Adsorption process of ion on amorphous ice surface

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In interstellar molecular clouds, various molecules (for instance, H_2O, NH_3, CO, CO_2, and so on) are formed from elements such as H, C, O, and N [1]. Most of H_2O exists as a thin shell of amorphous ice around dust grain. The molecules undergo chemical evolutions to organic molecules through various processes on the surface of amorphous ice [2]. Thus, the surface structure of amorphous ice is an important factor to understand the molecular evolution of organic molecules in molecular clouds. To investigate the effects of adsorption of ion on the surface structure of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice with NO_3^- were performed.

The MD calculations were performed using an atom-atom potential model, KAWAMURA potential model [3]. The amorphous ice was prepared by quenching of 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 ice at 10 K was controlled with the time period of the annealing at 235 K. To equilibrate the fundamental cell, the MD code was run for 40 ps at 10 K. Then, an ion (NO_3^-) was put in a position, such the center of nitrogen in ion was at a distance of 0.5 nm from the outermost hydrogen atom in surface. 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 0.5 nm in thickness from the outmost atom was analyzed as the surface layer.

The result shows that the atomic displacement parameters (ADP) of oxygen and hydrogen of water molecules in surface layer increase during the adsorption of NO_3^-. The values are diminished with formation of hydrogen bonds with surrounding water molecules, and gradually approach the values of pure amorphous ice without ions. For surface with NO_3^-, three oxygen atoms of NO_3^- form hydrogen bonds with hydrogen atoms in dangling bonds of water on the surface layer. When an ion is adsorbed, surrounding water molecules rotate to form hydrogen bonds with the ion. Thus, the rearrangement of water molecules occur even at low temperature. The result indicates that the thermal vibrations of water molecules are enhanced with adsorption and diffusion of ions on the surface. To investigate the effects of ion adsorption on smoothing of surface roughness, the potential map of surface layer were calculated. The results show that the potential map charges with a collision of ion on a convex position, whereas no charge was observed when the ion adsorbs on a concave position. This indicates that the smoothing of surface roughness of amorphous ice at low temperature results from ion collisions. The effects of ion adsorption might have important implications for surface reaction in interstellar molecular clouds.

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Surface Structures of Forsterite Crystal and Glass

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In interstellar molecular clouds, elements such as hydrogen, oxygen, carbon, and nitrogen deposit on dust grains, and form various molecules (e.g., H_2O, CO, CO_2, NH_3, CH_4, H_2CO, CH_3OH, and so on). These molecules undergo chemical evolutions to organic molecules through various processes on the surface of dust grains [1]. Forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) have been observed in interstellar molecular clouds and young stellar objects [2]. Although various studies have been performed for bulk structures of forsterite and enstatite, their surface structures are less conclusive [3]. To investigate the surface structures of forsterite in crystalline and glassy states, molecular dynamics (MD) calculations were performed. The surface structure is one of the important factors governing the chemical evolutions in interstellar molecular clouds.

The MD calculations were performed using an atom-atom potential model [4]. The potential parameters were empirically determined by constraining the model to reproduce the experimental results of density, thermal expansion coefficient, and bulk modulus [4]. The glass structure was prepared by quenching the liquid phase consisting of 2400 Mg_2SiO_4 from 3000 K to 10–1750 K with 2 K/fs in rate. 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 MD code was run with NTV ensemble at each temperature for 500 ps with a time step of 0.5 fs. The layer with 0.5 nm in thickness from the outmost atom was analyzed as the surface layer.

The result shows that the melting temperature of forsterite crystal with surface layer was 1927 K. This value is lower than the MD result of bulk state without surface (2418 K [4]) and experimental result (2171 K [5]). This depression of the melting temperature is attributed to the structure and thermal vibrations of atoms in surface layer of forsterite crystal. The nearest Si–Si distance, which was analyzed using the pair correlation functions of atoms, for surface layer of crystal is larger than that of internal part. Furthermore, the amplitudes of thermal vibrations of atoms in surface layer are larger than those of internal part. The results indicate that a surface layer with low density and high thermal vibrations exists in forsterite crystal. The amplitudes of thermal vibrations in surface layer increase with warming and approach the values of the bulk state at its melting point (i.e., 2418 K) at around 1927 K. This induces the depression of the melting temperature for system with the surface layer. For glassy state, a surface layer with short Si–Si distance exists, although the amplitudes of thermal vibrations of atoms are large in comparison with the values of the internal part. This inverted tendency may be resulted from an inhomogeneous structure of surface layer in the glassy state. The surface structures of crystalline and glassy forsterites have important implications for adsorption, diffusion, and chemical reaction in interstellar dust grains.

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Keywords: Forsterite, Surface, Interstellar molecular clouds, Molecular dynamics

N-heterocyclic compound synthesis from aldehydes and ketone with ammonia: A simulation of organic reactions on the meteorite parent bodies

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[Introduction]

Carbonaceous chondrites have the most primitive chemical compositions in the solar system and contain volatile components such as water and carbon. In spite of their primitive character, most carbonaceous chondrites have had experienced aqueous alteration on parent bodies, which was revealed by the occurrence of hydrous minerals. The meteoritic carbon are present mainly as organic matter, in which soluble organic matter (SOM, ˜1 to ˜30 wt%) consists of relatively low-molecular-weight compounds such as carboxylic acids and amino acids. The rest major carbon exists as insoluble organic matter (IOM) having high-molecular complicated structures. Therefore, the aqueous alteration must have influenced the organic-mineral interactions. In order to study the chemical evolution of organic matter in the solar system, the role(s) of minerals should be clarified. In this study, we performed simulation experiments of organic compound synthesis using ammonia (NH_3), formaldehyde (HCHO), acetaldehyde (CH_3CHO), propionaldehyde (C_2H_5CHO) and acetone (CH_3COCH_3), which are simple molecules found in molecular clouds, under the aqueous environment in the presence or absence of minerals.

[Materials and Methods]

The several aqueous mixtures with various ratios (by mol) of NH_3 (1 to 10) /HCHO (0.1 to 1) /CH_3CHO (0.01 to 0.1) /C_2H_5CHO (0.01 to 0.1)/CH_3COCH_3(0.01 to 0.1) were heated in the presence of powdered mineral including forsterite (San Carlos), magnetite (Utah), synthetic forsterite or amorphous silicate (Mg_2SiO_4 in composition) at 60 to 80℃ for 144 to 192 hours in N2-purged glass ampoules. A total of 20 runs of simulation experiments were performed. The reaction product was extracted with methylene chloride/methanol (2/1, by volume) and analyzed by high performance liquid chromatography/mass spectrometery.

[Results and Discussion]

Many compounds were observed at the range of m/z 100-400 in all reaction products. Of the identified compounds, alkylpyridines ($C_nH_{2n-5}N$), alkylimidazoles ($C_nH_{2n-3}N_2$) and hexamethylenetetramine ($C_6H_{12}N_4$, HMT) were the main products for each run. The compounds that have not been identified but represented by compositional having $C_nH_{2n-1}N_3O$ in composition were also identified as a main product. Although alkylpyridines and alkylimidazoles have been detected from carbonaceous chondrites (e.g. Yamashita and Naraoka, 2014). Although HMT has been reported as a main product during interstellar analog experiment by UV irradiation at low temperature (Vinogradoff et al., 2011), HMT has not been found in meteorites. HMT is relatively abundant in the products with the absence of minerals. However, the HMT amount decreased in the presence of the amorphous silicate and forsterite (San Carlos), instead of increasing production of alkylpyridines and alkylimidazoles. The minerals could control the reaction pathways as a catalyst. In particular, as amorphous silicate is the main solid phase in the interstellar environments (F. Kemper etal., 2004), it may have important roles for the evolution of extraterrestrial organic matter. Further experiments are needed to identify the intermediate compounds as well as to observe the change in mineral phases during the reactions.

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Keywords: Chemical Evolution, Mineral-organic interaction, Aqueous alterlation, N-Containing Compound, Carbonaceous chondrite

Meteoritic organic compound analysis by nano-liquid chromatography/mass spectrometry

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[Introduction]
Carbonaceous chondrites, which have the primitive chemical composition in the solar system, contain volatile materials including water and organic matter. Since biologically-relevant molecules such as amino acids, nucleobases were detected in meteorites(e.g. Burton et al., 2012), meteoritic organic matter has been investigated with respect to the origin of life. So far the organic compounds have been generally analyzed using the powder sample of sub-g to g meteorite with solvent extraction followed by chromatography. The powdered sample has lost its location information such as mineral textures, even though the primitive meteorites have heterogeneous composition in chemistry and mineralogy. Since most carbonaceous chondrites experienced aqueous alteration on the parent bodies, the understandig of mineral associaton with organic compounds is necessary to reveal chemical evolution in extraterrestrial environments. Futhermore, non-destructive organic analysis is preferred especially for precious samples. In this study, we will develop an analytical method of organic compounds using an intact micro-meter sized grain of extraterrestirial meterial with high-sensitive nano-liquid chromatography (nanoLC) coupled with high-resolution mass spectrometry(HRMS).
[Materials and Methods]
A single grain (~300 to 900 μm) was obtained by chipping from carbonaceous chondrites (Murchison and Murray; CM2). Each grain (0.168-2.392mg) was soaked in 5.0μL of methanol(MeOH) followed by sonication or mixing. One micro-litter of each extract was subjected to nanoLC/HRMS ($m/\Delta m$=~140,000 at m/z 200) with electrospray ionization (positive ion) using C18 reversed phase column or amide column. The eluent solvents were mixture of acetonitrile, water and formic acid. All analytical procedures were performed in a clean room.
[Results and Discussion]
Apparent changes were not observed on the grain surface before and after the analysis. Many alkylated homologous CHN and CHNO compounds were distinguished by every 14.0156 (m/z; $-CH_2-$) and peaks shift in the retention time of mass chromatogram. The occurence of homologous series is consistent with previous studies (Schmitt-Kopplin et al., 2010; Yamashita and Naraoka, 2014), suggesting the carbon-chain elongation by stepwise reactions from small molecules. The homologous series of $C_nH_{2n-5}N$(n=5-26), C_nH_{2n-7N}(n=9-28), $C_nH_{2n-1}N_2$(n=5-23), $C_nH_{2n-1}NO$(n=3-20), $C_nH_{2n-3}NO$(n=9-12) and $C_nH_{2n-5}NO$(n=6-26) were detected from the Murray meteorite. In contrast, the only series of $C_nH_{2n-5}N$(n=5-24) and $C_nH_{2n-7}N$(n=10-26) homologous series were detected in Murchison meteorite. The range of carbon number in the homologous series varied depending on the meteorites, whch may imply heterogeneity of organic compounds in the meteorites. Such a heterogeneous distribution may be associated with the mineral occurance. The fluid flow on the parent body may also affect the compound distribution by the (geo)chromatographic effect. Further investigations are needed to clarify the relationship between the meteoritic texture and the distribution of organic compounds.

Keywords: organic compound, carbonaceous chondrite, nanoLC/HRMS, heterogeneity

Isotopic Analysis of Presolar SiC Grains with the Post-Ionization SNMS

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For unveiling nucleosynthesis during stellar evolution, in-situ isotopic analyses of individual presolar grains have played important roles. So far, we have been developing a new mass spectrometer, Secondary Neutrals Mass Spectrometer (SNMS) with a femto-second laser, in order to enable further sensitive and higher mass/spatial-resolution measurements. At the conference, we' ll report our recent progress of development of SNMS and application to the analysis of SiC grains collected from Murchison meteorite. As preliminary results, we detected isotopic anomalies of major elements (Si and C), which is consistent with those of previous works. We will also refer the challenging isotopic measurements of other minor elements.

Keywords: Stellar Evolution, Presolar Grain, Isotopic Analysis

Formation of celestial body that was caused by the change of electronic states of matter

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Gravitational collapse of interstellar gas and condensation of cosmic dusts has been investigated [1]. But, electron-electron interactions increase by the increase of mass of celestial body. The change of electronic state increases bonding force. Large celestial body can become the core for gravitational collapse of hydrogen gas.

Coulomb force that binds neighboring atoms in vicinity of 10^{-10} m is about 10^{36} times powerful of gravitational force. Cold nanoparticles of interstellar medium can be clustered by the electron-electron interaction. Molecules of water contributed to growth of the cluster. The percentage of effect of short-range force on a cluster comprised of larger solid elements is decreased.

The gravity increases cumulatively with increase of mass regardless of the points of chemical bond. If planet becomes larger than $2.0\text{x}10^{9}$ kg, gravitational force of planet is more than short-range force. Large planetesimal captures small planetesimal by the gravity. Huge mass of celestial body can hold the hydrogen. Temperature of interior of planet become high by the gravitational potential energy.

Coulomb force and gravitational force work concurrently. Long period of growth is necessary in the early stages for the growth due to short-range force. While, gravitational collapse of interstellar gas is progressed in a short time due to existence of the gas of about 100 times mass of cosmic dust. The Sun is not the first generation of stars. The protostar of the Sun was growing before gravitational collapse of gas. There is metallic electronic state of hydrogen outside of core. The nuclear fusion begins at hydrogen layer. Radioactive substances contained in meteorite indicates that those were born from solid core by explosion due to nuclear fusion.

Please see more information at Website; “https://youtu.be/GMmvjU2CdKM ”, “https://youtu.be/HwBjqYpDdu0 ”.

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Keywords: protostar, cosmic dust, intermolecular bond, short-range force, gravitational collapse, nuclear fusion

Mid-infrared observations of the dust-forming classical nova V2676 Oph with Subaru/COMICS

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A dust-forming nova V2676 Oph (discovered in Mar 2012) was the first nova to provide evidence of both C_2 and CN molecules during its near-maximum phase and evidence of CO molecules during its early decline phase (Nagashima et al. 2014). The derived carbon- and nitrogen-isotopic ratios in the nova (Kawakita et al. 2015) are consistent with that the nova explosion was hosted by a CO-rich white dwarf (WD) star. To confirm a type of the hosting WD (CO-rich or ONe-rich), we performed the mid-infrared imaging and low-resolution spectroscopic observations of V2676 Oph with COMICS mounted on the Subaru telescope in June 2013 and May 2014 (482 days and 782 days respectively after its discovery). No clear [Ne II] emission line at 12.8 micron was observed. Based on the absence of [Ne II] emission, the WD hosting V2676 Oph is considered a CO-rich WD. Both types of dust grain, carbon-rich and oxygen-rich, were detected on both dates, although this nova is considered as a Carbon-rich ($C/O > 1$) based on the presence of C_2 observed earlier. The 11.4 micron unidentified infrared emission was also detected on these dates. Non-equilibrium processes are likely to be responsible for the grain formation in the nova.

Keywords: nova, dust, infrared

Silicate dust evolution in protoplanetary disks

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Silicate is the dominant solid component in circumstellar environments. Infrared spectroscopic observations have shown that both crystalline and amorphous silicate dust are present in protoplanetary disks, and crystalline silicate dust seems more abundant in the inner warm region of the disks. This suggests that thermal annealing of interstellar amorphous silicate dust occurred in the disk and changed the dust properties of disk dust temporally and spatially with disk evolution. Some of those processes occurred in the early Solar System may have been recorded in fine-grained matrices of less altered/metamorphosed chondrites, which contain abundant amorphous silicates and a small fraction of presolar silicate grains. Laboratory experiments help us extract the record of disk thermal processes from natural samples quantitatively. We have done experiments on crystallization and hydration experiments of amorphous silicates and evaporation and condensation experiments of crystalline silicates, focusing on kinetics of these processes. In this presentation, based on experimentally-obtained kinetic data, we will discuss the silicate dust evolution in protoplanetary disks.

Keywords: silicate, protoplanetary disk, kinetics