

## Astromineralogy from dust formation experiments, analysis of presolar grains, and infrared spectroscopy

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In these twenty years, space and ground based infrared spectroscopic observations have revealed the common presence of circumstellar and interstellar dust grains such as silicates, oxides, carbides, ice, and organics. Presolar grains are rare components of primitive meteorites identified on the basis of their highly anomalous isotopic compositions. They have formed around evolved stars as circumstellar dust grains and have survived the processing in the interstellar medium and the protosolar disk before their incorporation into the meteoritic parent bodies.

It is, however, difficult to directly compare presolar grains with circumstellar dust emissions because (1) infrared (IR) dust emission reflect an enormous number of dust grains with various composition, size, shape, crystallinity, and aggregation degree, (2) dust properties are poorly constrained due to lack of laboratory studies on dust formation processes, and (3) there are limited mineralogical and crystallographical studies on presolar silicates and oxides. The grain morphology and crystal structure of circumstellar dust may reflect condensation conditions in circumstellar envelopes of asymptotic giant branch (AGB) stars and that of presolar grains additionally reflect processing in the interstellar medium (ISM) and protosolar disk. Corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) is predicted to be the most abundant refractory dust species condensed in envelopes around oxygen-rich AGB stars. In this talk, we summarize our recent results of corundum condensation and evaporation experiments, calculation of the IR spectrum of condensed corundum around AGB stars, and analysis presolar alumina grains in order to link the mineralogical and astronomical investigations on circumstellar dust formation and evolution.

Evaporation experiments of single crystals of corundum in vacuum at 160-1785 deg C and condensation experiments at 1575 deg C and a supersaturation ratio of around 4 were performed to obtain anisotropic evaporation and condensation coefficients of corundum. The IR spectra of anisotropically condensed corundum grains were calculated assuming the ellipsoidal shapes. Presolar alumina grains were identified from acid residues of unequilibrated ordinary chondrites (QUE97008 LL3.05, RC075 H3.1, and Bishunpur LL3.15) by oxygen isotopic measurements. The focused-ion-beam sections of the presolar grains were prepared and observed with a transmission electron microscopes.

Evaporation coefficients of corundum are 0.02-0.2 at 1600-1785 deg C, which increase with temperature. The evaporation coefficient along the crystallographic m-axis is largest and that along the c-axis smallest irrespective of temperature. The obtained condensation coefficients along the c-, a-, and m-axes at 1575 deg C and a supersaturation ratio of about 4 are 0.04-0.06, 0.06-0.08, and 0.1-0.2, respectively. Eighteen presolar alumina grains were identified and the average size was 1  $\mu\text{m}$ , and neither whiskers nor extremely flat grains were observed. All presolar alumina grains are corundum but some of them have distorted crystal structures. Fifteen grains have irregular shapes covered with rough surfaces. The distorted crystal structures and rough surface structures may indicate that these grains have experienced the cosmic ray irradiation in the interstellar medium or solar wind irradiation in the early solar system.

The condensed corundum is most likely to be oblate slightly flattened to the c-axis, consistent with the fact that no presolar corundum with eccentric shapes has been found. The mass absorption coefficient of oblate corundum slightly flattened to the c-axis shows a peak at 13  $\mu\text{m}$  without any accompanying strong peaks, which correspond to the unidentified 13- $\mu\text{m}$  feature of around O-rich evolved stars. These results strongly indicate that corundum condensed anisotropically in circumstellar environments and have experienced space weathering prior to their incorporation into the meteoritic parent bodies.

Keywords: circumstellar dust, presolar grain, experiment, corundum, infrared spectroscopy, astromineral

## Ion-induced nucleation experiment III: Approach to reaction kinetics

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Mechanisms of grain nucleation have attracted many researchers in connection with the formation of atmospheric aerosols and cosmic dust grains. Many works have been performed assuming homogeneous nucleation in gas phase or heterogeneous nucleation on the bulk surfaces. For the homogeneous nucleation, very high supersaturation condition is often required to gain the efficient formation rate over a "critical size" of particle, while the heterogeneous nucleation on the bulk surface may not be relevant to the first stage of grain formation in realistic environments. It is therefore reasonable to propose another nucleation mechanism occurring in the realistic environments. Ion-induced heterogeneous nucleation would be one of important mechanisms for the gas phase nucleation, because ion-neutral interaction can overcome the difficulty of the critical size expected in neutral-gas-phase homogeneous nucleation. In this context, we have started a series of experiments to clarify the early stage of the ion-induced nucleation, that is, cluster ion formation. For the first step, using a newly-developed apparatus, we measured the free energies of water-cluster ions at each size, of which parameters are closely related to the cluster formation rates. These results were presented in this session last year. As a next step, in order to directly investigate the reaction kinetics of cluster ions, we further developed an ion trap apparatus where charged particle can be stored within the volume of  $\sim 0.5\text{cm}^3$  in vacuum for a long time. We will present the details of apparatus and the results of preliminary experiment.

Keywords: ion-induced nucleation, cluster ion, ion trap

## An experimental study on the effect of water vapor on crystallization of amorphous forsterite

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Infrared spectroscopic observations (e. g. ISO and Spitzer Infrared Telescope) have provided the evidence of existence of crystalline silicate dusts in comets and protoplanetary disks (Henning, 2010 and references therein). Wagstaff and Richards (1966) suggested that water vapor enhances the crystallization rate of SiO<sub>2</sub> glass by breaking [Si-O-Si] bonds and forming hydroxyl groups. Thus, if amorphous silicate dust is exposed to relatively water vapor-rich environments such as the post shock region of shock wave (Ciesla et al., 2003) and impact plumes generated by asteroid impacts (Fedkin & Grossman, 2013), amorphous silicates may crystallize more effectively with the aid of water.

In this study, in order to investigate the effect of water vapor on the crystallization kinetics of amorphous forsterite, crystallization experiments were conducted in vacuum condition ( $\sim 10^{-4}$  Pa) using a gold-image vacuum furnace (Thermo-Riko GFA430VN) at 500, 680, 730, 750 °C, and in sealed glass tubes, in which water vapor pressure is kept at 0.65 bar by a Ca(OH)<sub>2</sub> – CaO buffer system, at 500 °C in a box furnace. Amorphous forsterite powder, synthesized by a thermal plasma method, was provided by A. Tsuchiyama, Kyoto University. Temperature of both furnaces was calibrated against the melting points of NaCl, KBr, LiBr and In. Run products were analyzed with FT-IR (KBr pellet method). Quantitative analysis of the degree of crystallization was made with the spectral fitting of run products in the 10 μm band, where the structural evolution of amorphous forsterite can be observed as a change of Si-O stretching features.

The time-dependence of crystallization in vacuum was estimated by the Johnson-Mehl-Avrami equation for each temperature, and the Arrhenius plot of the time constant of crystallization,  $\tau$ , showed a linear correlation with the reciprocal temperature. The obtained value of  $E_a/k_B$  was  $4.94 \times 10^4$  K, where  $E_a$  is activation energy for crystallization and  $k_B$  is the Boltzmann constant. Kinetic parameter  $n$  in the Johnson-Mehl-Avrami equation obtained at 680, 730, 750 °C in vacuum were  $\sim 1.5$ . Assuming that the crystallization mechanism in vacuum does not change at lower temperatures, we can estimate the timescale of crystallization at 500 °C in vacuum, which is about 430 years for the crystallization degree of 26 %. On the contrary, experiments at  $P_{H_2O}=0.65$  bar showed that the degree of crystallization reached about 26 % only for 12 hours. It was also experimentally confirmed that amorphous forsterite remained unchanged by heating at 500 °C in vacuum for 72 hours. This clearly indicates that the crystallization of amorphous forsterite is promoted in the presence of water vapor. Kohara et al. (2004) reported the structure of Mg<sub>2</sub>SiO<sub>4</sub>-composition glass synthesized by a containerless liquid phase processing technique, and MgO<sub>X</sub> units act as a network former and SiO<sub>4</sub> units form polymer and dimer. We proposed that water molecules diffuse into the amorphous structure to break Si-O-Si bonds and MgO bonds by acting as a network modifier and promote the crystallization of amorphous forsterite.

Experiments at lower water vapor pressure conditions are needed for a direct application to the crystallization of amorphous silicates in canonical protoplanetary disks, but the present results imply that the crystallization of amorphous silicates might take place more effectively in the water-enriched regions compared with canonical solar nebula condition.

Keywords: amorphous silicate, forsterite, crystallization, water vapor, protoplanetary disk

## Small-scale structure of the zodiacal dust cloud observed in mid- and far-infrared with AKARI

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The zodiacal light emission (ZE) is the thermal emission from the interplanetary dust and the dominant diffuse radiation in the mid- to far-infrared wavelength region. The zodiacal dust cloud has a relatively smooth distribution. However, from the results of the Infrared Astronomy Satellite (IRAS) observations, it was found that there are many small-scale structures in the ZE distribution, such as asteroidal dust bands and a circumsolar resonance ring.

The Japanese infrared satellite AKARI, a dedicated satellite for infrared astronomical observations, is the mission to survey the whole sky in the mid- and far-infrared. AKARI detected the small-scale structure of the zodiacal cloud, such as the asteroidal dust bands and the circumsolar ring. There are three major bands ( $\pm 1.4$  degree,  $\pm 2.1$  degree, and  $\pm 9.3$  degree) among dust bands that form small-scale latitude features in the ZE. These three prominent asteroidal dust bands can be clearly seen in the AKARI far-infrared all-sky maps at 65 and 90 micron bands.

We also present spectra of the zodiacal light observed in mid-infrared wavelength region with Infrared Camera (IRC) onboard AKARI. The IRC spectra (5.5–12.5 micron) show a trapezoidal excess emission feature in 9–11 micron region which can be reasonably accounted for by a combination of amorphous and/or crystalline silicate. Although this excess feature is rather smooth and lacking sharp peaks, a possible 10.5 micron peak and small peaks around 9.3 and 11.35 micron can be seen at the shoulder of the trapezoidal excess. The spectrum around  $\beta=10$  degree toward the asteroidal dust band seems to have a slight different shape of the silicate feature from those of other regions.

Keywords: zodiacal light, interplanetary dust, AKARI, infrared

## Evolution of organic molecules in space: characteristics and properties of experimental organic residues.

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In the interstellar medium (ISM), dense clouds and circumstellar regions around young stars are favorable environments for the accretion of ice mantles around dust grains and their irradiation by energetic particles (UV-photons and cosmic rays). The partial collapse of dense cloud gives birth to stars generally surrounded by disks of dust and gas which can lead to planetary systems.

Organic-rich mantled dust is thus among the potential building blocks of our solar system and could be at the origin of a part of the organic matter found in comets and meteorites. However, it is not clear how the organic components formed in the ISM may have evolved before being incorporated in their parent bodies.

A new laboratory experimental apparatus PICACHU (Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University) was recently developed to simulate the formation and evolution of organic ice mantles. This apparatus is focused on organic compound evolution through UV irradiation and heating. Typical ISM gases (H<sub>2</sub>O, CO, NH<sub>3</sub>, CH<sub>3</sub>OH) are deposited onto the three faces of a refrigerated substrate (about 12K) and simultaneously irradiated by UV under ultra-high vacuum. The gases, desorbed from the ice during heating and post-irradiation, are monitored by a quadrupole mass spectrometer in the vacuum chamber. The final organic residues obtained after warm-up and/or post-irradiation are then characterized.

Here we report the first descriptions of the organic residues produced by the experiments. At the micron scale, the thin deposits are not homogenous showing desiccation-like networks. From atomic force microscope observation, it seems that the main deposits are made of the aggregation of round particles of some tens of nanometers. Porous membrane-like textures are also observed for post-irradiated sample. Transmission electron microscopy confirms the presence of round organic particles and shows their amorphous nature. These particles could resemble to the organic nanoglobules commonly found in the organic matter of carbonaceous chondrites, which contain isotopic anomalies and a dusty core [2, 3, 4]. Moreover, the porous nature of organic aggregates may enhance the efficiency of dust aggregation in the early solar system [5, 6].

[1] Herbst E. and van Dishoeck E. F. 2009. *Annu. Rev. Astron. Astrophys.* 47:427-480. [2] Garvie L. A. J. and Buseck P. R. 2004. *EPSL* 224:431-439. [3] Nakamura-Messenger et al. *Science* 314:1439-1442. [4] Hashiguchi M. et al. 2013. *GCA* 122:306-323. [5] Kouchi A. et al. 2002. *Astrophys. J.* 566:121-124. [6] Kudo T. et al. 2002. *Met. Plan. Sci.* 37:1975-1983.

Keywords: organic synthesis, low temperature experiment, UV irradiation, thermal evolution, Interstellar medium, meteorite & comet

## A LC/MS analysis of organic matter produced in the laboratory simulating interstellar molecular clouds

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Chemical and isotopic compositions of organics in astrophysical environments are important information not only to understand their origins and evolution, but one of key topics to discuss the origin and evolution of the solar system. This study focuses on the early step of the chemical evolution in interstellar molecular clouds, from primitive gaseous molecules to ice with organics, which is thought to be one of the precursors of extraterrestrial organic matter in the solar system.

Photochemical synthesis experiments were conducted using a high vacuum chamber "Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University" (PICACHU). In the chamber, a gold substrate (30 x 40mm) was set and cooled down to about 15K. Gaseous mixtures, prepared in a dedicated line, were admitted onto the surface of the substrate where they condensed forming ice samples. During the deposition the ice on the substrate was simultaneously irradiated UV light emitted from a deuterium lamp. After the photochemical process, the ice sample was warmed-up to room temperature, leading to form refractory organic residue that remained on the surface of the substrate. Then the substrate was stored in a sealed sample container under atmospheric air.

Each sample residue on the substrate was extracted with about 50 $\mu$ L of CH<sub>3</sub>OH (LC grade reagent) to analyze the contained organics by liquid chromatography coupled to mass spectrometry (LC/MS), using "Ultimate 3000" LC and "Q Exactive" MS (Thermo Fisher Scientific). 1 to 10 $\mu$ L of sample solution was injected to electrospray ionization (ESI) source. Both positive and negative mass spectra were acquired in the range of m/z 80 to 800 with its resolution (M/ $\Delta$ M) is 140,000 at m/z 200. The mass accuracy is generally less than ~0.001Da (1mDa) for positive ion.

This paper reports the results of 3 samples; A(H<sub>2</sub>O : CH<sub>3</sub>OH : NH<sub>3</sub> = 2 : 1 : 1, UV 71hours), B(H<sub>2</sub>O : CH<sub>3</sub>OH : NH<sub>3</sub> = 10 : 1 : 1, UV 165hours), and C(H<sub>2</sub>O : CO : CH<sub>3</sub>OH : NH<sub>3</sub> = 10 : 2 : 1 : 1, UV 240hours). All samples contained more than 1000 ion masses in the range of m/z 80 to 800. Major 1000 peaks were extracted using "Xcalibur" software (Thermo Fisher Scientific) for further data processing. The procedural background was calibrated using the mass spectra of CH<sub>3</sub>OH extracted from the blank surface of the other gold substrate which are not exposed to both gases and UV, but kept about 15K for 3days in PICACHU. 700 to 900 ion peaks less than m/z 700 were distinguished. About 70 to 80% of the mass spectra can be grouped in various series of alkyl homologues consisting of CHN, CHNO and CHO. The alkyl homologues are discrete with the interval of 14.0156Da that infers methylene chains (-CH<sub>2</sub>-)<sub>n</sub>. Various alkyl homologues were also reported in the literature, e.g. Danger *et al.* (2013).

The stoichiometric composition was estimated for each ion peaks by Xcalibur, and most of them have less than C<sub>30</sub>. More than a half of estimated C contained formulae also have both O and N. On the other hand, those without hetero elements (O and N) were minor. The distribution of m/z values of the mass spectra and their corresponding stoichiometric formula were different for each sample. That is due to both the composition of gaseous mixture, especially the existence of CO, and the duration time of UV irradiation.

### Reference:

Danger *et al.* (2013) *GCA* **118**, 184.

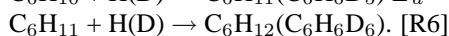
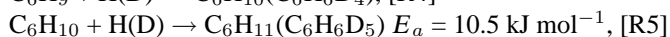
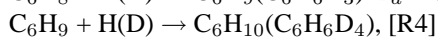
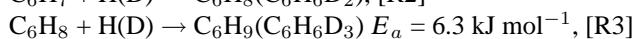
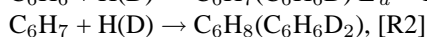
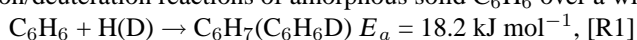
Keywords: Inter stellar organic analogs, Chemical evolution, LC/MS

## Hydrogenation and deuteration of solid aromatic hydrocarbon by quantum tunneling

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Surface tunneling reactions on interstellar dust (e.g., CO + H or D) are crucial to explain the abundances of organic molecules like methanol and their deuterated isotopologues observed in cold dense interstellar regions ( $\leq 100$  K), such as molecular clouds, where thermally activated reactions rarely occur at low temperatures. Aromatic and aliphatic hydrocarbons are two of the main components of interstellar and circumstellar dust, and benzene (C<sub>6</sub>H<sub>6</sub>) must be a precursor of interstellar polycyclic aromatic hydrocarbons (PAHs) and hydrogenated amorphous carbon grains. The present study investigates the following hydrogenation/deuteration reactions of amorphous solid C<sub>6</sub>H<sub>6</sub> over a wide temperature range (10-50 K).



$E_a$  is the activation barrier for H-atom addition in the gas phase. The radical recombination reactions R2, R4, and R6 are barrierless on the surface. We experimentally demonstrate that cold H and D atoms can efficiently add to solid benzene by tunneling at temperatures as low as 10-50 K. The present study is the first report on a nonenergetic deuteration process of aromatic hydrocarbons at low temperatures. In comparison to C<sub>6</sub>H<sub>6</sub>, PAHs tend to have lower activation barriers to H or D addition owing to the higher flexibility. Therefore, we suggest that interstellar aromatic hydrocarbons including PAHs and C<sub>6</sub>H<sub>6</sub> can be hydrogenated or deuterated by the tunneling of H or D atoms at low temperatures. The deuteration of interstellar aromatic hydrocarbons is of particular important, because these molecules represent a major carrier of deuterium enrichment observed in carbonaceous meteorites and interplanetary dust particles. As the gaseous atomic D/H ratio in molecular clouds can be also strongly enhanced for elemental ratios of  $1.5 \times 10^{-5}$  to  $10^{-2}$ - $10^{-1}$ , our results suggest that tunneling might represent a major deuteration mechanism for interstellar aromatic hydrocarbons, because surface tunneling is especially facilitated in the cold dense interstellar environments.

Keywords: Aromatic hydrocarbons, hydrogenation, deuterium enrichment, quantum tunneling, molecular clouds

## Laboratory Spectroscopy of Phenoxy Radical as a Candidate of Interstellar Matter

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The electronic transition of the phenoxy radical  $C_6H_5O$  produced in a discharge of anisole was measured by using a cavity ringdown (CRD) spectrometer.

Diffuse Interstellar Bands (DIBs) are optical absorption lines observed in diffuse clouds in interstellar space. They still remain the longest standing unsolved problem in spectroscopy and astrochemistry, although several hundreds of DIBs have been already detected. It is expected that identifications of DIBs can give us crucial information for extraterrestrial organic molecules. One of the best approaches to identify carrier molecules of DIBs is measurements of DIB candidate molecules produced in the laboratory to compare their absorption spectra with astronomically observed DIB spectra.

Aromatic radicals in a gas phase are potential DIB candidate molecules. The electronic transitions of aromatic radicals result in optical absorption. However, because the radicals are unstable, their electronic transitions are difficult to observe using a laboratory spectrometer system. To solve this difficulty, we have utilized a glow-discharge cell using a hollow cathode in which the radicals can be effectively produced as a high-density plasma.

The radicals produced in a discharge of anisole were measured by using CRD spectrometer, which is an apparatus to observe an high-resolution optical absorption spectrum. The bands observed in the 570 — 630 nm region in the discharge were assigned to the electronic transition of the phenoxy radical  $C_6H_5O$  on the basis of the reported low resolution spectra. Comparison studies of the phenoxy radical were made with known DIB spectra.

Keywords: Diffuse Interstellar Bands, interstellar molecule, cavity ring down, spectroscopy, molecular cloud, discharge



## Quantum chemical calculations of glycine formation in the interstellar medium

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Amino acids in the primitive earth may have been originated in the interstellar medium (ISM). Many amino acids and their precursors were found in the meteorites and were detected in laboratory experiments of UV irradiation on interstellar ice analogs. Moreover, various organic molecules were detected in molecular clouds; recently the detection of amino acid has been expected, especially by ALMA

In this study, we would like to make clear the mechanism of the simplest amino acid, glycine formation in the ISM using accurate quantum chemical calculation (density functional theory; DFT). Glycine formation pathway via hydantoin, which is glycine precursor detected in Murchison meteorite, were investigated. At first, the reactions in the gas-phase were examined. As a result, it was unlikely that glycine was formed during the lifetime of molecular clouds. However, there is a possibility that the reactions proceed with catalysis or the outside energies such as UV and heat.

Organic molecules in the ISM are considered to be generated on icy interstellar dust grains. In a previous study, the reaction barriers in aminoacetonitrile precursor formation pathway become lower with water molecules than those in the gas-phase, since water molecules on the ice core can play crucially a proton-transfer role, facilitating the basic transformations in the glycine formation pathways, [1]. We investigate the hydantoin and glycine formation pathway with one water molecule as a simplest model of ice.

[1] D. M. Koch, et.al. J. Phys. Chem. C112, 2972 (2008)

Keywords: interstellar medium, amino acid

## Adsorption experiments of ammonia and clay minerals to understand nitrogen isotopic fractionation in molecular clouds

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Nitrogen is the fifth abundant element in the universe and also essential component of organic molecules. Various nitrogen-containing organic compounds have been found by laboratory analysis of extraterrestrial materials. The stable isotopic composition of nitrogen (<sup>15</sup>N/<sup>14</sup>N ratio) will give information about evolutionary history of the organic molecules. Primitive solar system materials such as chondrites, comets, and interplanetary dust particles (IDPs) show various degrees of <sup>15</sup>N-enrichment compared to the solar system value of -400 ‰ [1]. They display up to +1500 ‰ in the bulk  $\delta^{15}\text{N}$  value (‰, normalized as vs. AIR) [2, 3]. Furthermore, anomalously high <sup>15</sup>N-enrichments, as called hot spots, have been frequently found within a single material with the highest  $\delta^{15}\text{N}$  values reaching as high as +5000 ‰ [4]. These <sup>15</sup>N-enrichments are considered to be originated in cold interstellar environments. However, the mechanisms of isotopic fractionation of nitrogen in the interstellar medium are not well understood and only a few models have been proposed [e.g., 5].

In this study, we focused on adsorption process of ammonia on grain surface of interstellar dusts as a potential mechanism for the extreme <sup>15</sup>N-enrichment and its high-heterogeneity found in extraterrestrial materials. Ammonia is a primitive nitrogen-containing compound and also one of major molecules in molecular clouds. Since ammonia is a highly reactive chemical, it is a precursor for nitrogen-involving organic molecules. The adsorption of ammonia on grain surface would be the first step for the formation of more complicated organic molecules. In order to examine the isotopic fractionation of nitrogen through adsorption of ammonia on grain surface, we performed experiments using ammonia gas and several adsorbents. For the experiments, six clay minerals (montmorillonite, saponite, dickite, kaolinite, pyrophyllite, and halloysite) were selected as the adsorbents. They were kept at 110 °C prior to the experiments to minimize adsorbed water. The each clay mineral was enclosed into a vacuumed glass vial and then ammonia gas (27 ‰, SI science) was introduced. A few days later, the glass vial was opened and the nitrogen isotopic composition of the adsorbed ammonia was determined by nanoEA/IRMS [6]. The results showed a relationship between  $\delta^{15}\text{N}$  values and the adsorbed ratio, which is explained by Rayleigh fractionation model. The adsorbents with low adsorption ratio have higher  $\delta^{15}\text{N}$  values compared to initial ammonia gas. The difference in the degree of <sup>15</sup>N-enrichment and adsorption property among clay minerals was also observed. These results imply that the adsorption of ammonia on grain surface should be considered as one of potential scenarios for <sup>15</sup>N-enrichment.

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Keywords: nitrogen isotopic fractionation, adsorption, ammonia, molecular clouds

## Do icy grains evaporate by an accretion shock?

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Gravitational collapse of a molecular cloud is a transient process to form protostars and protoplanetary disks. The infalling envelope onto the Keplerian disk often induces accretion shocks at their boundary. Recent ALMA observations suggested evaporation of icy grains at the shocked region [1,2]. The icy grain evaporation would considerably affect the chemical environment of the nebula. The shock conditions for the icy grain evaporation were calculated numerically in a few papers [3,4]. However, the effect of emissivity of icy grains has not been investigated systematically. The smaller the emissivity is, the higher the temperature of icy grains will become even in the same shock condition. The emissivity generally varies with the size, composition, and structure of icy grains, and then may change the evaporation condition. In this study, we revisited the evaporation condition for various icy grains using realistic emissivity.

We adopt a two-step calculation method to obtain the detailed thermal history of icy grains in the post-shock region. First we calculate the post-shock gas structure as a function of the distance from the shock front [5]. The shocked gas parameters just behind the shock front were determined by the Rankine-Hugoniot relation using the pre-shock parameters: a shock velocity and a pre-shock gas number density (J-type shock). The shocked gas is gradually cooled by line emissions from CO molecules and thermal collisions with non-evaporating sub-micron silicate grains. We consider a one-dimensional plane-parallel post-shock geometry, so the gas temperature and density are determined as a function of the distance from the shock front. Second we calculate the thermal evolution of icy grains using the post-shock gas structure obtained in the first step. The emissivity of icy grains was given by performing a Planck mean of a wavelength-dependent absorption efficiency, which was calculated from the dielectric function or the complex refractive index data. We solved the evaporative shrinkage of icy grains to obtain the evaporation condition, namely, the shock parameters with which the icy grain evaporates completely.

The numerical results indicate that the shock condition for the icy grain evaporation strongly depends on the emissivity. For example, the icy grain composed of pure CO<sub>2</sub> is evaporatable by the observed accretion shock [1,2] because of its small emissivity. However, if the icy grain contains considerable amount of silicate components, it has much larger emissivity and therefore hardly evaporates by the same accretion shock. Our results showed that the emissivity of the icy grains is one of the important factors to determine whether the icy grain evaporates by shock heating or not. This implies that it is possible to constrain the size, composition, and structure of the interstellar icy grains from the observational evidence of icy grain evaporation by accretion shocks.

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Keywords: Accretion shock, icy grain, Shock heating, Evaporation

## Diagnosing Evaporation of Icy Planetesimals due to Shock Heating in Protoplanetary Disks by ALMA Observations

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It is thought that eccentricities of planetesimals are excited due to gravitational interaction with protoplanets in protoplanetary disks. As a result, bow shocks are formed around the icy planetesimals and the ice is evaporated via the shock heating. Evaporation rates and orbital evolution of such planetesimals have been investigated (Tanaka et al. 2013, Nagasawa et al. 2014). In this work, we examine a possibility of diagnosing the shock heating and evaporation of icy planetesimals, using ALMA observations of lines of molecules evaporated from the planetesimals.

Evaporation of ice has been studied observationally and theoretically well, for example, at a shock front of outflows associated with young stellar objects. The evaporated molecules will be destroyed via chemical reactions with other species and/or depletion on dust grains. Destruction timescale via the reactions is about  $10^4$  years, while depletion time onto grains is much less than  $10^4$  years as far as the amount of grains is large enough. Therefore, the evaporated molecules can survive in gas-phase for around  $10^4$  years in the region hotter than their evaporation temperatures, while they freeze out immediately in the cold region. As parent species evaporated from ice, saturated nitrogen- or sulphur-bearing species and organic molecules are often considered. The evaporation temperatures are different depending on species; for example, the evaporation temperature of complex molecules are as high as that of water. In this work we focus on sulphur-bearing species whose evaporation temperature is not very high and gas-phase abundances are not high without evaporation of ice.

Our calculations show that evaporated  $H_2S$  is destroyed via gas-phase reactions, and SO and then  $SO_2$  are produced through reactions of atomic sulphur with molecular oxygen and OH. The timescale of these reactions is about  $10^4$  years. Therefore,  $H_2S$  and SO are good tracers of shock heating and evaporation of icy planetesimals if it occurs in the region hotter than the evaporation temperatures of  $H_2S$  and SO. The evaporation temperature of  $SO_2$  is higher than those of  $H_2S$  and SO. Thus, if the evaporation of icy planetesimals occurs in the region colder than the evaporation temperature of  $SO_2$ , the intensity of  $SO_2$  lines will be a good tracer of dust density since the depletion time on grains depends on it.

Molecular lines of  $H_2S$ , SO, and  $SO_2$  have not yet been detected towards protoplanetary disks by the previous radio observations. ALMA observations with high sensitivity and high spatial resolution, however, will make it possible to detect the lines of these molecules. Conditions that molecular lines of  $H_2S$  and SO becomes strong enough to be detected by ALMA observations will be discussed in the talk.

Keywords: protoplanetary disks, evaporation of icy planetesimals, astrochemistry

## Chemical Reactions in Protoplanetary Disks and Possibility of Detecting H<sub>2</sub>O Snowline using Spectroscopic Observations

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Inside H<sub>2</sub>O snowline in protoplanetary disks, H<sub>2</sub>O evaporates from the grain surface into gas. On the other hand, it is frozen out on the grain surface in the cold region beyond H<sub>2</sub>O snowline. H<sub>2</sub>O snowline is the line that divides the two different regions. H<sub>2</sub>O ice enhances the solid material in the cold outer part of a protoplanetary disk, which promotes the formation of cores of gaseous planets. We can also regard H<sub>2</sub>O snowline as the dividing line between forming regions of rocky planets and gas giant planets. In the disks around solar-mass T-tauri stars, H<sub>2</sub>O snowline is thought to exist at a few AU from the central star. Therefore, it is difficult to detect H<sub>2</sub>O snowline of exoplanetary systems by imaging observations, since their spatial resolution is insufficient.

In contrast, H<sub>2</sub>O emissions from protoplanetary disks are detected by recent observations of Spitzer and Herschel telescope. Zhang et al. (2013) estimated the position of H<sub>2</sub>O snowline by using the intensity ratio of different H<sub>2</sub>O lines, but the result depends on the model of temperature distribution in the protoplanetary disk. We consider that H<sub>2</sub>O snowline can be detected more directly by analyzing the velocity profiles of H<sub>2</sub>O line spectra that will be obtained by high dispersion spectroscopic observations in near future.

We have proposed the method of detecting H<sub>2</sub>O snowline by analyzing the velocity profiles of H<sub>2</sub>O line spectra that will be obtained by high dispersion spectroscopic observations.

First, we calculate chemical reactions using a self-consistent physical model of protoplanetary disks and investigate abundance distribution of H<sub>2</sub>O gas and the position of H<sub>2</sub>O snowline. We confirmed that the abundance of H<sub>2</sub>O is high not only in the inner region of H<sub>2</sub>O snowline near the equatorial plane but also in the hot surface layer of outer disk.

Second, we calculate the velocity profiles of H<sub>2</sub>O emission lines from protoplanetary disk, and found that we can obtain the information of H<sub>2</sub>O snowline through investigating the profiles of some emission lines that have small Einstein A coefficient and large excitation energy. The wavelengths of the useful H<sub>2</sub>O emission lines range from mid-infrared to sub-millimeter.

In addition, we investigate the effect of grain surface reactions and dust size growth.

When we include grain surface reactions in our calculations, the abundance of water vapor increases inside H<sub>2</sub>O snowline, while it decreases in the hot surface layer of outer disk. Hence, the line fluxes of H<sub>2</sub>O transitions with small Einstein A coefficient and high excitation energy become higher. It appears more significantly in the lines at the wavelengths of infrared than those at sub-millimeter. It is also shown that H<sub>2</sub>O lines with large Einstein A coefficient can be used to detect H<sub>2</sub>O snowline, since H<sub>2</sub>O emission from the hot surface layer of outer disk become small.

On the other hand, when we consider dust size growth, the abundance of water vapor increases in the hot surface layer of outer disk. Therefore, we need to select H<sub>2</sub>O transition lines with smaller Einstein A coefficients in order to identify the H<sub>2</sub>O snow line from the molecular line profiles.

We also discuss the possibility of future observations range from mid-infrared to sub-millimeter (e.g., ALMA, TMT, SPICA).

Keywords: H<sub>2</sub>O snowline, protoplanetary disk, calculation of chemical reactions, grain surface reaction, dust size growth, spectroscopic observation

## Temporal and spacial variation of organic materials in the proto-solar disk

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More than 80 distinct amino acids are discovered in meteorites, which, in addition to their precursors, are suggested to be extraterrestrial origin. Even the detection of glycine, the simplest amino acid, has been claimed in samples from comet 81P/Wild 2 returned by NASA's Stardust spacecraft. These discoveries suggest that interstellar chemistry can produce such complex molecules. Motivated by these studies, some observational search for complex molecules in the interstellar medium reported to detect acetic acid, acetamide, aminoacetonitrile, and ethyl formate in Sagittarius B2 molecular cloud. More recently, ALMA observation is expected to find more complexity of such organic materials.

Organic materials in the asteroids and comets may be partially derived from molecular clouds and partially processed in proto-solar disk. It is one of the critical problems whether organic materials in the interstellar dusts formed in molecular cloud could survive and accreted to planetesimals. Interstellar dusts were incorporated into the proto-solar molecular cloud and were heated to evaporate in the proto solar nebula. Since the degree of evaporation depends on temperature and pressure conditions of the solar nebula, the distribution and chemical compositions of the dusts in the solar nebula would vary from place to place and with time.

We calculated disk evolution and particle motion simultaneously in order to investigate temperature change of individual particles, which enables us to trace the change of average chemical composition of organics. The fundamental difference from the chemical network reactions on the surface of solid materials at lower temperatures of molecular clouds is that the reactions in this work are thermal processes at higher temperatures ( $T \geq 297\text{K}$ ).

We calculate viscous disk evolution model and particle-tracking model by Ciesla (2011). Particles are released at each 10AU at  $t = 0$ . Particles are supposed to be small enough to well couple with gas and they are thermally equilibrated.

The starting material is assumed to be *Greenberg particle*, which consists of silicate core and organics, and the chemical composition is taken from that for 297K of Nakano et al. (2003). When heated, the C and N composition of particles varies according to Nakano et al. (2003), but do not vary if temperature decreases. By summing up all the grains with different thermal history located at every 1AU at a certain time, the local bulk chemical composition of organics in the disk is obtained.

The temporal change of gas temperature and distribution of particles shows that particles initially located in the low-temperature outer region drift inward, and that thermally unprocessed organic particles were present in the inner region after  $10^6$  years because the temperature of disk decreases with time where particles from outer regions move.

The temporal-spatial variation of C and N contents and C/N ratio of organic particles indicates chemical variation of the inner region ( $\leq 10\text{AU}$ ). Silicate-organics complex grains from a molecular cloud were partially evaporated to be poor in organic materials inside 5AU at the early stage of the proto-solar disk. As temperature decreases with time, primitive grains are transported inward and chemical composition of organic materials in the inner regions of the disk changed from fractionated to unfractionated composition with disk evolution. A small amount of diffuse cloud organic materials survive at the most inner region and partially evaporated molecular cloud organic materials and diffuse cloud organic materials are mixed at C/N ratio-decreasing region. This result shows that composition of organic materials accrete to a planetesimal depend on when the planetesimal is formed.

Keywords: molecular cloud, protoplanetary disk, organic materials, interstellar dust

## Reproduction experiment of molecular formation based on Fischer-Tropsch-type catalytic reaction in the early solar nebula

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Catalytic reactions such as the Fischer-Tropsch type and Haber-Bosch type reactions are able to produce organic molecules efficiently on the surface of cosmic dust analogues, such as iron, magnetite, amorphous iron silicate and graphite at temperature above 573 K and pressure at  $10^5$  Pa in the laboratory [1-4]. In these experiments, organic molecules ranging from methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), benzene ( $\text{C}_6\text{H}_6$ ) and toluene ( $\text{C}_7\text{H}_8$ ), to more complex species such as acetone ( $\text{C}_3\text{H}_6\text{O}$ ), methyl amine ( $\text{CH}_3\text{NH}_2$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ) and N-methyl methylene imine ( $\text{H}_3\text{CNCH}_2$ ) have been produced so far. However, it is not obvious the reaction similarly works in the solar nebula and is able to extrapolate to the actual early nebula environment at lower temperature below 500 K and lower pressure under  $10^2$  Pa. Therefore, we developed a new experimental system to test the catalytic chemical reactions in the early nebula environment [lower temperature (100-500 K) and pressure ( $10^{-3}$ - $10^0$  Pa)] using a substrate of magnesium silicate or iron. Our experimental system has a temperature-controlled substrate, a Fourier transform infrared spectrometer (FT-IR), and two quadrupole mass spectrometers (Q-MSs). FT-IR measures the vibration modes of adsorbed and produced molecules on the surface and the Q-MSs detect volatile molecules, respectively. As a preliminary experiment, the substrate of a magnesium silicate thin film was used in a continuous gas flow of a mixture gas of  $\text{H}_2$  and CO for Fischer-Tropsch type reactions. Unfortunately, however, we do not find any signal of the Fischer-Tropsch type reaction and resulting organic molecules on the amorphous magnesium substrate, whereas the signal of CHO molecule and ethane ( $\text{C}_2\text{H}_6$ ) have been detected on the Q-MS spectra in some experimental condition on a different substrate. In the workshop, the detail results using iron substrate will be presented as a function of temperature and pressure.

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Keywords: organics, catalytic reaction, molecular formation, low temperature science, solar nebula

## Effects of olivine as a catalyst for the formation of organic compounds in meteorites

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### INTRODUCTION

Many classes of organic compounds have been identified in carbonaceous meteorites, which imply a complex history of chemical evolution in extraterrestrial environments. In the previous study (Yamashita and Naraoka, 2014), saturated- and unsaturated-alkylpyridines were reported with extensive homologous series ranging from C<sub>1</sub> to C<sub>20</sub> in the Murchison meteorite, which could be produced through aldol condensation of aldehydes in the presence of ammonia. The pyridine-derived compounds such as pyridine carboxylic acids (including nicotic acid) and alkylpiperidines were also found in Murchison, probably resulting from the alkylpyridines by oxidation and reduction, respectively, on the meteorite parent body.

### EXPERIMENTAL

The simulation experiments were performed in this study to pursue reaction mechanisms for the occurrence of alkylpyridines and their derivative compounds in meteorites. Aqueous solution containing aldehydes (HCHO and/or CH<sub>3</sub>CHO) and ammonia were heated in the presence or absence of olivine powder as a catalyst in a glass ampoule after N<sub>2</sub>-purging at 50-100 °C for 5-26 days. The reaction products were analyzed by high performance liquid chromatography/mass spectrometry with electrospray ionization.

### RESULTS AND DISCUSSION

Alkylpyridines were commonly observed in the reaction products. However, the alkylpyridine distribution was different depending in the presence or absence of olivine. Longer alkylated (up to C<sub>20</sub>) pyridines were produced with olivine, while only shorter alkylated (up to C<sub>7</sub>) ones were produced without olivine. The olivine surface can provide reaction sites to support elongation of alkylpyridines during aldol condensation. In addition, pyridine carboxylic acids were present with olivine, but absent without olivine. The chemical oxidation of alkylpyridines could be promoted by olivine. Thus, the effects of olivine are remarkable as catalysis to control the compound distribution observed in carbonaceous chondrites.

### REFERENCE

Yamashita, Y. and Naraoka, H. (2014) Two homologous series of alkylpyridines in the Murchison meteorite. *Geochem. J.* **48**, 519-525.

Keywords: carbonaceous chondrites, organic compounds, olivine, catalysis, aqueous alteration, molecular evolution