

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.

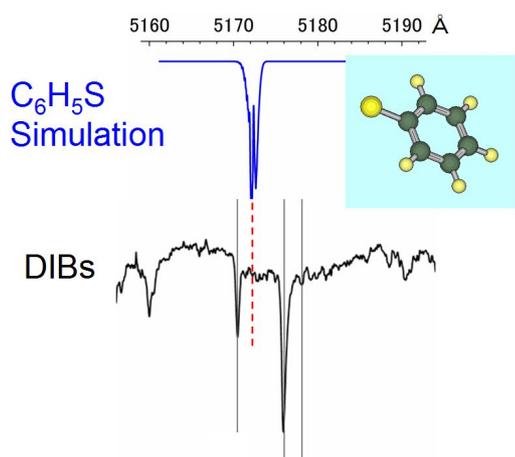
Radical in a gas phase is a potential DIB candidate molecule. The electronic transitions of polyaromatic hydrocarbon radicals result in optical absorption. However, because radicals are unstable, their electronic transitions are difficult to observe using a laboratory spectrometer system. To solve this 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.

A 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