Low temperature hydration experiments of cometary analog materials towards the Comet Astrobiology Exploration Sample Return (CAESAR) mission

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The Comet Astrobiology Exploration Sample Return (CAESAR) mission is a final candidate for selection as the fourth mission in NASA's New Frontiers Program. CAESARaims to acquire and return to Earth for laboratory analysis a minimum of 80 g of surface material from the nucleus of comet 67P/Churyumov-Gerasimenko (67P) (Squyres et al. 2018). Near-infrared spectra of a short-period comet 67P taken by the spectrometer onboard Rosseta spacecraft also indicate the absence of phyllosilicates in this comet (Capaccioni et al. 2015). In order to return anhydrated samples from 67P, optimal conditions for sampling should be determined because cometary dust particles especially amorphous silicates are highly reactive. Hydration process of anhydrous crystalline silicates such as olivine is already well-characterized, whereas reaction of water vapor or ice with amorphous silicates and organic matters at temperatures below H<sub>2</sub>O freezing points has been poorly understood. In this study, we performed incubation experiments of amorphous silicates and organic matters under low temperature conditions with ice or vapor of D<sub>2</sub>O/NH<sub>3</sub>.

Amorphous silicate nanoparticles with three different chemical compositions and textures (S1, S2, and S3), and commercial glycine and ribose powder were used in the experiments. S1 is composed of ~100 nm particles having MgSi<sub>2</sub>O<sub>5</sub>composition prepared with sol-gel processing. S2 and S3 are condensates from high temperature gases. S2 is amorphous Mg<sub>2</sub>SiO<sub>4</sub>nanoparticles of ~80 nm in size synthesized in a Radio Frequency plasma system (Koike et al. 2010). S3 is 30-100 nm sized amorphous silicate with Mg/Si~0.93 embedded with metallic Fe-Ni particles condensed from a high temperature vapor of the CI chondritic ratios of Mg, AI, Ca, Fe, and Nito Si in an induction thermal plasma system (Kim et al. 2017).

Two types of ice were used in the experiments to evaluate the effects of corrosive gases in 67P; (A) Pure D  $_2$ O ice (99.90% purity) and (B) Mixture D $_2$ O ice with 0.3% H $_2$ O and 0.15% NH $_3$ . Experiments with different ices were performed in different vacuum containers placed in a cryogenic box. About 5 mg of three silicate and glycine samples were put in different open-top glass bottles (2 ml). Approximately 50 mg of chipped ice fragments were put in the glass bottles and directly contact with the silicate and glycine samples. Roughly  $^{\sim}500$  mg of the same ice fragments were put in the vacuum containers as a vapor source. The temperature of the cryogenic box sets at -17 or -27°C. The samples were exposed with saturated vapor of ices for 10-120 days. As a comparison, exposure experiments of amorphous silicate samples (S1, S2, and S3) to H $_2$ O vapor were also conducted at 25 and 50°C for 10 days.

The exposed silicate samples were analyzed with a powder X-ray diffraction (XRD, Rigaku SmartLab) and Fourier-transform infrared spectroscopy (FT-IR; JASCO MFT-680, Thermo Nicolet iS5). The recovery rate of glycine (i.e., molar ratio of recovered glycine over starting glycine) and ribose were obtained by liquid chromatography tandem mass spectrometer (LC/MSMS; Shimadzu LCMS-8040).

No clear change of the XRD patterns and FT-IR spectra for S1, S2, and S3 was confirmed after the

experiments for <120 days at -17 and -27°C. The recovery of glycine exposed to  $D_2O$  ice and  $NH_3$  -containing  $D_2O$  ice for 10 days was 108±8 mol% and 105±8 mol%, respectively. The recovery of ribose exposed to  $D_2O$  ice and  $NH_3$ -containing  $D_2O$  ice for 10 days was 108±12 mol% and 105±12 mol%, respectively. Bicause the ice sublimation timescale is very short at the exoerimental temperatures, the present results indicate that cometary silicates at <-20°C in comets are pristine even if they have high surface to volume ratio and amorphous structures as GEMS grains in anhydrous CP-IDPs.

Keywords: comet, space exploration, hydration experiment