

## Space weathering in the interstellar medium by hydrogen ion irradiation

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Cosmic dust mainly forms around AGB stars and in ejecta of supernova explosions. Crystalline silicates are observed from some oxygen-rich AGB stars but almost absent in the interstellar medium (ISM). The low crystallinity of interstellar dust may be caused by amorphization of the crystalline silicate [1]. In this work, we focus on the irradiation of interstellar dust by accelerated ions by shock waves from supernovae. There are several irradiation experiments of dust analogue minerals such as olivine, enstatite, and diopside [1-4], but irradiation experiments with hydrogen ions, which is the most abundant gas species, are limited. Because structural and morphological changes may depend on irradiated gas species [5], we performed hydrogen ion irradiation experiments to constrain on the irradiation conditions to cause structural changes of ISM dust grains.

We used olivine (Fo<sub>80</sub>), enstatite, synthetic single crystal forsterite, serpentine ((Mg<sub>2.8</sub> Fe<sub>0.2</sub>)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), quenched glass with MgSiO<sub>3</sub> composition as substrates. Pyrrhotite (Fe<sub>0.9</sub>S) and iron meteorite were also used to observe the structural changes of FeS and metallic iron in IDP and primitive meteorites. Polished samples were cut into 3 x 5 x 0.5 mm sized pieces, and chemically etched to remove the surface deformation layers. Experiments were carried out in the Wakasa Wan Energy Research Center (WERC). We used H<sub>2</sub><sup>+</sup> ions accelerated to 40 keV and 10 keV. The dose for each energy was 10<sup>16</sup>-10<sup>18</sup> ions/cm<sup>2</sup> and 10<sup>17</sup> ions/cm<sup>2</sup>, respectively. Samples after irradiation were observed with a field-emission scanning electron microscope (FE-SEM).

All samples irradiated with 10 keV H<sub>2</sub><sup>+</sup> ions showed no the surface modification. The threshold dose for blister formation on Fe-rich olivine (Fo<sub>70</sub>) by 10 keV H<sub>2</sub><sup>+</sup> ion irradiation was 10<sup>17</sup> ions/cm<sup>2</sup> [4], in which condition we did not confirm any blister on relatively iron-poor olivine (Fo<sub>90</sub>). These results indicate that olivine with higher iron content easily occurs amorphization by the ion irradiation.

Elliptical shaped blisters were observed on the surfaces of olivine, enstatite, forsterite, serpentine, and pyrrhotite irradiated with 40 keV H<sub>2</sub><sup>+</sup> ions. The dose amount for blistering on olivine, enstatite, serpentine, and pyrrhotite was 10<sup>18</sup> ions/cm<sup>2</sup> and on forsterite was 10<sup>17</sup> ions/cm<sup>2</sup>. The blister sizes on forsterite were about 100 nm, on olivine and pyrrhotite were about 3 μm, and on serpentine were about 4-5 μm, respectively. Wavy shaped blisters were observed on enstatite, which were arranged at intervals of a few μm. No structural changes of the surfaces was observed on the iron meteorite and MgSiO<sub>3</sub> glass substrates. The dose amount for blistering on enstatite is an order of magnitude higher than that for amorphization [2]. We observed blisters on pyrrhotite, which is inconsistent with irradiation experiments of 1 MeV Kr<sup>+</sup> [6]. Ion mass and size may cause these differences, or the dose amount for blistering and amorphization may not be identical. We plan to observe the interior structures of the irradiated samples with a transmission electron microscope. In this presentation, we will report the results of SEM and TEM observations and discuss the structural changes due to ion irradiation.

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Keywords: Space weathering, Dust, Irradiation experiment, ISM

## Development of experimental setups for condensation experiments of enstatite and evaporation experiments of SiO<sub>2</sub>-MgO

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Enstatite whiskers elongated to the [001] axis were identified in chondritic porous interplanetary dust particles (CP-IDPs), Antarctica Micrometeorite (AMM), and samples from a comet Wild 2, while those elongated to the [100] axis are common in minerals occurred in the Earth and meteorites [1-4]. The condensation conditions of enstatite whiskers, however, have not been shown quantitatively. Moreover, the difference in the morphology of enstatite whiskers may reflect their different condensation conditions in the early solar system. In order to constrain on the formation conditions of enstatite whiskers with different crystal habits, we aim to construct the experimental setup that can control the condensation temperature, supersaturation ratio, and partial pressure of a hydrogen gas. In this presentation, we report the current status of our experimental setups and preliminary results of SiO<sub>2</sub>-MgO evaporation experiments.

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Keywords: experiment, condensation, evaporation, enstatite

## AKARI observations of asteroidal dust

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The zodiacal emission is the thermal emission from the interplanetary dust and the dominant diffuse radiation in the mid- to far-infrared wavelength region. From the results of the Infrared Astronomical Satellite (IRAS) observations, it was found that there are many small-scale structures in the zodiacal emission distribution, such as dust band pairs at the ecliptic latitudes of  $\pm 1.4$  and  $\pm 2.1$  degrees (the inner band) and  $\pm 9.3$  degrees (the outer band). It is suggested that recent disruption events among multikilometer bodies in the main asteroid belt within the last several million years are major supply sources of the dust particles in the dust bands, and they produce an edge-brightened toroidal distribution of dust. We conducted observations of the asteroidal dust bands with the Japanese infrared satellite AKARI in the mid- and far-infrared wavelength region. AKARI clearly detects the zodiacal dust-band structures. We derived the heliocentric distances of dust bands from the AKARI observations: 1.9 AU and 2.2 AU from the Sun for the inner and the outer bands, respectively. Based on the AKARI spectroscopic observations in the mid-infrared, the dust particles in the outer band show a slightly different spectral shape of the silicate feature from those of other regions which are thought to be cometary origins. It is highly probable that we obtain the mid-infrared spectra of micron-sized asteroidal dust grains for the outer band regions. We will discuss the size distribution and silicate composition for the dust grains in the outer bands.

Keywords: zodiacal light, silicate, asteroids

## Analyses of surface structure of amorphous ice using infrared spectroscopy

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In interstellar molecular clouds, water molecules deposit on dust grains, and forms amorphous ice. The amorphous ice includes various molecules such as CO, CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>CO, and so on. These molecules undergo chemical evolutions to organic molecules through various processes. Because the deposited amorphous ice has a large surface area due to its uneven structure, the surface of amorphous ice has an important role for chemical evolutions of included molecules in molecular clouds [1].

Structure of amorphous ice depends on formation condition [2], and has been mainly classified by density into two types: low-density amorphous (LDA) and high-density amorphous (HDA) ice. The densities of the LDA and HDA ice are  $0.94 \pm 0.03$  and  $1.1 \pm 0.1$  g cm<sup>-3</sup>, respectively. Although there are various studies for structures and properties of amorphous ice in bulk states, only a few studies have been reported for surface. In the present study, the surface structure of amorphous ice was analyzed by measurements of infrared (IR) spectra for thin film of vapor-deposited amorphous ice.

Amorphous ice was prepared with vapor deposition of distilled and degassed water on a substrate of oxygen-free copper at 43 K. The deposition rate was controlled to be a value in range of 0.02-0.61 nm/min. The inner pressure of the vacuum chamber during the deposition was about  $5.0 \times 10^{-5}$  Pa. The IR spectra were measured using Shimadzu IRPrestage-21.

The spectral features change with deposition. According to the assignments of IR spectra for amorphous ice [3], the O-H stretching vibration band observed in 2800-4000 cm<sup>-1</sup> was decomposed into three vibration modes (i.e., in-phase and out-of-phase modes of symmetric stretching, and asymmetric stretching mode). From the variations of the wave number of the out-of-phase mode, the variations in water structure of amorphous ice were analyzed.

The result shows that the wave number of the out-of-phase mode increases as the thickness of the amorphous ice increases, and gradually approaches a constant value of 3480 cm<sup>-1</sup>. From the observed variations, the thickness of the surface layer is estimated to be around 20 nm. Furthermore, the wave numbers of the surface layer and bulk state are estimated to be 3420 and 3480 cm<sup>-1</sup>, respectively. Because these values are close to those for HDA and LDA ice [4], the internal part of the sample is confirmed to be HDA ice. For the surface layer, the density is smaller than that of the internal part. Therefore, it is supposed that the structure is a close representation of LDA ice. Furthermore, it was found that the surface structure of the amorphous ice depends on deposition rate. From the results, we discuss the structure and dynamics of amorphous ice surface.

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## Effects of Density on Surface Structure of Amorphous Ice

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In interstellar molecular clouds, various molecules (for instance, H<sub>2</sub>O, NH<sub>3</sub>, CO, CO<sub>2</sub>, and so on) are formed from elements such as H, C, O, and N by deposition on dust grains [1]. Most of H<sub>2</sub>O exists as a thin shell of amorphous ice around dust grain. The deposited molecules undergo chemical evolutions to organic molecule through various processes [2]. The structure of amorphous ice surface is an important factor to understand the molecular evolution in molecular clouds. Amorphous ice is formed by vapor deposition of H<sub>2</sub>O gases [3] or compression of crystalline ice [4]. The structure of amorphous ice depends on formation processes and is classified into two types: high-density amorphous (HDA) and low-density amorphous (LDA) ices [4]. To investigate the effects of internal structure on surface structure, the molecular dynamics (MD) calculations of amorphous ice were performed.

The KAWAMURA potential model [5] was used for the MD calculations. The amorphous ice was prepared by quenching a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K. The density of amorphous was controlled with the time period of the annealing at 235 K. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 5 Å in thickness from the outmost atom was analyzed as the surface layer.

The calculations show that the density of amorphous ice at 10 K depends on the temperature history before the cooling to 10 K. In the case that the time period of annealing at 235 K was 1400 ps, for instance, the formed amorphous has the minimum density of 0.962 g/cm<sup>3</sup> at 10 K. For the case that the system was directly quenched from 300 to 10K without annealing at 235 K, the density reaches its maximum value of 1.095 g/cm<sup>3</sup>. Because a significant change of density was observed at 235 K, we controlled the density of internal part of amorphous ice with time period of the annealing at 235 K.

The result shows that the density of the surface layer is smaller than that of the internal part, and increases as the density of the internal part increases. The decrease in molecular density observed in the surface layer is attributed to the uneven structure and large amplitude of the thermal vibrations of water molecules. To investigate the contribution of the uneven structure, the radial distribution function (RDF) was calculated. The position of the second peak, which is observed at around 4.1 Å, of surface layer is about 0.3 Å large than that of internal part. This suggests that the surface layer has a lower density even if there is no unevenness. The amplitude of the thermal vibration is measured by the atomic displacement parameter (ADP). The calculation indicates that ADP of surface layer is larger than that of internal part, and depends on internal density. This result is consistent with the calculation of RDF. In the RDF result the broadening of peaks was observed for surface layer. It is concluded that the structure of surface layer is affected by density of internal part. This effect of internal structure on surface structure of amorphous ice might have important implications for molecular evolution in molecular clouds.

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## Formation of Carbon-Dioxide Clathrate Hydrates including Help Gases under Vacuum Conditions

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In interstellar molecular clouds, water molecules condense on dust grains. The condensed water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions of including molecules. Blake et al. [1] proposed the presence of clathrate hydrates in cometary ice. From the results using transmission electron microscopy and Fourier transformed infrared spectroscopy, they showed the phase transition of vapor deposited amorphous ice including CH<sub>3</sub>OH and CO<sub>2</sub> into type-II hydrate at around 120 K.

Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guest molecules. Most hydrates form one of two distinct crystallographic structures, type-I and -II, depending on the sizes and shapes of the guest molecules. The structure of CO<sub>2</sub> hydrate formed under a high-pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice by Blake et al. [1], the structure was type-II due to the help-gases effect of CH<sub>3</sub>OH. For the CO<sub>2</sub> hydrate grown epitaxially on a hydrate under vacuum condition, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of CO<sub>2</sub> hydrate including help-gases under vacuum conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O during warming.

The CO<sub>2</sub>/H<sub>2</sub>O ratios of the prepared gas mixtures were 0.13-16.8. The gas mixtures were deposited onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K. Infrared spectra were measured at approximately 1 min intervals during deposition at 43 K and at 2 K intervals during warming. Furthermore, CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O mixed hydrates were prepared from gas mixtures of H<sub>2</sub>O, CO<sub>2</sub>, and C<sub>3</sub>H<sub>6</sub>O with various compositions, and were measured spectra with the same procedures.

From the variation in spectral features of H<sub>2</sub>O-CO<sub>2</sub> ice with warming, remarkable changes were found at 82 K. The wave numbers of the O-H stretching modes of H<sub>2</sub>O and the C-O asymmetric stretching modes of CO<sub>2</sub> change significantly at this temperature. Furthermore, significant gas release and exothermic temperature rise were observed. These results suggest that the crystallization of amorphous ice begins at 82 K. From the wave numbers of C-O asymmetric stretching modes, the formed crystal is determined to be type-I hydrate. From the formation conditions of CO<sub>2</sub> hydrate, we propose the phase diagram of the H<sub>2</sub>O-CO<sub>2</sub> system under vacuum conditions. In addition, the formation processes of mixed hydrate including CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>O were analyzed. The result shows that the transition temperature of the mixed hydrate depends on the guest composition. From the results, we discuss the formation mechanisms of clathrate hydrates under vacuum conditions.

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## 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  $\delta^{15}\text{N}$  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  $^{15}\text{N}$ -enrichment up to +5000‰ [5, 6]. This  $\delta^{15}\text{N}$  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  $^{15}\text{N}$ -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  $^{15}\text{N}$ -enrichment in 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 clay 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°C) 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  $\delta^{15}\text{N}$  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  $\Delta^{15}\text{N}$  value. There was also a negative correlation observed between the adsorbed ratio (wt. %) and the  $\delta^{15}\text{N}$  value. When the glass vial was vacuumed for only 1 hour, the  $\delta^{15}\text{N}$  of the remaining ammonia increased (+64.1‰ for montmorillonite and +60.1‰ for saponite as  $\Delta^{15}\text{N}$  value). However, when the glass vial was vacuumed more than 1 hour, selective removal of  $^{15}\text{NH}_3$  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 ( $\Delta^{15}\text{N}=-1.6\sim+64.1\%$ ) and could be a potential mechanism for  $^{15}\text{N}$ -enrichment in interstellar environments.

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



## Amino acid analysis of photochemically processed interstellar ice analogues

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Amino acids are one of major constituent of living organisms on the Earth, so they are essential molecules for the origins of life. Many scenarios for the endogenous production of amino acids on the early Earth have been proposed [e.g., 1, 2]. On the one hand, the extraterrestrial delivery of them is also considered as a likely candidate [e.g., 3, 4]. Carbonaceous chondrites are known to contain abundant amino acids up to 250 ppm [5] and more than 80 species were identified [6]. In addition, the simplest amino acid: glycine was also detected in the cometary grains returned by stardust mission [7]. The extraterrestrial amino acids are considered to have been formed by aqueous alteration on the meteoritic parent bodies or in the presolar interstellar environments. Although, the formation process, as well as the place to be taken, is still on a debate, the existence of amino acid in comets as well as the isotopic signatures of them suggest that at least some amino acids and the precursors of them are interstellar origin [8].

In the study, we conducted laboratory experiments to synthesize interstellar ice analogues from typical interstellar gases and analyzed their amino acid composition. For the experiments that simulate the condition in the interstellar medium (ISM), we utilized an apparatus called PICACHU: Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University. In this PICACHU apparatus, the typical ISM gases ( $H_2O: CH_3OH: NH_3 = 2:1:1$ ) were introduced into the chamber and deposited onto the surface of a sappier glass there, which were refrigerated at  $\sim 12$  K. During the deposition of the ice, UV photons were continuously irradiated under highly vacuumed condition for 71 hours, because photochemical reactions in the ice, which were processed by stellar ultraviolet (UV) photons and cosmic rays, are important for the formation of complex organic molecules in ISM. In addition, we made two ice samples and one of them was further irradiated by UV for 232.5 hours after heated to room temperature in order to simulate subsequent decomposition in warmer environments. Then, the organic residues of the two ice samples were extracted by methanol and analyzed by GC-MS and GC/NPD after the derivatization for GC analysis.

The results showed that 11 species of amino acids were formed in the interstellar ice analogues, which were irradiated only at  $\sim 12$  K. The most abundant amino acid was glycine and the second most abundant one were  $\beta$ -alanine and alanine. Their abundances are about fourth of that of glycine. The abundance of each amino acid generally decreased with the increase of the carbon number of the amino acids. This trend was consistent with the previous study [9]. Then, the further irradiated sample showed the general decrease in the abundances of amino acids, but some of them were still remained. The survived ratio differed among amino acids and glycine was the most resistant to the irradiation ( $\sim 80\%$  remained.). These results indicate that amino acids can be formed by the UV irradiation to the interstellar ice and can survive subsequent irradiation in the warmer environments.

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