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

*Takaaki Noguchi[2], Hikaru Yabuta[3], Shoichi Itoh[4], Takuya Mitsunari, Naoya Sakamoto[5], Aya Okubo[1], Ryuji Okazaki[6], Tomoki Nakamura[7], Shogo Tachibana[8], Kentaro Terada[3], Mitsuru Ebihara[9], Naoya Imae[10], Makoto Kimura[11], Hiroko Nagahara[1]

1.Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 2.Faculty of Arts and Science, Kyushu University, 3.Department of Earth and Space Science, Osaka University, 4.Department of Earth and Plaentary Science, Kyoto University, 5.Creative Research Institution, Hokkaido University, 6.Department of Earth and Planetary Sciences, Graduate School of Science, Kyushu University, 7.Department of Earth Science, Tohoku University, 8.Department of Natural History Sciences, Hokkaido University, 9.Urban Liberal Arts, Tokyo Metropolitan University, 10.Antarctic Meteorite Research Center, 11.College of Science, Ibaraki University

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 $^{1}H^{-}$, $^{2}H^{-}$, $^{12}C^{14}N^{-}$, $^{12}C^{15}N^{-}$.

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}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

*Toshiki Koga[1], Hiroshi Naraoka[1]

1.Department of Earth and Planetary Sciences Kyushu University

[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. α-aminoisobutyric acid and β-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 μL) containing ammonia/formaldehyde/acetaldehyde or ketone (100/10/1 by mol) was heated at 60 °C for 6-28 days in a N_2-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 anhydrite. 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_5 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, β-alanine, β-(aminomethyl)succinic acid, β-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, β-alanine and β-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 α-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 α-amino acids detected in this experiment. In addition, larger amino acids ($> C_3$) are synthesized through aldol condensation, explaining the occurrence of α-, β-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

*Hitoshi Miura[1], Tetsuo Yamamoto[2], Hideko Nomura[3], Taishi Nakamoto[3], Kyoko K. Tanaka[2], Hidekazu Tanaka[2], Makiko Nagasawa[4]

1.Graduate School of Natural Sciences, Nagoya City University, 2.Institute of Low Temperature Science, Hokkaido University, 3.Graduate School of Science and Engineering, Tokyo Institute of Technology, 4.School of Medicine, Kurume University

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 sublimate 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 $f(E_\mathrm{d})$ 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 $E_\mathrm{d} + dE_\mathrm{d}$ is given by $f(E_\mathrm{d})dE_\mathrm{d}$. The desorption fraction $\langle P_\mathrm{d} \rangle$ is calculated by integrating a product of $P_\mathrm{d}(E_\mathrm{d})$ and $f(E_\mathrm{d})$ over E_d, where $P_\mathrm{d}(E_\mathrm{d})$ is the desorption probability of molecules as a function of E_d. In order to obtain $P_\mathrm{d}(E_\mathrm{d})$, 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 $f(E_\mathrm{d})$ is the normal (Gaussian) distribution with the mean E_d0 and the standard deviation ΔE_d. We investigate the dependence of on ΔE_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 meat the accretion shock with the pre-shock gas number density of 10^8 cm^{-3} and the shock velocity of 1 km/s. When the desorption energy has no deviation (ΔE_d = 0 K), we obtain $\langle P_\mathrm{d} \rangle = 1.7\times10^{-9}$. $\langle P_\mathrm{d} \rangle$ increases with the increase of ΔE_d: = 1.7×10^{-8}, 1.7×10^{-5}, and 1.5×10^{-2} for ΔE_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.

References: [1] N. Sakai et al. (2014), Nature 507, 78. [2] H.-W. Yen et al. (2014), ApJ 793, 1. [3] D. A. Neufeld and D. J. Hollenbach (1994), ApJ 428, 170. [4] T. Aota et al. (2015), ApJ 799, 141. [5] H. Miura et al. (2015), Japan Geoscience Union Meeting 2015, abstract PPS24-11. [6] T. Hama and N. Watanabe, 2013, Chem. Rev. 113, 8783. [7] H. Miura et al. (2010), ApJ 719, 642.

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

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

*Hideko Nomura[1], Takashi Tsukagoshi[2], Ryohei Kawabe[3], Daiki Ishimoto[4,1], Satoshi Okuzumi[1], Takayuki Muto[5], Kazuhiro Kanagawa[6], Shigeru Ida[7], Catherine Walsh[8], Tom J Millar[9], Bai Xue-Ning[10]

1.Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2.College of Science, Ibaraki University, 3.National Astronomical Observatory of Japan, 4.Department of Astronomy, Graduate School of Science, Kyoto University, 5.Division of Liberal Arts, Kogakuin University, 6.University of Szczecin, 7.Earth-Life Science Institute, Tokyo Institute of Technology, 8.Leiden Observatory, Leiden University, 9.Astrophysics Research Centre, School of Mathematics and Physics, Queen’s University Belfast, 10.Institute for Theory and Computation, Harvard-Smithsonian Center for Astrophysics

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 plants. 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

*Shota Notsu[1], Hideko Nomura[2], Daiki Ishimoto[1,2], Mitsuhiko Honda[3]

1.Department of Astronomy, Graduate School of Science, Kyoto University, 2.Department of Earth and Planetary Science, Tokyo Institute of Technology, 3.Department of Physics, School of Medicine, Kurume University

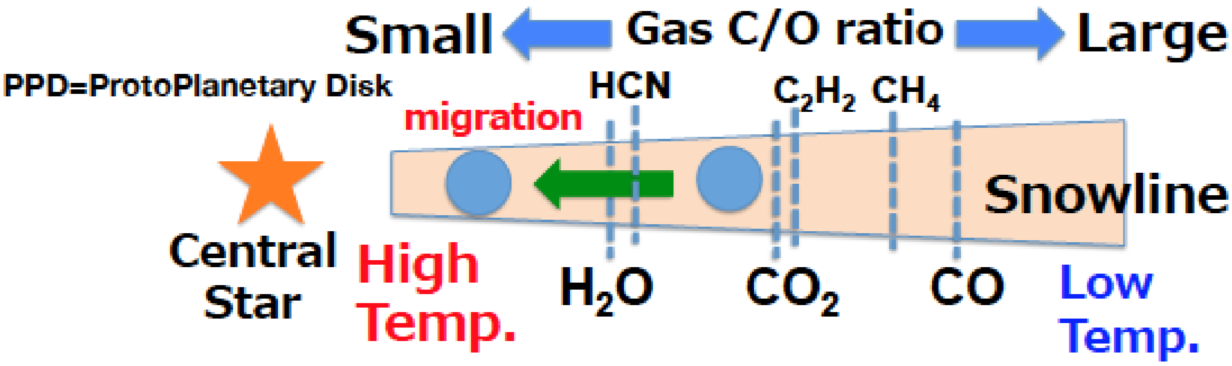
Protoplanetary disks are active environment for the creation of relativley simple molecules (e.g., H_2O, CO, CO_2, HCN) and complex organic molecules (COMs). The emission lines of these simple molecules from disks are detected by the infrared spectroscopic observations using Spitzer space telescope and 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_2O lines, and have proposed the method to locate the H_2O distributions of near the midplane of the inner disk, using spectroscopic observations. We have found that we can obtain the information on the H_2O 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_2O, CO, HCN, CO_2, 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 atomosphere 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 14μm band reflect gas distributions of inner disks. In contrast, HCN lines in 3μm 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-Tropsh-type catalytic reaction on an iron substrate

*Yuki Kimura[1], Rikako Sato[1], Akira Tsuchiyama[2], Hiroko Nagahara[3], Tetsuya Hama[1], Hiroshi Hidaka[1], Naoki Watanabe[1], Akira Kouchi[1]

1.Institute of Low Temperature Science, Hokkaido University, 2.Kyoto University, 3.University of Tokyo

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_4), ethane (C_2H_6), benzene (C_6H_6) and toluene (C_7H_8), to more complex species such as acetone (C_3H_6O), methyl amine (CH_3NH_2), acetonitrile (CH_3CN) and N-methyl methylene imine (H_3CNCH_2) have been produced at temperature above 573 K and relatively high pressure (10^5 Pa). In case of actual environment in the early nebula environment, the temperature and pressure should be below 500 K and under 10^2 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^{-3}-10^0 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_2 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_2O and CD_4, 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.

References

[1] H. G. M. Hill, J. A. Nuth, *Astrobiology*, 3 (2003) 291.
[2] J. A. Nuth, N. M. Johnson, S. Manning, *The Astrophysical Journal,* 673 (2008) L225.
[3] N. M. Johnson, M. McCarthy, J. A. Nuth III, *45th Lunar and Planetary Science Conference*, (2014) 2702.
[4] J. A. Nuth, Y. Kimura, C. Lucas, F. Ferguson, N. M. Johnson, *The Astrophysical Journal Letters*, 710 (2010) 98.
[5] Y. Kimura, J. A. Nuth, N. M. Johnson, K. D. Farmer, K. P. Roberts, S. R. Hussaini, *Nanoscience and Nanotechnology Letters*, 3 (2011) 4.

Keywords: catalytic reaction, organic molecule, experiment

The precise determination of the ^{13}C isotopic ratios for carbon chain molecule HC_3N in the low-mass star forming region L1527 by radio observations

*Mitsunori Araki[1], SHURO TAKANO[2], NAMI SAKAI[3], SATOSHI YAMAMOTO[4], TAKAHIRO OYAMA[1], NOBUHIKO KUZE[5], KOICHI TSUKIYAMA[1]

1.Infrared Free Electron Laser Research Center, Tokyo University of Science, 2.Nihon University, 3.The Institute of Physical and Chemical Research (RIKEN), 4.The University of Tokyo, 5.Sophia University

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 HC_3N 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 HC_3N 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 ±0.03 : 1.35 ±0.04 : 86.4 ±2.2 for [$H^{13}CCCN$] : [$HC^{13}CCN$] : [$HCC^{13}CN$] : [HCCCN], where the errors are in one standard deviations. The ratios of [$HCC^{13}CN$]/[$HCCC^{15}N$] and [HCCCN]/[$HCCC^{15}N$] were obtained to be 5.26 ±0.24 and 338 ±15, respectively. It was found that the abundance of $H^{13}CCCN$ is almost equal to that of $HC^{13}CCN$, and it was concluded that HC_3N in L1527 is mainly formed by the reaction schemes *via* C_2H_2 and $C_2H_2^+$, *i.e.* dicarbide chemistry. The obtained ratios are quite similar to those reported in the cyanopolyyne peak in the starless dark cloud Taurus Molecular Cloud-1 [2]. Thus this similarity would suggest a universality of dicarbide chemistry producing HC_3N irrespective of evolutional phases from a starless dark cloud to a class 0 object for a low-mass star forming region.

[1] Sakai, N., Sakai, T., Hirota, T., & Yamamoto, S. 2008, ApJ, 672, 371
[2] Takano, S., Masuda, A., Hirahara, Y., et al. 1998, A&A, 329, 1156

Keywords: radio, carbon chain molecule, isotopic ratio

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

Laurette Piani[1], *Shogo Tachibana[1], Tetsuya Hama[2], Iyo Sugawara[1], Yasuhiro Oba[2], Hidekazu Tanaka[2], Yuki Kimura[2], Akira Miyake[3], Junya Matsuno[3], Akira Tsuchiyama[3], Hisayoshi Yurimoto[1], Akira Kouchi[2]

1.Department of Natural History Scieces, Hokkaido University, 2.Institute of Low Temperature Science, Hokkaido University, 3.Department of Geology and Mineralogy, Graduate School of Science, Kyoto University

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_2O, CO, NH_3, and CH_3OH) 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 ($H_2O:NH_3:CH_3OH$ = 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 (~ 10^14 photons cm-2 s-1) at room temperature for 3-10 days, which corresponds to ≤10^4-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

Space weathering in the interstellar medium by hydrogen ion irradiation

*Haruka Uchida[1], Aki Takigawa[1,3], Akira Tsuchiyama[1], Koutaku Suzuki[2], Yoshinori Nakata[2], Akira Miyake [1], Akiko Takayama[1]

1.Department of Geology and Mineralogy, Division of Earth and Planetary Sciences, Faculty of Science,Kyoto University, 2.The Wakasawan energy research center, 3.The Hakubi Center for Advanced Research, Kyoto University

Cosmic dust mainly forms around AGB stars and in ejecta of supernova explosions. Crystalline silicates are observed from some oxygen-rich AGB stars but almost absent in the interstellar medium (ISM). The low crystallinity of interstellar dust may be caused by amorphization of the crystalline silicate [1]. In this work, we focus on the irradiation of interstellar dust by accelerated ions by shock waves from supernovae. There are several irradiation experiments of dust analogue minerals such as olivine, enstatite, and diopside [1-4], but irradiation experiments with hydrogen ions, which is the most abundant gas species, are limited. Because structural and morphological changes may depend on irradiated gas species [5], we performed hydrogen ion irradiation experiments to constrain on the irradiation conditions to cause structural changes of ISM dust grains.

We used olivine (Fo_{80}), enstatite, synthetic single crystal forsterite, serpentine ($(Mg_{2.8} Fe_{0.2})_3Si_2O_5(OH)_4$), quenched glass with $MgSiO_3$ composition as substrates. Pyrrhotite ($Fe_{0.9}S$) and iron meteorite were also used to observe the structural changes of FeS and metallic iron in IDP and primitive meteorites. Polished samples were cut into 3 ×5 ×0.5 mm sized pieces, and chemically etched to remove the surface deformation layers. Experiments were carried out in the Wakasa Wan Energy Research Center (WERC). We used H_2^+ ions accelerated to 40 keV and 10 keV. The dose for each energy was 10^{16}-10^{18} ions/cm^2 and 10^{17} ions/cm^2, respectively. Samples after irradiation were observed with a field-emission scanning electron microscope (FE-SEM).

All samples irradiated with 10 keV H_2^+ ions showed no the surface modification. The threshold dose for blister formation on Fe-rich olivine (Fo_{70}) by 10 keV H_2^+ ion irradiation was 10^{17} ions/cm^2 [4], in which condition we did not confirm any blister on relatively iron-poor olivine (Fo_{90}). These results indicate that olivine with higher iron content easily occurs amorphization by the ion irradiation.

Elliptical shaped blisters were observed on the surfaces of olivine, enstatite, forsterite, serpentine, and pyrrhotite irradiated with 40 keV H_2^+ ions. The dose amount for blistering on olivine, enstatite, serpentine, and pyrrhotite was 10^{18} ions/cm^2 and on forsterite was 10^{17} ions/cm^2. The blister sizes on forsterite were about 100 nm, on olivine and pyrrhotite were about 3 μm, and on serpentine were about 4-5 μm, respectively. Wavy shaped blisters were observed on enstatite, which were arranged at intervals of a few μm. No structural changes of the surfaces was observed on the iron meteorite and $MgSiO_3$ glass substrates. The dose amount for blistering on enstatite is an order of magnitude higher than that for amorphization [2]. We observed blisters on pyrrhotite, which is inconsistent with irradiation experiments of 1 MeV Kr^+ [6]. Ion mass and size may cause these differences, or the dose amount for blistering and amorphization may not be identical. We plan to observe the interior structures of the irradiated samples with a transmission electron microscope. In this presentation, we will report the results of SEM and TEM observations and discuss the structural changes due to ion irradiation.

[1] Carrez et al. (2002), MAPS, 37, 1599. [2] Jäger et al. (2003), A&A, 401, 57.
[3] Demyk et al. (2001), A&A, 368, L38. [4] Matsumoto (2014), ph.D Thesis. [5] Muto and Enomoto (2005), Materials Trans., 46, 2117. [6] Christoffersen and Keller, (2011), MAPS 46, 950.

Keywords: Space weathering, Dust, Irradiation experiment, ISM

Development of experimental setups for condensation experiments of enstatite and evaporation experiments of SiO_2-MgO

*Aki Takigawa[1,2]

1.Division of Earth and Planetary Sciences, Kyoto University, 2.The Hakubi Center for Advanced Research, Kyoto University

Enstatite whiskers elongated to the [001] axis were identified in chondritic porous interplanetary dust particles (CP-IDPs), Antarctica Micrometeorite (AMM), and samples from a comet Wild 2, while those elongated to the [001] axis are common in minerals occurred in the Earth and meteorites [1-4]. The condensation conditions of enstatite whiskers, however, have not been shown quantitatively. Moreover, the difference in the morphology of enstatite whiskers may reflect their different condensation conditions in the early solar system. In order to constrain on the formation conditions of enstatite whiskers with different crystal habits, we aim to construct the experimental setup that can control the condensation temperature, supersaturation ratio, and partial pressure of a hydrogen gas. In this presentation, we report the current status of our experimental setups and preliminary results of SiO_2-MgO evaporation experiments.

[1] J. P, Bradley , D. E. BrownLee , D, R, Veblen, Nature 301, 473 (1983).
[2] Noguchi et al . (2008), MAPS, Abst# 5129.
[3] Ishii H.A. et al. (2008), *Science* 319, 447-450.
[4] Nakamura-Messenger et al. (2009) , MAPS, Abst# 5330.

Keywords: experiment, condensation, evaporation, enstatite

AKARI observations of asteroidal dust

*Takafumi Ootsubo[1], Fumihiko Usui[2]

1.Graduate School of Arts and Sciences, University of Tokyo, 2.Graduate School of Science, University of Tokyo

The zodiacal emission is the thermal emission from the interplanetary dust and the dominant diffuse radiation in the mid- to far-infrared wavelength region. From the results of the Infrared Astronomical Satellite (IRAS) observations, it was found that there are many small-scale structures in the zodiacal emission distribution, such as dust band pairs at the ecliptic latitudes of +/-1.4 and +/-2.1 degrees (the inner band) and +/-9.3 degreed (the outer band). It is suggested that recent disruption events among multikilometer bodies in the main asteroid belt within the last several million years are major supply sources of the dust particles in the dust bands, and they produce a edge-brightened toroidal distributions of dust. We conducted observations of the asteroidal dust bands with the Japanese infrared satellite AKARI in mid- and far-infrared wavelengths region. AKARI clearly detects the zodiacal dust-band structures. We derived the heliocentric distances of dust bands from the AKARI observations: 1.9 AU and 2.2 AU from the Sun for the inner and the outer bands, respectively. Based on the AKARI spectroscopic observations in mid-infrared, the dust particles in the outer band show a slight different spectral shape of the silicate feature from those of other regions which are thought to be cometary origins. It is highly probable that we obtain the mid-infrared spectra of micron-sized asterodial dust grains for the outer band regions. We will discuss the size distribution and silicate composition for the dust grains in outer bands.

Keywords: zodiacal light, silicate, asteroids

Analyses of surface structure of amorphous ice using infrared spectroscopy

*Akimichi Kinjo[1], Rentaro Netsu[1], Tomoko Ikeda-Fukazawa[2]

1.Graduate School of Science and Technology, Meiji University, 2.Department of Applied Chemistry, Meiji University

In interstellar molecular clouds, water molecules deposit on dust grains, and forms amorphous ice. The amorphous ice includes various molecules such as CO, CO_2, NH_3, CH_4, H_2CO, and so on. These molecules undergo chemical evolutions to organic molecules through various processes. Because the deposited amorphous ice has a large surface area due to its uneven structure, the surface of amorphous ice has an important role for chemical evolutions of included molecules in molecular clouds [1].

Structure of amorphous ice depends on formation condition [2], and has been mainly classified by density into two types: low-density amorphous (LDA) and high-density amorphous (HDA) ice. The densities of the LDA and HDA ice are 0.94 ±0.03 and 1.1 ±0.1 g cm^{-3}, respectively. Although there are various studies for structures and properties of amorphous ice in bulk states, only a few studies have been reported for surface. In the present study, the surface structure of amorphous ice was analyzed by measurements of infrared (IR) spectra for thin film of vapor-deposited amorphous ice.

Amorphous ice was prepared with vapor deposition of distilled and degassed water on a substrate of oxygen-free copper at 43 K. The deposition rate was controlled to be a value in range of 0.02-0.61 nm/min. The inner pressure of the vacuum chamber during the deposition was about 5.0×10^{-5} Pa. The IR spectra were measured using Shimadzu IRPrestage-21.

The spectral features change with deposition. According to the assignments of IR spectra for amorphous ice [3], the O-H stretching vibration band observed in 2800-4000 cm^{-1} was decomposed into three vibration modes (i.e., in-phase and out-of-phase modes of symmetric stretching, and asymmetric stretching mode). From the variations of the wave number of the out-of-phase mode, the variations in water structure of amorphous ice were analyzed.

The result shows that the wave number of the out-of-phase mode increases as the thickness of the amorphous ice increases, and gradually approaches a constant value of 3480 cm^{-1}. From the observed variations, the thickness of the surface layer is estimated to be around 20 nm. Furthermore, the wave numbers of the surface layer and bulk state are estimated to be 3420 and 3480 cm^{-1}, respectively. Because these values are close to those for HDA and LDA ice [4], the internal part of the sample is confirmed to be HDA ice. For the surface layer, the density is smaller than that of the internal part. Therefore, it is supposed that the structure is a close representation of LDA ice. Furthermore, it was found that the surface structure of the amorphous ice depends on deposition rate. From the results, we discuss the structure and dynamics of amorphous ice surface.

References:

[1] J. M. Greenberg and J. I. Hage, Astrophys. J., 361 (1990) 260.
[2] A. H. Narten, C. G. Venkatesh, and S. A. Rice, J. Chem. Phys., 64 (1976) 1106.
[3] E. Whalley, Can. J. Chem., 55 (1977) 3429.
[4] L. Schriver-Mazzuoli, A. Schriver, and A. Hallou, J. Mol. Struct., 554 (2000) 289.

Effects of Density on Surface Structure of Amorphous Ice

*Norifumi Hara[1], Riku Togashi, Yu Kumagai[1], Tomoko Ikeda-Fukazawa[2]

1.Graduate School of Science and Technology, Meiji University, 2.Department of Applied Chemistry, Meiji University

In interstellar molecular clouds, various molecules (for instance, H_2O, NH_3, CO, CO_2, and so on) are formed from elements such as H, C, O, and N by deposition on dust grains [1]. Most of H_2O exists as a thin shell of amorphous ice around dust grain. The deposited molecules undergo chemical evolutions to organic molecule through various processes [2]. The structure of amorphous ice surface is an important factor to understand the molecular evolution in molecular clouds. Amorphous ice is formed by vapor deposition of H_2O gases [3] or compression of crystalline ice [4]. The structure of amorphous ice depends on formation processes and is classified into two types: high-density amorphous (HDA) and low-density amorphous (LDA) ices [4]. To investigate the effects of internal structure on surface structure, the molecular dynamics (MD) calculations of amorphous ice were performed.

The KAWAMURA potential model [5] was used for the MD calculations. The amorphous ice was prepared by quenching a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K. The density of amorphous was controlled with the time period of the annealing at 235 K. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 5 Åin thickness from the outmost atom was analyzed as the surface layer.

The calculations show that the density of amorphous ice at 10 K depends on the temperature history before the cooling to 10 K. In the case that the time period of annealing at 235 K was 1400 ps, for instance, the formed amorphous has the minimum density of 0.962 g/cm^3 at 10 K. For the case that the system was directly quenched from 300 to 10K without annealing at 235 K, the density reaches its maximum value of 1.095 g/cm^3. Because a significant change of density was observed at 235 K, we controlled the density of internal part of amorphous ice with time period of the annealing at 235 K.

The result shows that the density of the surface layer is smaller than that of the internal part, and increases as the density of the internal part increases. The decrease in molecular density observed in the surface layer is attributed to the uneven structure and large amplitude of the thermal vibrations of water molecules. To investigate the contribution of the uneven structure, the radical distribution function (RDF) was calculated. The position of the second peak, which is observed at around 4.1 Å, of surface layer is about 0.3 Ålarge than that of internal part. This suggests that the surface layer has a lower density even if there is no unevenness. The amplitude of the thermal vibration is measured by the atomic displacement parameter (ADP). The calculation indicates that ADP of surface layer is larger than that of internal part, and depends on internal density. This result is consistent with the calculation of RDF. In the RDF result the broadening of peaks was observed for surface layer. It is concluded that the structure of surface layer is affected by density of internal part. This effect of internal structure on surface structure of amorphous ice might have important implications for molecular evolution in molecular clouds.

References:

[1] A. Kouchi, T. Yamamoto, T. Kuroda, J. M. Greenberg, Astron. Astrophys. 1994, 290, 1009-1018.
[2] N. Watanabe, A. Kouchi, Surface Science, 2008, 83, 439-489.
[3] A. Kouchi, J. Cryst, Growth. 1990, 99, 1220-1226.

[4] O. Mishima, L. D. Calvert, E. Whalley, Nature, 1984, 310, 393-395.
[5] N. Kumagai, K. Kawamura, and T. Yokokawa, Mol. Simul. 1994, 12, 177.

Formation of Carbon-Dioxide Clathrate Hydrates including Help Gases under Vacuum Conditions

*Rentaro Netsu[1], Tomoko Ikeda-Fukazawa[2]

1.Graduate School of Science and Technology, Meiji University, 2.Department of Applied Chemistry, Meiji University

In interstellar molecular clouds, water molecules condense on dust grains. The condensed water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions of including molecules. Blake et al. [1] proposed the presence of clathrate hydrates in cometary ice. From the results using transmission electron microscopy and Fourier transformed infrared spectroscopy, they showed the phase transition of vapor deposited amorphous ice including CH_3OH and CO_2 into type-II hydrate at around 120 K.

Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guest molecules. Most hydrates form one of two distinct crystallographic structures, type-I and -II, depending on the sizes and shapes of the guest molecules. The structure of CO_2 hydrate formed under a high-pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice by Blake et al. [1], the structure was type-II due to the help-gases effect of CH_3OH. For the CO_2 hydrate grown epitaxially on a hydrate under vacuum condition, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of CO_2 hydrate including help-gases under vacuum conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO_2 and C_3H_6O during warming.

The CO_2/H_2O ratios of the prepared gas mixtures were 0.13-16.8. The gas mixtures were deposited onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K. Infrared spectra were measured at approximately 1 min intervals during deposition at 43 K and at 2 K intervals during warming. Furthermore, CO_2 and C_3H_6O mixed hydrates were prepared from gas mixtures of H_2O, CO_2, and C_3H_6O with various compositions, and were measured spectra with the same procedures.

From the variation in spectral features of H_2O-CO_2 ice with warming, remarkable changes were found at 82 K. The wave numbers of the O-H stretching modes of H_2O and the C-O asymmetric stretching modes of CO_2 change significantly at this temperature. Furthermore, significant gas release and exothermic temperature rise were observed. These results suggest that the crystallization of amorphous ice begins at 82 K. From the wave numbers of C-O asymmetric stretching modes, the formed crystal is determined to be type-I hydrate. From the formation conditions of CO_2 hydrate, we propose the phase diagram of the H_2O-CO_2 system under vacuum conditions. In addition, the formation processes of mixed hydrate including CO_2 and C_3H_6O were analyzed. The result shows that the transition temperature of the mixed hydrate depends on the guest composition. From the results, we discuss the formation mechanisms of clathrate hydrates under vacuum conditions.

References

[1] D. Blake, L. Allamandola, S. Sandford, D. Hudgins, F. Freund, Science 254, 548 (1991).

[2] T. Ikeda, S. Mae, O. Yamamuro, T. Matsuo, S. Ikeda, R. M. Ibberson, J. Phys. Chem. A 104, 10623 (2000).

[3] F. Fleyfel, J. P. Devlin, J. Phys. Chem. 95, 3811 (1991).

Nitrogen isotopic fractionation of ammonia accompanied with adsorption-desorption process on montmorillonite and saponite

*Haruna Sugahara[1], Yoshinori Takano[1], Nanako O. Ogawa[1], Yoshito Chikaraishi[1], Naohiko Ohkouchi[1]

1.Japan Agency for Marine-Earth Science and Technology

Solar system objects show wide variation in the nitrogen isotopic composition. The $\delta^{15}N$ value (‰, normalized as vs. Air) ranges from -400‰ in the solar wind [1] and Jovian atmosphere [2] to around +1500‰ of comets, chondrites, and interplanetary dust particles (IDPs)[3, 4]. These pristine solar system materials also show occasional extreme ^{15}N-enrichment up to +5000‰ [5, 6]. This $\delta^{15}N$ variation in the solar system objects is considered to have been inherited from the cold interstellar environments [7]. However, only a few models can explain the interstellar chemistry to enhance ^{15}N-enrichments, such as photodissociation of nitrogen molecules and subsequent formation of ammonia [8], and conceivable isotopic fractionation processes have not well understood.

In the study, we conducted simple adsorption-desorption experiments using ammonia gas and two clay minerals (montmorillonite and saponite). From the results, we propose the adsorption-desorption process of ammonia on grain surface of interstellar dusts as a potential mechanism for ^{15}N-enrichmentin interstellar environments. Ammonia is a simple nitrogen-containing molecule and one of major nitrogen carriers in the molecular clouds. It is a highly reactive chemical and regarded as a precursor for other complex nitrogen-containing molecules. Thus, adsorption of ammonia could be a first step for grain surface chemistry to form more complex organic molecules. The adsorption-desorption experiments were performed to examine the possibility of nitrogen isotopic fractionation of ammonia by adsorption and desorption on the clay minerals. Each clay mineral sample, with controlled amount of water (0, 5, 10, 20 wt.% vs. dry cry minerals), was sealed into the glass serum bottles with ammonia gas (+27‰, SI Science). The glass vial was rested for a week under room temperature (25℃) to reach a stable state before analysis. After the initial analysis was completed, the glass vial was vacuumed for 1 to 8 hours to examine the results under vacuumed environment. The nitrogen isotopic composition of the adsorbed ammonia at each step of the experiments was determined by nanoEA/IRMS technique [9].

The results showed that adsorbed ammonia generally had larger $\delta^{15}N$ value than the initial ammonia gas. The degree of isotopic fractionation from the initial ammonia were +2.4~+40.3‰ for montmorillonite and -1.6~44.4‰ for saponite as $\Delta^{15}N$ value. There was also a negative correlation observed between the adsorbed ratio (wt. %) and the $\delta^{15}N$ value. When the glass vial was vacuumed for only 1 hour, the $\delta^{15}N$ of the remaining ammonia increased (+64.1‰ for montmorillonite and +60.1‰ for saponite as $\Delta^{15}N$ value). However, when the glass vial was vacuumed more than 1 hour, selective removal of $^{15}NH_3$ was observed. The water content of the sample was not an influential factor throughout the experiments. The results suggest that adsorption and desorption of ammonia on clay minerals causes significant nitrogen isotopic fractionation ($\Delta^{15}N$=−1.6~+64.1‰) and could be a potential mechanism for ^{15}N-enrichment in interstellar environments.

Reference: [1] Marty B. et al. (2011) Science 332, 1533. [2] Abbas M. M. et al. (2004) APJ 602, 1063 [3] Bonal L. et al. (2010) GCA 74, 6590. [4] Manfroid J. et al. (2009) A&A 503, 613. [5] Briani G. et al. (2009) PNAS 106, 105222. [6] Hashiguchi M. et al. (2015) Geochem. J. 49, 377. [7] Rogers S. D. & Charnley S. B. (2008) Mon. Not. R. Astron. Soc. 385, L48. [8] Chakraborty S. et al. (2014) PNAS 111, 14704. [9] Ogawa N. O. et al. (2010) in Earth, Life, and Isotopes. pp.339.

Keywords: nitrogen isotopic fractionation, adsorption, ammonia, molecular clouds, grain surface chemistry

Amino acid analysis of photochemically processed interstellar ice analogues

*Haruna Sugahara[1], Yoshinori Takano[1], Shogo Tachibana[2], Akira Kouchi[3]

1.Japan Agency for Marine-Earth Science and Technology, 2.Department of Natural History Scieces, Hokkaido University, 3.Institute of Low Temperature Science, Hokkaido University

Amino acids are one of major constituent of living organisms on the Earth, so they are essential molecules for the origins of life. Many scenarios for the endogenous production of amino acids on the early Earth have been proposed [e.g., 1, 2]. On the one hand, the extraterrestrial delivery of them is also considered as a likely candidate [e.g., 3, 4]. Carbonaceous chondrites are known to contain abundant amino acids up to 250 ppm [5] and more than 80 species were identified [6]. In addition, the simplest amino acid: glycine was also detected in the cometary grains returned by stardust mission [7]. The extraterrestrial amino acids are considered to have been formed by aqueous alteration on the meteoritic parent bodies or in the presolar interstellar environments. Although, the formation process, as well as the place to be taken, is still on a debate, the existence of amino acid in comets as wall as the isotopic signatures of them suggest that at least some amino acids and the precursors of them are interstellar origin [8].

In the study, we conducted laboratory experiments to synthesize interstellar ice analogues from typical interstellar gases and analyzed their amino acid composition. For the experiments that simulate the condition in the interstellar medium (ISM), we utilized an apparatus called PICACHU: Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University. In this PICACHU apparatus, the typical ISM gases (H_2O: CH_3OH: NH_3 = 2:1:1) were introduced into the chamber and deposited onto the surface of a sappier glass there, which were refrigerated at ~12 K. During the deposition of the ice, UV photons were continuously irradiated under highly vacuumed condition for 71 hours, because photochemical reactions in the ice, which were processed by stellar ultraviolet (UV) photons and cosmic rays, are important for the formation of complex organic molecules in ISM. In addition, we made two ice samples and one of them was further irradiated by UV for 232.5 hours after heated to room temperature in order to simulate subsequent decomposition in warmer environments. Then, the organic residues of the two ice samples were extracted by methanol and analyzed by GC-MS and GC/NPD after the derivatization for GC analysis.

The results showed that 11 species of amino acids were formed in the interstellar ice analogues, which were irradiated only at ~12 K. The most abundant amino acid was glycine and the second most abundant one were β-alanine and alanine. Their abundances are about fourth of that of glycine. The abundance of each amino acid generally decreased with the increase of the carbon number of the amino acids. This trend was consistent with the previous study [9]. Then, the further irradiated sample showed the general decrease in the abundances of amino acids, but some of them were still remained. The survived ratio differed among amino acids and glycine was the most resistant to the irradiation (~80% remained.). These results indicate that amino acids can be formed by the UV irradiation to the interstellar ice and can survive subsequent irradiation in the warmer environments.

References: [1] Janda M. et al. (2008) Orig. Life Evol. Biosph. 38, 23 [2] Holm N.G. and Andersson E. (2005) Astrobiology 5, 444. [3] Chyba C. and Sagan C. (1992) Nature 355, 125. [4] Ehrenfreund P. et al. (2002) Rep. Prog. Phys. 65, 1427. [5] Martins Z. et al. (2008) MAPS 42, 2125. [6] Burton A. S. et al. (2012) Chem. Soc. Rev. 41, 5459. [7] Elsila J. E. et al. (2009) MAPS 44, 1323. [8] Pizzarello S. and Huang Y. (2005) GCA 69, 599. [9] Munõz Caro G. M. et al. (2002) Nature 416, 403.

Keywords: Amino acid, interstellar medium, interstellar ice, photochemical reaction