: nitrogen isotopic fractionation, adsorption, ammonia, molecular clouds, grain surface chemistry

