PHOTOCHEMISTRY IN MOLECULAR CLOUD AND PROTOPLANETARY DISK: EVOLUTION OF ICE AND ORGANIC RESIDUES THROUGH WARMING AND UV-IRRADIATION. L. Piani[1*], S. Tachibana[1], T. Hama[2], I. Sugawara[1], Y. Oba[2], H. Tanaka[2], Y. Kimura[2], A. Miyake[3], J. Matsuno[3], A. Tsuchiyama[3], H. Yurimoto[1] and A. Kouchi[2], [1]Department of Natural History Sciences, Science faculty, Hokkaido University, Japan ([*]corresponding author: laurette@ep.sci.hokudai.ac.jp), [2]Institute of Low Temperature Science, Hokkaido University, Japan. [3]Division of Earth and Planetary Science, Kyoto University, Japan.

Introduction: In the dense and cold parts of the interstellar medium (ISM), photochemical reactions in ice lead to the formation of relatively complex organic molecules. Experimental simulations of molecular cloud conditions showed that complex organic compounds remain after the warming-up of ultraviolet (UV)-photoprocessed ice [e.g. 1]. These compounds are among the potential building blocks of our Solar System and could be the precursors of a part of the organic matter found in comets and meteorites. However, 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 the Solar System.

Method: To simulate the formation and evolution of organic ice and remaining compounds through UV irradiation and heating, we developed an experimental apparatus called PICACHU, an acronym for Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University (schematic view, Fig. 1) [2]. Typical ISM gases (H_2O, CO, NH_3, and CH_3OH) are mixed, deposited onto the three faces of a refrigerated substrate (~12 K) and simultaneously irradiated by three UV lamps under high vacuum.

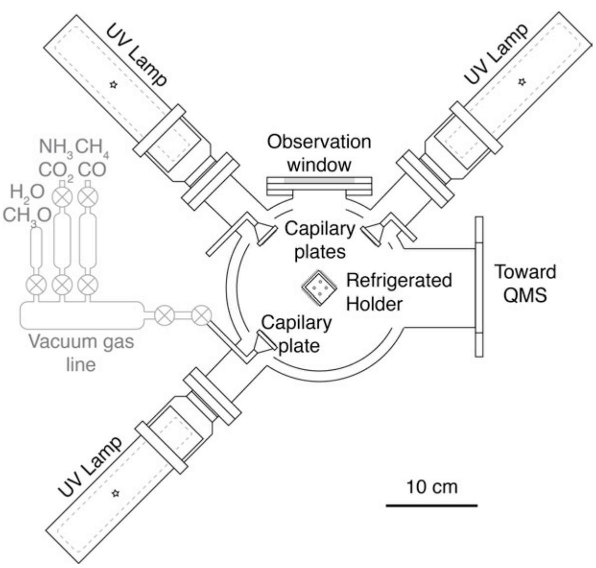

Fig. 1. Schematic view of the main vacuum chamber of PICACHU apparatus.

Gases, desorbed from the ice during heating and post-irradiation, are monitored by a quadrupole mass spectrometer (QMS) in the vacuum chamber. The morphological evolution of the ice deposits during warm-up and/or irradiation is observed *in situ* using a microscope looking though the top observation window and correlated with desorbed gases measured by the QMS. A part of the organic residues formed after the ice sublimation were re-irradiated with UV photons at room temperature. We also have replicated the experimental conditions with another experimental apparatus equipped with an *in situ* Fourier-Transform Infrared spectrometer (FTIR) to monitor the evolution of the ice. The residual organic materials were examined with a laser microscope, an atomic force microscope (AFM), a field-emission secondary electron microscope (FE-SEM) and transmission electron microscopes (TEM). Viscoelastic measurements were performed with a nano-indentation technique.

Results and discussion: *Ice and released gases.* 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 surface deformations and appearance of bubbles from ~ 65 to about 140 K with the microscope (Fig. 2). The bubbling is associated with outbursts of gases mostly composed of H_2. With non-irradiated ice of similar compositions, bubbling and gas outbursts were not observed and H_2 signal on QMS is much lower.

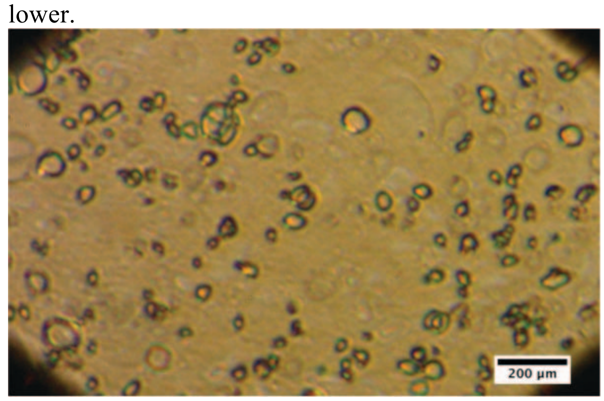

Fig. 2. *In situ* observation of bubble formation and blow up in the UV-photoprocessed ice at 120 K (initial gases H_2O:NH_3:CH_3OH = 5:1:1, gas deposition rate = 1.10^{14} molec.cm^{-2}.s^{-1}, UV-photon flux 7. 10^{13} ph.cm^{-2}.s^{-1}, deposition duration 96 hrs).

The presence of bubbles indicates that the ice at low temperature behaves like a supercooled liquid from 65 K and with a viscosity similar to a dacitic magma at about 1000°C. Gas outbursts occurring with the blowing up of bubbles may be responsible of grain and gas ejections. These observations might help to characterize grain and gas ejection processes observed on cometary and some icy satellite surfaces [3-4].

Photo-processing of organic residues. After warming up of the ice, the remaining organic residue was irradiated again by UV-photon (UV-photon flux of ~ 10^{14} ph.cm^{-2}.s^{-1}) at room temperature during 3 to 10 days. The total UV-doses correspond to short residence durations in diffuse cloud ($\leq 10^4$ yrs). Nevertheless, significant morphological changes were observed in the residue comparing to the residues recovered directly after warming: increase of porosity (Fig. 3A), increase of roughness (Fig. 3B) and, appearance of discrete and round nanoparticles (Fig. 3C) that may be similar to some nanoglobules found in the organic matter within chondrites and cometary rocks [e.g. 5-7]. Viscoelastic properties were also changed by the UV-irradiation of the residue. As a whole, the viscoelastic properties of the organic residues indicate that organic-coating on inorganic dust could play as efficient glue on dust aggregation [8] but, at the same time, could also enhance the aggregate brittleness [9].

References: [1] Greenberg 2002. Surf. Sci. 500, 793–822. [2] Piani et al. 2014. Met. Plan. Sci. Suppl. abstract #5189 [3]Laufer et al., 2013. Icarus 222, 73–80. [4] Loeffler and Baragiola, 2012. Astrophys. J. 744:102 (7pp). [5] Nakamura et al., 2002. Int. J. Astrobiol. 1, 179–189. [6] Garvie and Buseck, 2004. Earth Planet. Sci. Lett. 224, 431–439. [7] De Gregorio et al., 2010. Geochim. Cosmochim. Acta 74, 4454–4470. [8] Wada et al., 2013. Astron. Astrophys. 559, 62. [9] Sirono, 1999. Astron. Astrophys. 347, 720–723.

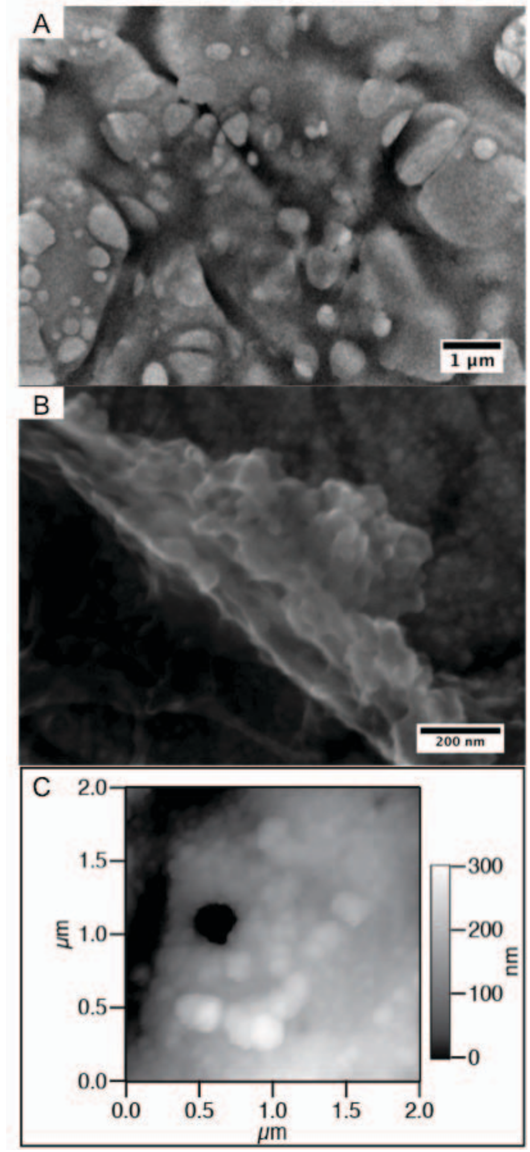

Fig. 3. Morphology of the UV-irradiated organic residues: (A) TEM image showing a high porosity with pores diameters from ≤ 10 nm to some microns, (B) FE-SEM image showing the roughness and asperities of the residue and, (C) AFM topographic map showing discrete and round nanoparticles with diameter of some 10s of nm at the surface of the deposit.