

## Evolution of inorganic and organic matters during the early stages of aqueous activity in a cometary body recorded in Antarctic micrometeorites

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Introduction: The interactive evolution of inorganic and organic materials is one of the hot issues of planetary science with a special interest to the search of possibility of life in planetary systems. Micrometeorites (MMs) recovered from surface snow of the Antarctica are extremely primitive, which contains ultracarbonaceous and chondritic porous MMs (CP MMs), and we have made a systematic investigation of MMs by using SEM, TEM, XANES, and SIMS to get through understanding of the evolution and interaction of inorganic and organic materials in planetary environments.

Samples and methods: We collected ~400 MMs preserved in ~300 kg snow, and selected seven porous MMs, which were embedded in annealed Au sheet with a hydraulic press in the clean room and coated by Pt, from which ~100 nm-thick FIB sections were prepared without using organic epoxy resin. The FIB sections were processed with a low voltage argon ion milling machine to minimize the damage during FIB sample preparation. Carbon-, N-, and O-XANES spectra of the FIB sections were acquired using STXM, and then, TEM observation was performed. Isotope imaging was performed for the remainder of D10IB009 CP MM pressed into a Au sheet for isotopographs of  $^1\text{H}^-$ ,  $^2\text{H}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ ,  $^{12}\text{C}^{15}\text{N}^-$ .

Results and discussion: The MMs show evidence for very early stages of aqueous activities for both inorganic and organic components, and we recognize three stages based on mineralogy and chemistry of organic and inorganic materials. Stage I is characterized by alteration only in organic materials, but inorganic materials do not show evidence for aqueous alteration. The inorganic materials are totally anhydrous including GEMS and enstatite whiskers/platelets, which are almost identical to those in anhydrous IDPs. Organic materials in two MMs at this stage have abundant high carboxyl functionality, and one of them contains nitrile and/or nitrogen heterocyclic groups with D and  $^{15}\text{N}$  enrichments, which are thus highly pristine. However, other two CP MMs are poorer in organic materials and show high aromaticity, which are indistinguishable from those of hydrated carbonaceous chondrites. Stage II is characterized by alteration of inorganic matter. GEMS was changed into GEMS-like amorphous silicate by hydration and oxidation, and the GEMS-like amorphous silicate in Stage II has relatively homogenous compositions than GEMS in Stage I. Nano-phase Fe metal that was abundant in the stage I was depleted, and instead, Fe-rich phyllosilicate was found coexisting with GEMS-like amorphous silicate. Stage III is defined by the appearance of Mg-rich phyllosilicate and Mg-Fe carbonate, which indicates reactions among Fe-rich phyllosilicate in Stage II, Mg-rich olivine and pyroxene, and organic materials and/or C-bearing ice.

The MMs are porous and "freeze-dry" processes took place during and after aqueous alteration, where liquid water was sublimated. The temperature of the reaction would be kept at near zero degree C. Possible parent bodies would be comets or icy asteroids. If further aqueous alteration took place, magnetite would be formed, which is often observed as framboidal aggregates and

plaquettes in IDPs. The aqueous alteration in comets and porous icy bodies differ from that in chondrite parent bodies in that it took place locally and heterogeneously. On the other hand, aqueous alteration in chondrite parent bodies took place more homogeneously due to pervasive liquid water distribution in more compact bodies.

Keywords: comet, aqueous alteration, inorganic-organic matter

## Amino acid synthesis from aldehydes and ammonia in the presence of olivine

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## [Introduction]

Carbonaceous chondrites, which have primitive chemical compositions in the Solar System, contain a diverse suite of extraterrestrial amino acids. Since the discovery of the building blocks of terrestrial life in the extraterrestrial materials, the amino acids have been most investigated among meteoritic organic compounds. In particular, the degree of aqueous alteration on meteorites appears to have correlation to the amino acid distribution (e.g.  $\alpha$ -aminoisobutyric acid and  $\beta$ -alanine) and L-enantiomeric excess (Lee) of isovaline. Although these results suggest that aqueous alteration have influence on amino acid synthesis on the meteorite parent body, the detailed formation mechanisms remains unclear. In this work, we performed the amino acid synthesis experiments simulating the condition of meteorite parent body to investigate their distribution and enantiomeric composition to infer the formation mechanism of meteoritic amino acids.

## [Materials and Methods]

Aqueous solution (300  $\mu$ L) containing ammonia/formaldehyde/acetaldehyde or ketone (100/10/1 by mol) was heated at 60 °C for 6-28 days in a N<sub>2</sub>-purged glass ampoule with or without olivine powder (San Carlos, 27.0 mg). The reaction product was extracted with hot water, and the supernatant was divided into two fractions. Then one was subjected to acid hydrolysis with 6M HCl, the other was not hydrolyzed. After purification using ion exchange column, both fractions were derivatized with iPrOH/HCl and trifluoroacetic anhydride. The resultant amino acid derivatives were analyzed by gas chromatography/mass spectrometry. The amino acids were identified and quantified based on their retention times and mass spectra of standards.

## [Results and Discussion]

Totally 16 amino acids up to C<sub>5</sub> were identified, in which glycine was the most abundant (up to approximately 3500 ppm relative to carbon amount of reactants). Other amino acids are composed mainly of serine, isoserine, alanine,  $\beta$ -alanine,  $\beta$ -(aminomethyl)succinic acid,  $\beta$ -aminobutyric acid, homoserine, aspartic acid and glutamic acid (up to approximately 600, 250, 240, 240, 160, 110, 60, 60 and 50 ppm, respectively). In the absence of olivine, relatively small amounts of glycine, serine, isoserine, alanine,  $\beta$ -alanine and  $\beta$ -aminobutyric acid were detected (up to approximately 840, 30, 110, 80, 90, and 90 ppm, respectively) from the hydrolyzed fraction. In contrast, in the presence of olivine, the concentration of most of the amino acids (up to approximately 3500, 600, 250, 240, 240 and 110 ppm, respectively) increased significantly in the hydrolyzed fraction. The amino acid concentration increased significantly after hydrolysis, which is similar to the occurrence of meteoritic amino acids.

The amino acid distribution (e.g. absence of  $\alpha$ -aminoisobutyric acid and isovaline) implies a different formation pathway from the Strecker-type reaction, which has been proposed for meteoritic amino acid synthesis. We propose other formation mechanisms: iminium cation produced from aldehydes and ammonia is subjected to nucleophilic addition by formyl anion followed by chemical oxidation, giving  $\alpha$ -amino acids detected in this experiment. In addition, larger amino acids (> C<sub>3</sub>) are synthesized through aldol condensation, explaining the occurrence of  $\alpha$ -,  $\beta$ -amino acids detected.

Further experimental studies are needed to reveal the detailed formation mechanism of amino acids from aldehydes and ammonia with olivine.

Keywords: amino acids, carbonaceous chondrite, aqueous alteration process, olivine, aldol reaction

## Thermal desorption of molecules from grain surface by accretion shocks: the effect of distribution of desorption energy

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Gravitational collapse of a molecular cloud is a transient process to form protostars and protoplanetary disks. The in-falling envelope onto the Keplerian disk often induces accretion shocks at their boundary. Recent ALMA observations suggested sublimation of various molecules, such as SO, from the icy grain surfaces (host grains) at the shocked region [1,2]. The sublimation would considerably affect the chemical environment of the nebula. The shock conditions for the sublimation were calculated numerically in a few papers [3-5]. However, these results were negative for the sublimation of molecules because the shock condition speculated from the ALMA observations is insufficient to sublime SO molecules from the host grains [4,5].

The numerical models assumed that the desorption energy of a certain molecular species is a single (average) value. However, temperature-programmed desorption (TPD) experiments indicated that the desorption energy is not well represented by a single value because of the heterogeneity of the host grain surfaces [e.g., 6]. If the desorption energy has a deviation from its average value, the sublimation from adsorption sites having smaller desorption energies may occur even by weaker shock heating. In this study, we revisit the desorption fraction when the distribution of the desorption energy is taken into consideration.

Let  $f(E_d)$  be the distribution of the desorption energy,  $E_d$ , of a certain species. The fraction of molecules that have the desorption energies in a range from  $E_d$  to  $E_d + dE_d$  is given by  $f(E_d)dE_d$ . The desorption fraction  $\langle P_d \rangle$  is calculated by integrating a product of  $P_d(E_d)$  and  $f(E_d)$  over  $E_d$ , where  $P_d(E_d)$  is the desorption probability of molecules as a function of  $E_d$ . In order to obtain  $P_d(E_d)$ , we numerically calculate the thermal history of host grains based on the one-dimensional plane-parallel shock-wave heating model [e.g., 7]. In addition, we assume that  $f(E_d)$  is the normal (Gaussian) distribution with the mean  $E_{d0}$  and the standard deviation  $\Delta E_d$ . We investigate the dependence of  $\langle P_d \rangle$  on  $\Delta E_d$  for various shock conditions.

Let us introduce the numerical results of when molecules adsorbed on 0.1 micron-sized host grains with  $E_{d0} = 2000$  K meet the accretion shock with the pre-shock gas number density of  $10^8 \text{ cm}^{-3}$  and the shock velocity of 1 km/s. When the desorption energy has no deviation ( $\Delta E_d = 0$  K), we obtain  $\langle P_d \rangle = 1.7 \times 10^{-9}$ .  $\langle P_d \rangle$  increases with the increase of  $\Delta E_d$ :  $\langle P_d \rangle = 1.7 \times 10^{-8}$ ,  $1.7 \times 10^{-5}$ , and  $1.5 \times 10^{-2}$  for  $\Delta E_d = 100$ , 200, and 400 K, respectively. The deviation of the desorption energy increases the desorption fraction of molecules by orders of magnitudes. This result suggests that molecules adsorbed on the host grains in molecular clouds can desorb more easily than that expected before.

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Keywords: Accretion shock, Icy grain, Shock heating, Adsorbed molecules, Sublimation

## ALMA observations of CO gas depletion in the protoplanetary disk around TW Hya

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Protoplanetary disks are the natal place of planets and ALMA observations are now revealing the physical and chemical structure of planet forming regions in the disks. Understanding chemical components of gas, dust and ice in the disks is essential to investigate the origins of materials in the planets. In the talk, I shall report our recent ALMA Band 7 observations of CO isotopologue lines from the protoplanetary disk around TW Hya. The result shows a significant decrement in CO gas throughout the disk even inside the CO snowline, indicating freeze-out of gas-phase CO onto grain surfaces and possible subsequent surface reactions to form larger molecules. Complex organic molecules could be efficiently produced in the observed CO gas depleted regions.

Keywords: protoplanetary disks, CO line emission, formation of organic molecules

## How to measure snowlines and C/O ratio distributions in protoplanetary disks using infrared spectroscopic observations

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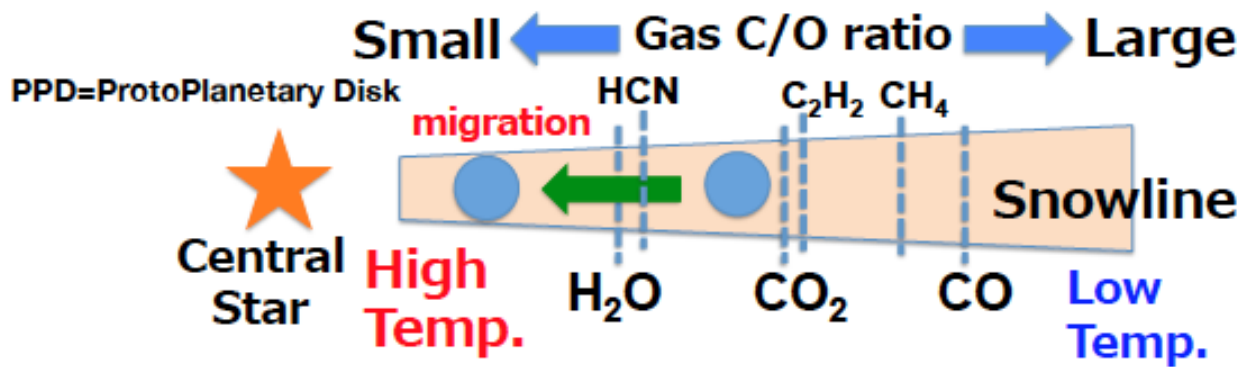
Protoplanetary disks are active environment for the creation of relatively simple molecules (e.g., H<sub>2</sub>O, CO, CO<sub>2</sub>, HCN) and complex organic molecules (COMs). The emission lines of these simple molecules from disks are detected by the infrared spectroscopic observations using Spitzer space telescope and large ground-based telescopes like VLT, Keck (e.g, Pontoppidan et al. 2010a&b, Mandell et al. 2012).

Since protoplanetary disks rotate with keplerian velocity, the emissions from disks have characteristic profiles due to doppler shift. Analyzing the profiles of lines, we will obtain the information on the distance from the central star of the line emitting regions. We have calculated the chemical structures of protoplanetary disks and radiative transfer of H<sub>2</sub>O lines, and have proposed the method to locate the H<sub>2</sub>O distributions of near the midplane of the inner disk, using spectroscopic observations. We have found that we can obtain the information on the H<sub>2</sub>O snowline through investigating the profiles of some emissions that have small Einstein A coefficient and relatively large energy in the upper level (e.g., Notsu et al. 2016a, ApJ submitted, 2016b, in prep.).

It is thought that difference in snowlines of oxygen- and carbon-bearing molecules, such as H<sub>2</sub>O, CO, HCN, CO<sub>2</sub>, will result in systematic variations in the C/O ratio both in the gas and ice (e.g., Oberg et al. 2011, Pontoppidan et al. 2014). In addition, the C/O ratio of atmosphere of some exoplanets (e.g., Hot Jupiter) were measured by recent studies (e.g, Madhusudhan et al. 2014). Therefore, the planet forming regions could be confined through comparing the radial distributions of C/O ratio in disks and those of planetary atmospheres.

In this study, we developed our calculations of disk chemical structures for T Tauri disk, and investigate the abundance distributions of simple molecules. We then calculated radiative transfer of various lines of simple molecules. We found that through investigating the profiles of lines with various Einstein A coefficients and excitation energies, we can detect C/O ratio distributions of various molecules in disks. For example, HCN lines from a T Tauri disk in 14 $\mu$ m band reflect gas distributions of inner disks. In contrast, HCN lines in 3 $\mu$ m bands reflect those of outer disks. We also discuss the possibility to measure such molecular lines with future near- and mid-infrared spectroscopic observations. In addition, we will discuss the results for Herbig Ae disk case, if we have a time.

Keywords: snowline, protoplanetary disk, chemical reactions, C/O ratio, infrared spectroscopic observation, planet formation



There are radial dependences of Gas & Dust  
C/O ratio in Protoplanetary disks.

e.g., Pontoppidan et al. 2014



## Temperature dependence of reaction efficiency in the Fischer-Tropsch-type catalytic reaction on an iron substrate

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Fischer-Tropsch type catalytic reaction has been believed to be one of simplest and most fundamental formation processes of organic molecules, which dominantly occurred on the surface of cosmic dust particles, such as iron, magnetite, amorphous iron silicate and graphite, in the period from the late stage of molecular cloud to the solar nebula. Experimental approaches to find the environment, where catalytic reaction was progressed efficiently, have been attempted in laboratories [1-5]. In the experimental studies, organic molecules ranging from methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), benzene (C<sub>6</sub>H<sub>6</sub>) and toluene (C<sub>7</sub>H<sub>8</sub>), to more complex species such as acetone (C<sub>3</sub>H<sub>6</sub>O), methyl amine (CH<sub>3</sub>NH<sub>2</sub>), acetonitrile (CH<sub>3</sub>CN) and N-methyl methylene imine (H<sub>3</sub>CNCH<sub>2</sub>) have been produced at temperature above 573 K and relatively high pressure (10<sup>5</sup> Pa). In case of actual environment in the early nebula environment, the temperature and pressure should be below 500 K and under 10<sup>2</sup> Pa, respectively. It is not obvious that the results of the reaction experiments are able to extrapolate to the actual early nebula environment. Therefore, we newly developed an experimental system to test the catalytic chemical reactions in the lower temperature (100-800 K) and pressure (10<sup>-3</sup>-10<sup>0</sup> Pa) using an iron substrate. Our experimental system has a temperature-controlled substrate, a Fourier transform infrared spectrometer (FT-IR), and two quadrupole mass spectrometers (Q-MSs). Although FT-IR is able to measure the vibration modes of adsorbed and produced molecules on the surface, we have not been used it during the first experiment at higher temperature. We found a strong signal of mass 20 in the Q-MSs spectra in a continuous gas flow of a mixture gas of D<sub>2</sub> and CO. The intensity of the signal decreases as temperature decrease from 800 to 400 K and becomes weaker than the detection limit below 300 K. The mass 20 corresponds to D<sub>2</sub>O and CD<sub>4</sub>, which are first products in the Fischer-Tropsch type reaction. In our presentation, the detail results using iron substrate will be presented as a function of temperature.

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Keywords: catalytic reaction, organic molecule, experiment

The precise determination of the  $^{13}\text{C}$  isotopic ratios for carbon chain molecule  $\text{HC}_3\text{N}$  in the low-mass star forming region L1527 by radio observations

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Linear carbon chains have been found in dark clouds. Recently a lot of carbon chains have also been detected in the class 0 object L1527, which is a low-mass star forming region. We observed the normal and isotopic species of the fundamental carbon-chain molecule  $\text{HC}_3\text{N}$  in L1527 with the high signal-to-noise ratios using Green Bank 100 m telescope and Nobeyama 45 m telescope to explore the production scheme of  $\text{HC}_3\text{N}$  in the region having a warm carbon chain chemistry (WCCC). The spectral lines of the rotational transitions in the 44–109 GHz region were used to study the abundances of the normal and isotopic species. The ratios were precisely determined to be  $1.00 : 1.01 \pm 0.03 : 1.35 \pm 0.04 : 86.4 \pm 2.2$  for  $[\text{H}^{13}\text{CCCN}] : [\text{HC}^{13}\text{CCN}] : [\text{HCC}^{13}\text{CN}] : [\text{HCCCN}]$ , where the errors are in one standard deviations. The ratios of  $[\text{HCC}^{13}\text{CN}]/[\text{HCCC}^{15}\text{N}]$  and  $[\text{HCCCN}]/[\text{HCCC}^{15}\text{N}]$  were obtained to be  $5.26 \pm 0.24$  and  $338 \pm 15$ , respectively. It was found that the abundance of  $\text{H}^{13}\text{CCCN}$  is almost equal to that of  $\text{HC}^{13}\text{CCN}$ , and it was concluded that  $\text{HC}_3\text{N}$  in L1527 is mainly formed by the reaction schemes *via*  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_2^+$ , *i.e.* dicarbide chemistry. The obtained ratios are quite similar to those reported in the cyanopolyne peak in the starless dark cloud Taurus Molecular Cloud-1 [2]. Thus this similarity would suggest a universality of dicarbide chemistry producing  $\text{HC}_3\text{N}$  irrespective of evolutionary phases from a starless dark cloud to a class 0 object for a low-mass star forming region.

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Keywords: radio, carbon chain molecule, isotopic ratio

## Formation and evolution of molecular cloud organic matter: Thermal and photo-irradiation effects

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Simulation experiments on UV-photochemistry of molecular cloud ice have shown that complex organic matter remains as a residue after warming up to room temperatures [e.g. Greenberg, 2002]. These compounds could be the precursors of a part of the organic matter found in comets and meteorites, but it is not clear how the organic-bearing ice formed in the ISM may have evolved through temperature increase and irradiations by UV-photons and cosmic rays until their incorporation into Solar System bodies.

We developed an experimental apparatus called PICACHU, an acronym for Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University [Piani et al., 2014] in order to simulate the formation and evolution of ice and organic residues through UV irradiation and heating. Typical ISM gases (a mixture of H<sub>2</sub>O, CO, NH<sub>3</sub>, and CH<sub>3</sub>OH) were deposited onto the substrate cooled down to ~12 K and simultaneously irradiated by UV photons under high vacuum. Gases, desorbed from the ice during heating and post-irradiation, were monitored by a quadrupole mass spectrometer (QMS). In-situ observation of the deposited ice during warm-up and/or irradiation was also made with an optical microscope. A part of the organic residues formed by warming-up was re-irradiated with UV photons at room temperature. The residual organic materials were examined with a laser microscope, an atomic force microscope, a field-emission secondary electron microscope and transmission electron microscopes. Viscoelastic measurements were performed with a nano-indentation technique.

During the warming-up of the UV-photoprocessed ice (H<sub>2</sub>O:NH<sub>3</sub>:CH<sub>3</sub>OH = 2:1:1, 5:1:1, 10:1:1 and, 2:1:0), we observed the deformation of ice film and the formation of bubbles at ~ 65 -140 K, which was not observed for non-irradiated ice. The formation of bubbles was associated with outbursts of gases mostly composed of hydrogen. The formation of bubbles indicates that the ice at low temperature behaves like a supercooled liquid.

The organic residue irradiated by UV-photon (~ 10<sup>14</sup> photons cm<sup>-2</sup> s<sup>-1</sup>) at room temperature for 3-10 days, which corresponds to ≤10<sup>4</sup>-year irradiation in diffuse clouds, showed a significant morphological change from the residues with no room-temperature UV irradiation. The porosity and roughness of the residue increased and discrete and round nanoparticles were observed that may be similar to some nanoglobules found in meteorites. Viscoelastic properties were also changed by the room-temperature UV-irradiation, indicating that organic-coating on inorganic dust could play as efficient glue on dust aggregation but, at the same time, could also enhance the aggregate brittleness.

Keywords: molecular cloud, organic matter, photochemical reaction