

Crystal structure, morphology, and isotopic compositions of presolar alumina grains in unequibrated ordinary chondrites

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Corundum, the thermodynamically stable phase of Al₂O₃, is predicted to be the most abundant refractory dust species condensed in envelopes around oxygen-rich asymptotic giant branch (AGB) stars. Many presolar Al₂O₃ grains, which are the survival circumstellar dust grains, have been identified from acid-residues of chondrites. The grain morphology and crystal structure of presolar grains may reflect condensation conditions in circumstellar envelopes of AGB stars and processing in the interstellar medium (ISM) and protosolar disk.

Using scanning electron microscopy (SEM) we obtained detailed secondary electron images, energy dispersive X-ray spectroscopy (EDS), electron backscattered diffraction (EBSD) patterns, and cathodoluminescence (CL) spectra of each Al₂O₃ grain prior to isotopic measurements. Focused ion beam (FIB) lift-out sections were made from the identified presolar grains and the interior structures were observed with a transmission electron microscope (TEM).

The Al₂O₃ grains were identified from acid residues of QUE97008 (LL3.05) by EDS and observed in detail by field emission (FE) SEM at the Carnegie Institution of Washington (CIW). Previously identified alumina grains from Semarkona (LL3.0), Roosevelt County 075 (H3.1), and Bishunpur (LL3.15) were also used in this study. CL spectra were obtained with a FE-SEM equipped with a Gatan Mono CL4 system at NIST. EBSD analysis was performed with an FEI Nova 600 FIB-SEM equipped with an HKL EBSD system at the Naval Research Laboratory (NRL). Isotope measurements were performed with the Cameca NanoSIMS 50L ion-microprobe at CIW. Oxygen isotopes of 163 grains were measured using ~100 nm Cs⁺ beam rastered over each of the grains. An O⁻ beam was used to measure the Mg-Al isotopic compositions of the presolar and some solar Al₂O₃ grains. Ultra-thin sections of presolar grains QUE053, 060, and 067 were prepared with the NRL FIB-SEM. TEM studies were carried out at NRL with a JEOL 2200FS field-emission scanning transmission electron microscope (STEM).

Eight presolar grains from QUE97008 and one from RC 075 were newly found. Grain QUE060 is classified into Group 2 and has a subhedral shape with clear flat facets. The surface is smooth except for a face with a cavity. TEM diffraction patterns of the FIB section indicated that the grain consists of multiple corundum crystallites. Dark-field TEM image showed large (>100 nm) and small (<30 nm) scale orientation variation. The large-scale misorientation observed on the right side of the grain seems to relate to the cavity. Small-scale distortions occur uniformly within the grain. EDS spectra showed that the Mg/Al ratio of QUE060 is ~0.01, and the NanoSIMS measurement revealed this high Mg content to be essentially pure radiogenic ²⁶Mg, with inferred initial ²⁶Al/²⁷Al ~0.01, similar to other Group 2 grains.

QUE067 is a thin Group 4 grain with very irregular morphology. Its ²⁷Al/²⁴Mg ratio was three times lower than in QUE060, but its inferred ²⁶Al/²⁷Al ratio was similar. No EBSD patterns of crystals were obtained from the grain surface but TEM observation on the FIB section showed that the interior of QUE067 was corundum, not amorphous.

The subhedral shape and smooth surface of QUE060 suggest that this grain was likely single crystalline corundum when it condensed in a circumstellar envelope of a low-mass AGB star, and that the polycrystalline nature, voids and distorted crystal structure inside the grain are secondary features.

A possible process to form large-scale misorientation and the cavity is grain-grain collisions in a SN shock in the ISM. A high velocity collision creates a shockwave propagating inside the grain, finally forming a crater. Small-scaled distortions may have also formed by collisions with small particles in the ISM. Such collisions are less destructive than with larger grains, but their probability is high. Ion bombardment in the ISM may also contribute to the small-scale distortions.

Keywords: dust, early solar system, chondrite, presolar grain, transmission electron microscopy, evolved star

3-D observation of GEMS by electron tomography

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Amorphous silicates in chondritic porous interplanetary dust particles (CP-IDPs) coming from comets are dominated by glass with embedded metal and sulfides (GEMS). GEMS grains are submicron-sized rounded objects (typically 100-500 nm in diameter) with nanometer-sized (10-50 nm) Fe-Ni metal and sulfide grains embedded in an amorphous silicate matrix. Several formation processes for GEMS grains have been proposed so far, but these models are still being debated [2-5].

Bradley et al. proposed that GEMS grains are interstellar silicate dust that survived various metamorphism or alteration processes in the protoplanetary disk and that they are amorphization products of crystalline silicates in the interstellar medium by sputter?deposition of cosmic ray irradiation, similar to space weathering [2,4]. This consideration is based on the observation of nano-sized crystals (~10 nm) called relict grains in GEMS grains and their shapes are pseudomorphs to the host GEMS grains.

On the other hand, Keller and Messenger proposed that most GEMS grains formed in the protoplanetary disk as condensates from high temperature gas [3,5]. This model is based on the fact that most GEMS grains have solar isotopic compositions and have extremely heterogeneous and non-solar elemental compositions. Keller & Messenger (2011) also reported that amorphous silicates in GEMS grains are surrounded by sulfide grains, which formed as sulfidization of metallic iron grains located on the GEMS surface.

The previous studies were performed with 2D observation by using transmission electron microscopy (TEM) or scanning TEM (STEM). In order to understand the structure of GEMS grains described above more clearly, we observed 3D structure of GEMS grains by electron tomography using a TEM/STEM (JEM-2100F, JEOL) at Kyoto University. Electron tomography gives not only 3D structures but also gives higher spatial resolution (~a few nm) than that in conventional 2D image, which is restricted by the sample thickness (>50 nm). Three cluster IDPs (L2036AA5 cluster4, L2009O8 cluster13 and W7262A2) were used for the observations. IDP W7262A2 was collected without silicon oil, which is ordinary used to collect IDPs, so this sample has no possibility of contaminations caused by silicon oil or solvent to rinse it [6].

The samples were embedded in epoxy resin and sliced into ultrathin sections (50-300 nm) using an ultramicrotome. The sections were observed by BF-TEM (bright field-TEM) and HAADF-STEM (high angle annular dark field-scanning TEM) modes. Images were obtained by rotating the sample tilt angle over a range of ±65 degree in 1 degree steps. The obtained images were reconstructed to slice images. Mineral phases in the slice images were estimated by comparing with a 2D elemental map obtained by an EDS (energy dispersive X-ray spectroscopy) system equipped in the TEM/STEM.

Careful examination of the slice images confirmed that iron grains are embedded in the amorphous silicate matrix of the GEMS grains, but sulfide grains were mainly present on the surface of the amorphous silicate. These results are consistent with the model that GEMS grains formed as condensates [3,5], although more data are needed to conclude the origin of GEMS grains. The present study is the first successful example adapting the electron tomography to the IDPs. This type of analysis will be important for planetary material sciences in the future.

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- [4] Bradley (2013) *GCA*, 107, 336
- [5] Keller and Messenger (2013) *GCA*, 107, 341
- [6] Messenger et al. (2012) 43rd LPSC, 2696 (abstr.)

Keywords: IDP, GEMS, TEM, tomography

Condensation experiments of Si-rich gas into the chondrule melt for rapid low-Ca pyroxene formation using a new furnace

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Introduction

Low-Ca pyroxenes (mainly enstatites) and the high-pressure polymorphs are the most major phases constituting rocks in the solar system. The formation mechanism of low-Ca pyroxenes in the solar nebula is problematic. It has been thermodynamically predicted that enstatite forms from forsterite by the reaction with Si-rich gas since enstatite and the preceding condensate Mg-silicate, forsterite, are in reaction relation (Grossman, 1972). However, the rate of the reaction is sluggish because of the solid diffusion-controlled in the enstatite layer, and the reaction is nearly treated as maximum fractional condensation (Imae et al., 1993). Also, the amount of enstatite condensed directly from the residual gas is very small. Tissandier et al. (2002) experimentally showed that pigeonite (CaO~5-7 wt%) crystallized from chondrule melt by the interaction with Si-rich gas. In the present study, a new technique to simulate the solar nebula was developed and massive low-Ca pyroxenes (CaO~1 wt%) were produced using the furnace.

Experiments

The total pressure was mainly controlled to be 100Pa under the hydrogen gas flow, using a butterfly valve indicated from the diaphragm-seal type pressure gauge. The maximum temperature for each run was 1200-1450°C, in which pyroxene is in stable region and the cooling rate was mainly 100°C/h. A tiny fragment of the Allende meteorite (~30-50 mg for each run) was used as a starting material of the experiments. The starting material and silica powder were put avoiding the direct contact into the alumina crucible with the 1 mm orifice. The experiments without silica powder were also carried out as reference experiments.

Result

Minor amount of low-Ca pyroxenes were found mainly with dominant olivines under the experiments without Si-rich gas source. While, a drastic change was observed from the experiments with Si-rich gas source: completely changed to low-Ca pyroxenes poikilitically enclosing rounded olivines were observed for the charges at 1450°C, and low-Ca pyroxenes were observed mainly on the rim for the charges at 1350°C and 1250°C. The iron content increased on the decreasing temperatures.

Discussion

The collision frequency of the Si-rich gas on the melt of the Allende chondrite as a starting material is not so large to derive the crystallization of the massive low-Ca pyroxenes from the melt. Rather, the Si-rich gas helped the nucleation of low-Ca pyroxenes in the stability field of low-Ca pyroxene. Massive crystallization of pyroxenes did not occur for the experiments without Si-rich gas source and here the forsterite continued to grow under metastable condition.

References

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Keywords: primordial solar nebula, condensation, low-Ca pyroxene, Si-rich gas, low-pressure experiments, chondrule

Hydration of amorphous forsterite grains in protoplanetary disks

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Hydrous silicate dust can be thermodynamically stable at low temperatures ($\sim 200\text{K}$) in protoplanetary disks with the solar-system abundance of elements. Theoretical and experimental investigation (Fegley and Prinn, 1989; Imae et al., 1999) have shown that the hydration reaction between crystalline Mg-silicates and water vapor is too sluggish to occur during a lifetime of protoplanetary disks. However, infrared spectroscopic observation and investigation of extraterrestrial materials have shown that both crystalline and amorphous Mg-silicates may be present in protoplanetary disks and in the protosolar disk. Amorphous silicates are thermodynamically unstable, and thus could be hydrated more rapidly at higher temperatures than crystalline silicates (Nagahara and Ozawa, 2011). If hydration of amorphous silicates occurs within a disk lifetime, hydrated dust could be a source of water to terrestrial planets.

In this study, in order to investigate hydration of amorphous Mg-silicates, we conducted closed-system reaction experiments of amorphous forsterite and water vapor in sealed glass tubes at temperatures of 1023-423K and $P_{\text{H}_2\text{O}}$ of 0.05 -50 bar for 2-1344 hours. Run products were analyzed with FT-IR and XRD. We found that samples reacted at temperatures below 723K and $P_{\text{H}_2\text{O}}$ of 5-50 bar showed sharp $3\mu\text{m}$ absorption features, clearly suggesting the formation of hydrous phase(s). XRD analyses of some run products showed that the hydrous phase was serpentine. Because the stable temperature of hydrous phase(s) at $P_{\text{H}_2\text{O}}$ of 5-50 bar is $\sim 523\text{K}$, the present results indicate that hydrous Mg-silicates can be formed metastably from amorphous forsterite at higher temperatures than the thermodynamic prediction. Moreover, hydration of amorphous forsterite occurred after 2-hour heating at 623K and $P_{\text{H}_2\text{O}}$ of 5 and 50 bar, implying that the activation energy for hydration of amorphous forsterite is much smaller than that for crystalline forsterite.

Hydration reaction seems to have little $P_{\text{H}_2\text{O}}$ dependence at $P_{\text{H}_2\text{O}}$ of 5-50 bar, indicating that hydration is controlled by a reaction between amorphous forsterite with saturated adsorbing water molecules. No hydration occurred, however, at 523K and $P_{\text{H}_2\text{O}} < 1$ bar, which could be due to less effective adsorption of water molecules at low-pressure conditions.

Keywords: protoplanetary disk, Mg-silicate, crystalline, amorphous, forsterite, hydrous mineral

Sticking probability for homogeneous nucleation of iron dust

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Nucleation theories have been used to understand the condensation sequence, number density and size of cosmic dust in a gas outflow of dying stars or a gas plume after shock wave heating in the primitive solar nebula. However, it has been well known that nucleation rates obtained by nucleation theories and by experiments have a large difference. We believe that the reason is uncertainties of the physical parameters of nanometer sized particles. Therefore, it is still not successful to explain the characters of cosmic dust by a nucleation theory. To determine the physical parameters of nanoparticles and evaluate nucleation theories, we constructed an in-situ observation system of temperature and concentration during homogeneous nucleation in vapor phase using interferometry for both of ground based and microgravity experiments.

Nanoparticles are formed from a supercooled vapor after evaporation by electrical heating in a controlled gas atmosphere. Using the new system in lab, we succeeded to determine surface free energy and sticking probability of manganese nanoparticle from timescale for gas cooling and condensation temperature based on nucleation theories [1]. In this laboratory experiment, convection of gas atmosphere caused by thermal heating generates heterogeneity of nucleation environment, such as temperature and concentration profiles around evaporation source. If same kinds of experiments are performed in microgravity, evaporated vapor defuses uniformly and the temperature profile becomes concentric around the evaporation source. As the result, nucleation will occur at concentric position. Then, we can obtain physical properties with relatively smaller error bars and then we may be able to evaluate nucleation theories more precisely. Therefore, we also performed a microgravity experiments using an aircraft and the sounding rocket S-520-28 launched on December 17th, 2012.

We prepared specially designed Mach-Zehnder-type interferometers with an evaporation chamber and camera recording systems to fit the space and weight limitations of the rocket. Three systems, named DUST 1 to 3, with same configuration except evaporation source and gas pressure in the chamber were installed into the nosecone of the rocket. The evaporation source and gas atmosphere were tungsten and gas mixture of oxygen (4000 Pa) and argon (36000 Pa) for DUST 1, iron and argon (20000 Pa) for DUST 2, and iron and argon (40000 Pa) for DUST 3. The experiments were run sequentially and automatically started from 100 s after launch of the rocket. The evaporation source of iron was electrically heated under microgravity. Evaporated iron vapor was diffused, cooled and condensed in the gas atmosphere. The temperature and concentration at the nucleation site are determined from the movement of the fringe in the interferogram. Here, we will show the results of the homogeneous nucleation and determine the sticking probability of iron atoms into a nanoparticle based on nucleation theories. The results will be compared with that by ground based experiment.

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Keywords: Nucleation, Sounding Rocket, Interferometer, In-situ Observation, Cosmic Dust

Ion-Induce nucleation experiment I: development of a new apparatus

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Mechanisms of grain nucleation have attracted researchers in various fields of science in connection with e.g. atmospheric aerosols and cosmic dust grains. Although there have been many theoretical and experimental works approaching this issue, the details of nucleation mechanism is still in debate. Most of works are performed assuming homogeneous nucleation in gas phase or heterogeneous nucleation on the bulk surfaces. The homogeneous nucleation often suffers from a "critical size" of particle and requires high supersaturation condition to gain the efficient formation rate, while the nucleation on the bulk surface may not be relevant to the first stage of grain formation in realistic environments. It is known that ion-induced heterogeneous nucleation would play an important role in the particle formation because in this mechanism ion-neutral interaction overcomes difficulties expected in neutral-gas-phase homogeneous nucleation. We recently developed a new experimental apparatus to investigate the elementary process of the ion-induced nucleation. We present the importance of ion-induced nucleation and advantages of the newly developed apparatus. Using this apparatus, we have been successful in obtaining an important physical parameter, free energy, of water cluster ions.

Keywords: cluster ion, ion-induced nucleation

Mid-infrared Observation of sungrazing comet C/2012 S1 (ISON) with Subaru+COMCIS

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Comets are the frozen reservoirs of the early solar nebula and are made of ice and dust. Dust grains in comets have been used to investigate the formation conditions of the solar system. A silicate feature is often observed in comet spectra in mid-infrared region, for example 11.3-micron, and may be used for probing early history of the solar system. In most cases the feature shows the existence of crystalline silicate together with amorphous silicate. Since the crystalline silicate grains are generally made through high-temperature annealing above 800K from amorphous ones, it is believed that the crystalline silicate grains produced at the inner part of the disk were transported to the outer cold regions where comet nuclei formed.

Comet C/2012 S1 (ISON) is a long-period Oort cloud comet, discovered in September 2012. In particular, comet ISON is a sungrazing comet, which is predicted to pass close by the Sun and Earth and becoming a bright object. Mid-infrared observations of this new comet and investigation of the 10-micron silicate feature help us to understand the formation of crystalline silicate grains in the early solar nebula.

We observed comet ISON in mid-infrared wavelength region using Cooled Mid-Infrared Camera and Spectrometer (COMICS) mounted on the Subaru Telescope on Mauna Kea, Hawaii. The observation of comet ISON was carried out on 2013 October 19th and 21st UT. Since the weather condition was not so good when we observed, we carried out N-band imaging observations (8.8 and 12.4 micron) and N-band low-resolution spectroscopy. The spectrum of C/ISON can be fit with 260–265 K blackbody spectrum when we use the 7.8–8.2 and 12.4–13.0 micron region as the continuum. The spectrum has only a weak silicate excess feature, which may be able to attribute to small amorphous olivine grains. We could not detect a clear crystalline silicate feature in the spectrum. We will compare the spectrum with other Oort cloud comets, such as comets C/2011 L4 (PanSTARRS) and C/2013 R1 (Lovejoy), and discuss the dust properties and the birthplace of the comet C/ISON.

Keywords: comet, dust, silicate, infrared

Observation of surface structure of amorphous solid water by atomic force microscope at low temperatures

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Amorphous solid water (ASW) is one of the important materials in space because it exists an abundant and effects to evolution of interstellar molecules. In molecular clouds, it is well known that chemical reactions on icy interstellar dust grains which consist of ASW mantle and mineral particle core are key processes in the formations of important organic molecules (ie. H₂CO, CH₃OH) and deuterium-enriched molecules. Although ASW surface play an important role as a field of chemical reactions, the surface structure of ASW has yet to be revealed.

Recently, we developed a low temperature atomic force microscope (AFM) for study of the surface structure of ASW. AFM is a powerful tool to study the surface structure of ASW because it can work even if the surface do not have a conductive property. In this presentation, we show AFM images of ASW surfaces which were formed at several conditions. ASW were formed on Si(111) 7×7 at 103-135 K with various deposition rate (0.08-0.8 nm/min) and various thickness(2.5-22 nm). From the observations of surface structure, we discuss the relation between the surface structure and the condition of ASW formation.

Keywords: amorphous ice, interstellar dust, molecular clouds, atomic force microscopy

Experimental approach to the formation of organic molecules following vacuum-ultraviolet irradiation of interstellar ice

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Cosmic gases and dust grains ejected from dying stars gradually assemble under the influence of gravity to form interstellar clouds. Among these gases, heavy elements such as magnesium (Mg) and silicon (Si) are incorporated in dust. Lighter and chemically active elements (e.g., hydrogen, carbon, oxygen, and nitrogen; H, C, O, N, respectively) play important roles in the chemistry of interstellar clouds. After the temperature and photon field decrease when the density of dust particles increases in interstellar clouds, atoms (e.g., H, O, C, N) and molecules (e.g., CO) deposit onto the dust surfaces. Cold-surface reactions proceed on the grain surface, and an ice mantle, which is predominantly composed of H₂O combined with other molecules such as CO, CO₂, NH₃, CH₄, H₂CO, and CH₃OH, is formed.

The ice mantles are also subjected to substantial energetic processing by the prevailing ultraviolet radiation during the lifetime of an interstellar cloud. Followed by repeated processing when cycling between diffused clouds and dense clouds, new refractory organic molecules are formed in the ice mantles. The ice mantles undergo further photon radiations upon the formation of protoplanetary disks, and finally evolve to non-volatile complex organic residues by irradiation and thermal processing. However, the detail of the chemical evolution of the organic molecules has still been ambiguous. Although the previous laboratory studies using infrared spectroscopy can provide the presence of polar compounds such as amines, carboxylic acid or amides functions, it often suffers from the low sensitivity and the difficulty to obtain precise identifications of molecular species due to the overlapping of broad solid-state bands. Since dust grains and ice mantles are the precursors of planetary material, studying the photoprocesses is essential to understanding the origin of our solar system, and more powerful analytical techniques are required to unveil rich chemistry of the ices in interstellar clouds and protoplanetary disks.

Here, we are going to present a talk about a new apparatus which is now under construction to shed light on the chemical evolution of organic molecules in interstellar clouds and protoplanetary disks. The apparatus consists of three basic parts, i.e., a vacuum system, a copper-substrate equipped with a closed cycle helium refrigerator, and a vacuum ultraviolet source. Multi-component interstellar ice analogues are created on the cold (10 K) substrate by vapor deposition, and subjected to irradiation by the ultraviolet. The irradiated ice is subsequently heated up to 800 K. The gas composition desorbed from the ice during heating is analyzed by a high-resolution quadrupole mass spectrometer in the vacuum chamber. The survived organic residue from heating are studied using gas chromatography coupled to mass spectrometry (GC-MS) and high performance liquid chromatography coupled to mass spectrometry (HPLC-MS).

Keywords: interstellar cloud, protoplanetary disk, ice mantles, complex organic molecules

Hydrogen addition reactions of C_2H_2 on cold grains; clue to the formation mechanism of cometary C_2H_6

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Volatiles incorporated into comets were formed in the pre-solar molecular cloud and probably chemically altered in the proto-planetary disk of the Sun. Although physico-chemical evolution from a molecular cloud to the disk is basically understood, detailed evolutionary processes are still in debate; e.g., the fraction of the materials originated in the molecular cloud incorporated into the disk without physico-chemical alterations (some fraction of materials might sublime via accretion shock) and physical conditions (temperature, densities of materials, etc.). To reveal those links, we focused on the molecules formed through grain surface reactions, which occurred under quite low temperature conditions like 10K. We discuss the origin of such molecules in comets (icy small body of the Solar system), which might preserve the information about chemical and physical conditions of proto-planetary disk. Cometary ethane (C_2H_6) and acetylene (C_2H_2) have been observed in multiple comets since 1996 and their abundances relative to H_2O (the major component of cometary ices) is $\sim 10^{-3}$ but with variations. This variation might be caused by the difference in the mixing ratios between the materials originated in the molecular cloud and the disk-processed materials. C_2H_6 has never been detected in the molecular cloud and the formation mechanism of C_2H_6 detected in comets is still in debate. One of the candidates of formation reactions of C_2H_6 is the hydrogen addition reaction of C_2H_2 on the cold grain surface ($C_2H_2 \rightarrow C_2H_3 \rightarrow C_2H_4 \rightarrow C_2H_5 \rightarrow C_2H_6$). In the previous experimental studies, those reactions were evaluated qualitatively and it was concluded that the reaction from C_2H_4 to C_2H_6 occurred more rapidly than the reactions from C_2H_2 to C_2H_4 and it would be a reason for the nondetection of C_2H_4 . To investigate these reactions more quantitatively in realistic conditions for molecular clouds, we performed the laboratory measurements of hydrogen addition reactions of C_2H_2 and C_2H_4 on the amorphous solid water (ASW), respectively.

The experiments were conducted by using laboratory setup for surface reaction in interstellar environment (LASSIE) at the institute of low temperature science, Hokkaido University³. A cryogenic aluminum substrate is located in the center of the main chamber and surrounded by a large copper shroud connected to a liquid-nitrogen reservoir. Atomic hydrogen used for the reactions were produced by the dissociation of H_2 molecules in microwave-induced plasma. The kinetic temperature of hydrogen atoms were ~ 120 K and the H-atom flux was $\sim 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The samples of pure solid C_2H_2 , C_2H_4 , and those on ASW were produced on the substrate at 10, 15 and 20K. Infrared absorption spectra of the ices were measured by FTIR before and during the exposure of H-atom.

Our measurements show basically the same trend as shown in the previous studies. We will discuss the temperature and thickness dependence of the time constant for the sample ices in the poster.

Keywords: molecular formation, grain surface chemistry, Inter Stellar Medium

High Resolution Spectroscopy of Laboratory-Produced Interstellar Molecule having Response to Visible Light

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Diffuse interstellar bands (DIBs) 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 molecule. One of the best approaches to identify carrier molecules of DIBs is a measurement of DIB candidate molecule produced in the laboratory to compare their absorption spectra with astronomically observed DIB spectra.

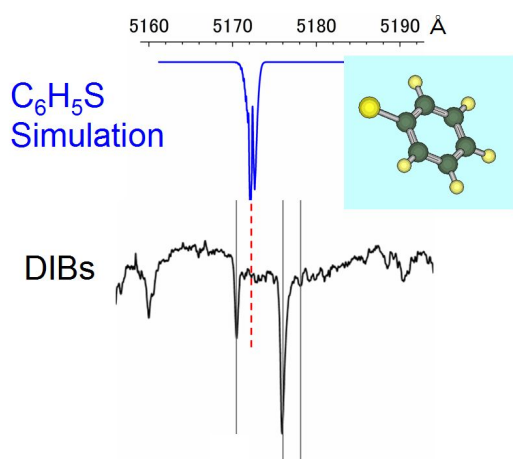
Radical in a gas phase is a potential DIB candidate molecule. The electronic transitions of polyaromatic hydrocarbon radicals result in optical absorption. However, because radicals are unstable, their electronic transitions are difficult to observe using a laboratory spectrometer system. To solve this difficulty, we have developed a glow-discharge cell using a hollow cathode in which radicals can be effectively produced as a high-density plasma. The radicals produced were measured by using the cavity ringdown (CRD) spectrometer and the discharge emission spectrometer.

The CRD spectrometer, which consists of a tunable pulse laser system, an optical cavity and a discharge device, is an apparatus to observe an high-resolution optical absorption spectrum. The electronic transition of thiophenoxy radical C_6H_5S was observed in the discharge emission of thiophenol C_6H_5SH . The frequency of the electronic transition of thiophenoxy radical was measured.

An optical discharge emission was examined by a HORIBA Jobin Yvon iHR320 monochromator. We detected the phenoxy radical C_6H_5O in the discharge of phenol C_6H_5OH . The band observed at 6107 Å in the discharge was assigned to the electronic transition of phenoxy radical on the basis of the sample gas dependences and the reported low resolution spectra. The frequency of the electronic transition of phenoxy radical was measured.

Comparison studies of thiophenoxy and phenoxy radicals were made with known DIB spectra.

Keywords: Diffuse Interstellar Band, interstellar molecule, spectroscopy, cavity ringdown, molecular cloud, discharge



Variation of organic compounds in the polar extract of Murchison meteorite

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Various organic compounds have been found in carbonaceous chondrites, in which water-soluble bio-related organic compounds such as amino acids and carboxylic acids are fully studied mainly because of their great interests to origins of life in the universe and standards available for the analyses. The concentrations of these acids increase significantly after acid hydrolysis of the water extract. Even though a few studies attempted to identify the chemical structures of their precursors (Cooper and Cronin, 1995), the original structures remain largely unclear. The aqueous activity on the meteorite parent body also could proceed in a chemical oxidation (i.e. incorporation of oxygen by hydrous reaction), resulting in the alteration of original organic matter (Oba and Naraoka, 2009). The large abundance of carboxylic acids in the water extract may be attributable to such oxidation processes.

In contrast to the water extract, less polar methanol extract of chondrites has not been characterized well in spite of relatively high content of organic matter with the D- and ¹⁵N enrichment. Recently, ultrahigh-resolution mass spectral analysis on various solvent extracts of the Murchison meteorite (CM2) was performed by electrospray ionization (ESI) using Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) to reveal significant chemical diversity to tens of thousands of different mass peaks having CHO, CHOS, CHNO and CHNOS elemental compositions (Schmitt-Kopplin et al., 2010). With the assumption for molecular formulae calculation and no chromatographic separation, however, the detailed chemical structures of the compounds cannot be determined. In particular, the organic compounds with their elemental compositions of CH and CHN were not discussed. In this study, we performed high-performance liquid chromatography/high resolution mass spectrometry (HPLC/HRMS) analysis of organic compounds in polar solvent extracts of the Murchison meteorite.

Homologous series of alkylpyridines have been identified in the polar solvent extracts of the Murchison meteorite by liquid chromatography/high-resolution mass spectrometry. The wide range of saturated- and unsaturated-alkylated (C1 to C21) pyridines is more diverse relative to that previously found, which could be produced by aldehydes and NH₃ through aldol condensation and Chichibabin-type synthesis on the meteorite parent body. This finding implies a high aldehyde activity under an alkaline condition with ammonia for the chemical evolution of organic matters in carbonaceous meteorites. In addition to the compound distribution of alkylpyridines, the occurrence of other compounds in the water extract will be also discussed with respect to their formation mechanisms in carbonaceous meteorites.

Keywords: polar organic compounds, carbonaceous meteorite, Murchison, high-resolution mass spectrometry

Heating and evaporation of icy dust in transient heating events induced by nebular shocks

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Icy dust plays an important role in chemical evolution from molecular clouds to protoplanetary disks. Simple organic molecules such as formaldehyde (H₂CO) and methanol (CH₃OH) can form in H₂O-CO ice by consecutive addition of hydrogen atoms to CO molecule (Watanabe & Kouchi 2002). Deuterium enrichment in these organic molecules was confirmed to occur by H-D substitution on icy dust surfaces (Nagaoka et al. 2005). More complex organic molecules such as amino acids were detected in the room-temperature residue of an interstellar ice analogue that was ultraviolet-irradiated in a high vacuum at 12 K (Munoz Caro et al. 2002). Sublimation of such icy dust will change the chemical composition of a gas phase in molecular clouds or protoplanetary disks. It is important to elucidate the thermal history of icy dust because it affects the chemical evolution of these organic molecules significantly.

In this paper, we investigated the transient heating event of icy dust induced by nebular shocks. In protostellar or protoplanetary disks, gas accretion from its parent molecular cloud or formation of planetary systems induces shock waves in various conditions. When icy dust passes through the shock front together with the ambient gas, the gas changes its velocity suddenly but the icy dust retains its velocity because of its large inertia. This results in a large relative velocity between them. The high-velocity collision of gas molecules to the icy dust surface raises the dust temperature and leads to its evaporation. Since the relative velocity is reduced by collisions with gas molecules, the heating event should cease within a short period of time. We calculated thermal history and evaporation experienced by icy dust during shock passage for various shock conditions systematically.

The physical model is as follows. We assume that the temperature and density of the post-shock gas are uniform. For simplicity, we consider a spherical icy dust composed of pure H₂O or CO. The icy dust temperature changes much faster than its velocity because of its small thermal inertia. It is shown that the evaporation fraction of individual icy dust defined by the ratio of the decrease in radius to the initial one depends only on the post-shock gas density (ρ_g) and the relative velocity between icy dust and gas just behind the shock front (v_0). We calculated the equations of motion and evaporative shrinkage of the icy dust to obtain the peak temperature and evaporation fraction experienced by the icy dust.

In general, icy dust experiences high temperature and significant evaporation for large v_0 and ρ_g . In addition, we obtained the results as follows: (i) Icy dust does not evaporate completely before it stops relative to the ambient gas even for quite large v_0 and ρ_g . This is due to a negative feedback between the evaporative shrinkage and the duration of heating. (ii) Icy dust hardly evaporates if v_0 is smaller than a certain value. For example, when $v_0 < \sim 3$ km/s for pure H₂O ice or $v_0 < \sim 1$ km/s for pure CO ice, the icy dust shrinks less than by 1% in radius for any gas density. (iii) Icy dust can experience an extremely high temperature at which it would evaporate completely if it were in equilibrium. This is a remarkable feature of the transient heating event that the short heating duration allows the icy dust to survive against superheating.

We elucidated the conditions of icy dust evaporation induced by nebular shocks for various shock conditions systematically. Our results would be useful to discuss the relation between the changes in chemical composition of molecular clouds or protostellar/protoplanetary disks and the evaporation of icy dust by shocks.

Keywords: icy dust, shock heating, evaporation, chemical evolution, protostellar disk, protoplanetary disk

Importance of deuterium fractionation of ethanol by grain surface reactions: experiment of H-D tunneling substitution

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Since we have demonstrated the importance of tunneling grain surface reactions in deuterium fractionation of molecules, many works have targeted this process. To date, we have shown that the grain surface reactions play a crucial role in deuterium enrichments of water, formaldehyde, methanol, and methylamine. In this talk, we present the results of experiment on H-D substitution tunneling reactions of ethanol on cryogenic surfaces. Although C₂H₅OH was observed toward interstellar clouds, its deuterated species have not been detected. However, it was found that its homologous, CH₃OH can be highly deuterated by H-D substitution reactions on grain surfaces and thus it should be reasonable to focus on the potential importance of this process for ethanol. We demonstrated that deuterated methanol is efficiently produced by tunneling reaction of H atoms at very low temperatures relevant to grain surfaces in clouds. H-D reactions predominantly occur in CH₃-CH₂- groups but were hardly observed in an -OH group which is consistent with the methanol case.

Keywords: deuterium enrichment, ethanol, grain surface reaction

Ion-Induce nucleation experiment II: free energy of the water-cluster ion

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Ion-Induce nucleation in gas phase is an important mechanism for grain formation in various circumstances. However, the number of works regarding this formation mechanism is very limited. To investigate the elementary processes of ion-nucleation mechanism, we recently developed a new apparatus (See, the presentation by N. Watanabe in this session). Using this apparatus, the cluster ion formation with an ion core mass-selected, which is the first stage of nucleation, can be observed quantitatively. In this presentation, we show the results of experiment on water-cluster ion formation in which free energies with the size of cluster have been determined. The experiment was performed at temperatures in range of 230-400 K with the supersaturation ratio of about 10^{-3} - 10^{-2} .

Keywords: interstellar grain, cluster ion, nucleation

Detection of levitation dust around the asteroid by Hayabusa-2 LIDAR

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The micron-size particles are continuously produced at the surface of airless bodies like the Moon and asteroids by innumerable micro impacts and thermal stress related to large temperature difference between daytime and nighttime. Previous asteroid missions have revealed smooth appearance of topography on 951 Gaspra, 243 Ida, and 433 Eros suggesting that these asteroids are covered with particles smaller than resolution of camera images. Particularly, the exploration of Eros by NEAR Shoemaker has revealed as smooth surface as a liquid water at the base of craters whose diameter is between 20 and 300 m. This "pond" is consistent with stagnant dusts of diameter smaller than 50 microns. Based on this observation, dust levitation hypothesis was proposed. According to this hypothesis, a photoelectric effect of solar UV positively charges both dust and the surface. Then a balance between electric repulsion and gravity causes 0.5-microns dusts to oscillate vertically over the surface of Eros long period of time. When a dust has a horizontal velocity, it transfers laterally until it reaches to a shadow of topography where electrostatic field is weaker than surroundings. Thus topographic depression such as a crater becomes a sink of levitating dusts.

LIDAR is one of four remote-sensing instruments onboard Hayabusa-2, and is used to measure altitudes of the spacecraft from a surface of the asteroid, 1999 JU3, for not only secure navigation but also scientific investigation of a C-type asteroid. Hayabusa-2 LIDAR has been improved from that onboard Hayabusa which explored and returned samples from asteroid 25143 Itokawa. A new function called dust count mode is implemented to Hayabusa-2 LIDAR to observe spatial distribution of dust number density in 8 levels with resolution of 20 m in bore sight direction. LIDAR can hardly observe lateral distribution of dusts, but distinguish a weak reflection of thin dust cloud from that of the surface. To plan an operation of the dust count mode observation is difficult because the number density of asteroid dust is not known at all. Instead, we evaluate the lower bound of number density that is geologically important for morphology of asteroid surface. For a given number density of dusts and under an assumption that a characteristic time of levitation is the rotation period of 1999 JU3, the rate of embayment of craters is calculated. If this rate of embayment is greater than that of crater production, we need to take into account a modification process for the study of crater morphology and crater counts of 1999 JU3. This lower bound is calculated to be 10^6 m^{-3} for a cloud of dusts whose radius is larger than a few microns. Then we set this value as a target of the dust count mode observation.

A detectability of dust count mode is dependent on sensitivity of Hayabusa-2 LIDAR and an altitude of the spacecraft. We calculate a reflection from dusts using Mie scattering model assuming that a diameter of dust particle is constant and is larger than the wavelength of laser, that is, 1064 nm. A characteristic distance between dusts is also assumed to be sufficiently larger than the wavelength so that interaction between dust particles is negligible. Using a lidar equation, we calculate a peak power of backscattering light from a dust cloud for various sets of the distance, the number density, and the dust radius. The peak power of reflection is generally stronger than noise level of the detector. The reflection from dust cloud is so weak that the targeted number density of 10^6 m^{-3} is hardly higher than the detection limit. Even at the lowest altitude, the reflection from a dust cloud of 10-microns radius for 10^6 m^{-3} number density is equivalent to the detection limit. If the dust radius is 5 microns, number density more than 10^7 m^{-3} is necessary to be detected. Therefore we plan to start the dust count operation from the HP and attempt to conduct as much operations as possible at low altitude.

Condensation of forsterite under protoplanetary disk conditions

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Meteoritic evidence indicates that dust condensation occurred in the early stage of solar system evolution. In this study, we succeeded in performing condensation experiments of forsterite under controlled protoplanetary-disk conditions, which will make significant contribution to understanding silicate formation and chemical fractionation in protoplanetary disks.

Condensation experiments were carried out in the system of Mg_2SiO_4 - H_2 - H_2O . A mixed gas of H_2 and H_2O was flowed into a continuously evacuated infrared vacuum furnace at a controlled rate to keep a pressure constant. Synthetic forsterite powder in an Ir crucible was heated as a gas source. A part of evaporated gases were condensed on a Pt mesh located at a cooler region in the chamber. The pressure and temperature conditions were close to those of protoplanetary disks. The total pressure of the system was 5.5 Pa, and the substrate temperature ranged from 1320 to 1160 K. The H_2O/H_2 ratio was set at 0.015, which was about 15 times larger than the solar ratio. The SiO/H_2 ratio was evaluated to be about 0.7-2 % of the solar ratio from the weight loss rate of the gas-source forsterite. Experimental duration ranged from 6 to 237 hours.

Sub-micron to micron-sized condensates covered with Pt substrates at 1160 and 1275 K, but no condensates were found at 1320 K. The typical size of condensates at 1160 K was less than 1 micron irrespective of experimental duration and no effective growth of each condensed grain was observed. Condensates at 1275 K for >40 hours partly had several micron-sized flat regions. EDS analyses showed that chemical compositions of condensates were consistent with the stoichiometry of forsterite, and their EBSD patterns were well fitted with the patterns from crystalline forsterite. Coincident EBSD patterns were obtained from the flat region of condensates at 1275 K, suggesting that the area was covered with a single crystal. TEM observation of condensates at 1160 K also found that the condensates were polycrystalline forsterite with a thickness of 30-150 nm, and infrared absorption spectra of condensates show clear 10-micron absorption features resembling those of crystalline forsterite. These evidence indicates that polycrystalline forsterite condensed at 1275 and 1160 K.

The mean free path of gas molecules under the present experimental conditions is less than 1 mm, and the evaporated forsteritic gas and the ambient H_2 - H_2O gas are expected to be well mixed. Supersaturation ratios (S) for experiments at 1320, 1275, and 1160 K are thus estimated to be <1.2, <10, and <1000-2000. These supersaturation ratios correspond to the supercooling of <5, <60 and <170 K, respectively.

No condensates were found at 1320 K because the degree of supersaturation was too small for nucleation of forsterite or even the vapor was not saturated with forsterite ($S < 1$). The condensates at the supercooling of <170 K (1160 K) imply that heterogeneous nucleation of new grains occurred successively on preexisting grains. On the other hand, with the supercooling of <60 K (1275 K), some grains seem to have grown up to several microns, and some seem to have newly nucleated on preexisting grains, suggesting that both nucleation and growth of each condensate occurred.

These differences would result in a structural difference in forsterite dust condensed in protoplanetary disks. Fluffy aggregates of sub-micron sized fine particle would form with a supersaturation of >1000, while aggregates of micron-sized grains would form with S of 10 that could be an analogue of amoeboid olivine aggregates in chondrites.

Keywords: forsterite, condensation, protoplanetary disk

A New Experiment for Organic Molecule Formation by Catalytic Reactions on the Surface at Low Temperature and Pressure

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Abundant H₂, CO and N₂ gases react to be more complex molecules mainly on the cooled surface of cosmic dust particles in the molecular cloud and/or primitive solar nebula [1]. The production of organic molecules and subsequent evolution to organic materials in the solar nebula may contribute to the primordial organic system of the Earth. Catalytic chemical reactions are possible production pathway of organic materials in the solar nebula after the formation of simple molecules on nanometer sized cosmic dust particles in the molecular clouds. Experimentally, organic molecules ranging from methane (CH₄), ethane (C₂H₆), benzene (C₆H₆) and toluene (C₇H₈), to more complex species such as acetone (C₃H₆O), methyl amine (CH₃NH₂), acetonitrile (CH₃CN) and N-methyl methylene imine (H₃CNCH₂) have been produced using such as the Fischer-Tropsch type (FTT) and Haber-Bosch type (HBT) reactions on analogs of naturally occurring grain surfaces [2]. Previous studies were performed at higher-temperature (>573 K) and pressure (~1 atm) than the expected conditions in the solar nebula [3-6]. However, since the actual environment is at lower temperature and pressure, it is not clear whether the previous experimental results can be extrapolated to the solar nebula. Our group seeks to elucidate the reaction rates of chemical reactions including isotopic fractionation at lower temperature (100-500 K) and pressure (10⁻³-10⁰) and their contribution to the primordial organic system of the Earth.

We are constructing a vacuum chamber based on a new concept to conduct the experiments mentioned above. The chamber with a differential pumping system has a temperature-controlled substrate, a Fourier transform infrared spectrometer (FT-IR), and two quadrupole mass spectrometers (Q-MSs). The substrate has an iron or silicate thin film for FTT and HBT reactions and the FT-IR measures the vibration modes of adsorbed and produced molecules on the surface and the Q-MSs detect volatile and nonvolatile molecules, respectively. As a result, reaction rates of molecules such as H₂, CO, N₂ and NH₃ on iron or silicate substrate will be obtained as a function of temperature and pressure.

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Keywords: Organic molecules, Catalytic reactions, Protoplanetary system

Dust movement and chemical evolution of proto-solar disk

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Origin and evolution of the protoplanetary system have been developed mostly from the dynamic point of view, which includes two competing theories, and which has been improved by astrophysical observation of exoplanets and extrasolar planetary systems. On the other hand, examination of meteorites and samples by planetary explorations such as lunar samples, cometary particles, and regolith particles of the asteroid Itokawa enable us to gain insight into the evolution of the Solar System. Although those primitive materials give various information, they are not linked to the physical processes in the primary Solar System.

The purpose of this study is to demonstrate how chemical composition distribution evolves over time in the early stage of the proto-solar disk. In order to combine physical processes and chemistry, we have developed a new model consisting of chemical equilibrium calculation and particle tracking equations. At first, we calculate the chemical composition of starting particles at each position in the protoplanetary disk, to track their each motion in the evolving disk, and to analyze the bulk composition of particles that came from various positions in particular time and space. Then, the dynamic evolution of individual particles is calculated in one-dimensional steady-state disk model. In an early stage, particle located in the inner region of the disk have a composition rich in refractory components and those outside have unfractionated CI-like composition. Particles in average move inward by the angular momentum conservation, but a little fraction of them move outward by the turbulent diffusion. Therefore, mixing of refractory particles from inside and CI-like materials from outside takes place, and the mixing ratio vary with time and space.

Because of inward movement of many particles, the relative fraction of particles from outside increases with time for one particular region in the disk, that is, the bulk chemical composition of particles is getting more CI-like. Similarly, the bulk chemical composition of particles at particular place is getting more CI-like with time. Calculations with model parameters of higher temperature of the disk suggest that longer time is needed to replace refractory-rich compositions by a CI-like composition. It is because the radial distance between fractionated particles with refractory-rich composition and unfractionated CI-like materials is longer in a high temperature disk.

Comparing these results and the composition of CM, CO, CV chondrites, it is concluded that CV composition can be reproduced at the most inner region, CO in the next, and CM most outer region in the disk. The present work shows that the composition of carbonaceous chondrites were formed at the asteroid belt region at the early stage of disk evolution with the wide spread of high temperature region.

Keywords: protoplanetary disk, chemical evolution, dust movement, chemical equilibrium