Exposure Experiments of Amorphous Silicates and Organics to Cometary Ice and Vapor Analogs

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Abstract

Hydration is a major mineral alteration process in primitive asteroids and it might occur in comet nuclei; however, it is poorly understood at low temperatures, especially below the freezing point of water. Long-duration experiments were performed with exposures of amorphous silicate nanoparticles and organic compounds (glycine and ribose) to D2O and D2O + NH3 ices and vapors at temperatures of −17°C and −27°C for 10–120 days; and with exposure of amorphous silicates to H2O vapor/liquid at >25°C for 10 days. The amorphous silicates were analyzed by X-ray diffraction and Fourier-transform infrared spectroscopy, and recovery of organic molecules was determined by liquid chromatography–mass spectrometry. No hydration of amorphous silicates or organic compounds was observed after exposure at temperatures below −17°C for 120 days to ices with or without NH3, whereas hydration of the amorphous silicates was observed in experiments above room temperature. The estimated thermal history of the nucleus of the short-period comet 67P/Churyumov–Gerasimenko indicates that the surface temperature does not exceed −45°C, even in a region exposed to strong solar illumination during the perihelion passage. Assuming hydration is controlled by the collision frequency between H2O molecules and dust particles, the present results indicate that cometary dust does not hydrate for more than 25–510 periods of comet 67P. This is consistent with the absence of phyllosilicates on 67P and suggests that amino acids and sugars have not been altered.

Key words: comets: general – comets: individual (67P/Churyumov–Gerasimenko) – interplanetary medium – meteorites, meteors, meteoroids

1. Introduction

The occurrence of hydrated silicates in many C- and D-type asteroids indicates that hydration of anhydrous silicate rocks is a common alteration process in primitive asteroids. Reflectance spectra of these asteroids display absorption features characteristic of structural water in hydrated silicates, such as the 2.7 μm band (e.g., Usui et al. 2018). C-type asteroid 162173 Ryugu shows the 2.7 μm band from an entire surface, indicating pervasive aqueous alteration on this asteroid (Kitazato et al. 2019). CI, CM, CR, and Tagish Lake carbonaceous chondrites from these asteroids contain phyllosilicates, serpentine, and saponite as major mineral phases (e.g., Zolensky et al. 1993). The mineralogy and oxygen isotopic signatures of the hydrated carbonaceous chondrites indicate that aqueous alteration occurs very early in hydrous asteroids (∼5 Myr after formation of Ca-Al-rich inclusions (CAIs); e.g., Fujiya et al. 2012), at temperatures of 20°C–100°C and with water/rock ratios of ∼1 (e.g., Clayton & Mayeda 1984). The chemical structure of carbon in insoluble organic matter and the amount of some soluble organic compounds vary with the amounts of phyllosilicates in meteorites, indicating that aqueous processes on the parent body also affect organic compounds (e.g., Cody & Alexander 2005; Glavin et al. 2011).

The short-period comet 9P/Temple 1 displays mid-infrared spectra suggestive of the presence of phyllosilicates, amorphous silicates, carbonates, and organic matter when the copper impactor from the NASA Deep Impact spacecraft hit the comet surface to produce gaseous ejecta (Lisse et al. 2006). While this detection of phyllosilicates is controversial (Davidsson et al. 2016), a phyllosilicate presence on Tempel 1 might have been caused by hydration induced due to solar-radiation heating rather than radioactive decay, because the surface temperature exceeds 60°C during the perihelion passage (Groussin et al. 2007). Another short-period comet 81P/Wild 2 displays no evidence of extensive aqueous alteration forming phyllosilicates, as shown by return sample analysis (e.g., Nakamura et al. 2008). Near-infrared spectra of short-period comet 67P/Churyumov–Gerasimenko, recorded by the Rosetta spacecraft, indicate the absence of phyllosilicates on this comet as well (Capaccioni et al. 2015).

The hydration of anhydrous silicates such as olivine is well characterized. Wegner & Ernst (1983) performed hydration experiments with forsterite to form serpentine and brucite, and obtained reaction rates as a function of temperature (190°C–360°C), pressure (1–3 kbar), grain size (37–149 μm), and water/rock ratios. Malvoisin et al. (2012) also determined the hydration reaction rates depending on size and temperature ranges of 1–150 μm and 250°C–300°C, respectively. Lafay et al. (2012) studied the pH dependency of hydration reactions in highly alkaline solutions (pH 13.5) at temperatures of 150°C–200°C. All these experiments were conducted at relatively high temperatures to simulate hydrothermal reactions on Earth. Low-temperature hydration reactions are expected to occur on asteroids and comets but are poorly understood, and have been studied only above room temperature. Nakamura-
Messner et al. (2011) conducted hydration experiments with interplanetary dust particles (IDPs) at temperatures of 25°C–160°C and with a pH range of 7–13, and found that glass embedded with metal and sulfide (GEMS) and enstatite are replaced by serpentine and saponite within 12 hr in an alkaline solution at 25°C. Chizmadia (2007) showed aqueous hydration of Mg–Si–O and Fe–Si–O smokes at 5°C and 25°C. Yamamoto & Tachibana (2016) reported serpentine formation by reactions between water vapor and amorphous Mg$_2$SiO$_4$ particles at 50°C–100°C.

Organic compounds are also constituents of primitive asteroids and comets, with amino acids having attracted attention as possible life precursors. A number of amino acids have been found in carbonaceous chondrites (e.g., Burton et al. 2012), but few in cometary samples. Only glycine, the simplest amino acid, was detected on the aluminum foil of the NASA Stardust sampler, which captured dust from comet Wild 2 (Elsila et al. 2009). Glycine was also detected in the coma of comet 67P during the Rosetta mission (Altweeg et al. 2016).

The kinetics of glycine degradation in a high-temperature aqueous solution (200°C–340°C) has been investigated (Sato et al. 2004), although the stability of glycine below 0°C remains unclear. Ribose is a pentose and a constituent of ribonucleic acid (RNA). It has not been detected in comets and meteorites, but could be present in comets (Meinert et al. 2016). The stability of ribose at pH 4–8 and temperatures of 40°C–120°C has been investigated and found to be lower than that of amino acids (Larralde et al. 1995).

It remains uncertain whether aqueous alteration occurs in comets. It seems likely that alteration would occur during the perihelion passage when temperatures are the highest since formation of the comet, but temperature–time reaction requirements are unknown. This study investigated reactions of amorphous silicates and organic compounds exposed to ices and vapors at low temperatures. The thermal history of the nucleus of comet 67P was also investigated to set limits on reaction conditions.

2. Experimental

Amorphous silicate nanoparticles with different chemical compositions and textures (silicates S1, S2, and S3), representing the most reactive silicates in cometary dust particles, were used in the exposure experiments. Silicate S1 comprises ~100 nm particles of Mg$_2$SiO$_4$ prepared by sol–gel processing. Mg powder was dissolved in concentrated HNO$_3$ and the acid was removed by evaporation. Tetraethyl orthosilicate (TEOS; Wako Pure Chemical Industries, Japan), ethanol, and an ammonia solution were added to the Mg residue. The mixture was heated at 700°C for 20 hr to completely dry and remove NH$_3$NO$_3$, without crystallization (Murata et al. 2009). Silicates S2 and S3 are condensates from high-temperature plasma gases at ultra-high cooling rates (1–10 × 10$^4$ K s$^{-1}$) synthesized in a radio-frequency plasma system (Koike et al. 2010) and in an induction thermal-plasma system (Kim et al. 2017), respectively. S2 comprises amorphous Mg$_2$SiO$_4$ nanoparticles of ~80 nm diameter. S3 comprises 30–100 nm diameter amorphous silicate particles embedded with metallic Fe, Fe–Ni, and Fe$_2$Si$_3$ particles. The bulk chemical composition of S3 is the CI-chondritic ratio of Mg, Al, Si, Ca, Fe, and Ni. S1 may have short-range structures of SiO$_4$ tetrahedra like so-called glassy silicate because it is synthesized by sol–gel processing but S2 and S3 have more disordered structures because of the high quenching rate of the thermal plasma. In this paper, we refer to S1, S2, and S3 as amorphous silicates because all three samples have no long-range order structure and short-range structures of the silicate samples were not determined. The stabilities of glycine (C$_2$H$_5$NO$_2$) and ribose (C$_3$H$_7$O$_3$) were also studied. Commercial glycine and ribose (Wako Pure Chemical Industries) were used in the exposure experiments.

Two types of ice were used in experiments: (A) pure D$_2$O ice (99.90% purity); and (B) an ice mixture of D$_2$O, H$_2$O (0.3%), and NH$_3$ (0.15%). NH$_3$ is one of the major cometary volatiles that might potentially react with silicates and labile organic compounds (particularly ribose). D$_2$O was used to distinguish experiment products from contaminants reacting with air moisture.

Experiments with the different ices were performed in separate vacuum containers in a cryogenic box (Figure 1). About 5 mg of each of the three silicates and two organic samples were placed in separate open glass bottles (2 mL) and cooled to approximately −40°C in the cryogenic box. Approximately 50 mg of chipped ice fragments, prepared by scraping bulk ice in the same cryogenic box, were placed in the glass bottles to have direct contact with the samples. Fragments of the same ice (∼0.5 g) were placed in the vacuum containers as a vapor source (Figure 1). During sample preparation, the temperature of the cryogenic box was kept below −35°C, with a flow of dry nitrogen gas preventing frost formation. To remove residual air, the vacuum container was evacuated to ~10$^{-4}$ Pa using a turbo molecular pump and an oil-free scroll pump. Sublimation of chipped ice fragments in the vacuum container was negligible during the preparation. After evacuation, the container was closed and the temperature of the cryogenic box was maintained at −2°C, −17°C, or −27°C for each set of reaction conditions. Samples were exposed to saturated ice vapors for 10–120 days. Vapor pressures of D$_2$O at −2°C, −17°C, and −27°C correspond to those of H$_2$O ice at −5°C, −20°C, and −30°C, respectively (Table 1). Experimental conditions are summarized in Table 2.

After each experiment, the temperature of the cryogenic box was again set at −40°C and the vacuum container evacuated to completely remove the ice. The vacuum container was then
removed from the cryogenic box and allowed to equilibrate with room temperature under continuing evacuation. Total evacuation time was >12 hr.

Experiments involving exposure of the amorphous silicate samples to H$_2$O vapor and liquid were conducted at temperatures of >0°C. In the vapor experiments, three 15 mL open glass bottles containing ~5 mg of the sample were placed in a closed 250 mL polystyrene container with 30 mL of distilled water, and kept at 25°C (room temperature) or 50°C for 10 days. In the liquid H$_2$O experiments, ~10 mg of each silicate sample and 50 mL of distilled water (water/rock ratio = 5) were placed in separate 1.5 mL microtubes for 10 days. After which the samples were dried under vacuum. Water vapor pressures during the experiments are given in Table 1.

The exposed silicate samples were analyzed by powder X-ray diffraction (XRD, Rigaku SmartLab) using Ni-filtered Cu Kα radiation (λ = 1.5418 Å) with an accelerating voltage of 40 kV and tube current of 40 mA. Silicon zero-diffraction plates were used as sample holders. The 2θ range, scan step interval, and scan speed were set at 4°–95°, 0.02°/step, and 0.3 s$^{-1}$, respectively. For Fourier-transform infrared spectroscopy (FT-IR; JASCO MFT-680 and Thermo Nicolet iS5) analyses, samples were embedded in a KBr matrix (pellet) with a sample: KBr mass ratio of 1:200.

Residual glycine and ribose were dissolved in 1 mL of distilled water. Glycine and ribose were derivatized with AccQ Tag reagent (Waters Co.), and derivatization products analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS) to determine sample recoveries (i.e., molar ratio of recovered sample over starting sample), using a Shimadzu LC–MS 8040 and Waters LC–MS/MS system (2695 separation module and Quatromicro API). The LC–MS/MS method has been reported previously (Furukawa et al. 2013, 2015).

### 3. Results

XRD patterns of silicate S1, S2, and S3 samples before and after experiments are shown in Figure 2. Significant changes in XRD patterns were observed after 10 days of exposure to saturated H$_2$O vapor (at 25°C and 50°C) and liquid H$_2$O (at 25°C). For silicate S1, an XRD peak originally at 22° shifted to ~22°; peaks at 34°9 and 60°4 did not shift but their intensities increased. S2 displays peaks at ~10°, 24°0, 35°5, and 59°7 after experiments at 25°C and 50°C, which were not observed in XRD spectra of the starting material. XRD patterns of S3 display peaks at ~10°, 23°, 35°4, and 60° in addition to peaks seen with the starting material. The peak positions and broad shapes of XRD patterns at about 10°, 22°–24°, 35°, and 60° observed for all samples after high-temperature experiments do not match those of phyllosilicates, but are similar to those of magnesium silicate hydrate (MSH) at 9°7, 26°7, 35°0, and 59°9 (e.g., Nied et al. 2016).

The XRD patterns of samples after experiments at −17°C and −27°C do not display peaks of either MSH or hydrous silicate. A small amount of D$_2$O adsorbed on the samples may have remained after the evacuation process but this effect was negligible. The sharp peaks in the XRD spectrum of S1 after the 120 day experiment at −17°C are due to contaminated glycine. The slight differences in spectral slope at <20° after low-temperature experiments are not due to hydration but rather to differences in instrument operating conditions and amounts of sample used in the analyses. This is most apparent with S3 samples because S3 displays a weak amorphous halo that causes a low sample/background intensity ratio. It was also difficult to fill the XRD holder with the same amount of S3 sample because of its 30 nm particle size and metal nanoparticles, which caused problems with static electricity. FT-IR spectra of S1, S2, and S3 are shown in Figure 3. All FT-IR spectra of amorphous silicates exposed to H$_2$O vapor at 25°C and 50°C, and liquid H$_2$O at 25°C display clear changes at 10 and 14–16 μm. The formation of phyllosilicates is incomplete but hydration has clearly occurred. FT-IR spectra after low-temperature experiments (−17°C and −27°C) display no changes indicating hydration, even after 120 days with NH$_3$. These results are consistent with those of XRD analyses. FT-IR peaks due to vibrations related to hydration of silicates (i.e., SiO–H(D) formation) and absorption of H$_2$O and D$_2$O are expected at 4000–2400 cm$^{-1}$. However, H$_2$O absorption peaks are strong and close to SiO–H features, which makes it difficult to resolve hydration signatures. After acquisition of the FT-IR

### Table 1

| Temperature (°C) | −30 | −27 | −20 | −17 | −5  | −2  | 25  | 50  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| H$_2$O (Pa)    | 51  | 67  | 125 | 162 | 572 | 421 | 3164| 12328|
| D$_2$O (Pa)    | 38  | 50  | 96  | 125 | 428 | 339 | 2737| 11121|

### Table 2

| Ice/vapor | D$_2$O | D$_2$O+NH$_3$ | D$_2$O | D$_2$O+NH$_3$ | D$_2$O | D$_2$O+NH$_3$ | D$_2$O | D$_2$O+NH$_3$ | D$_2$O | D$_2$O+NH$_3$ | D$_2$O | D$_2$O+NH$_3$ | H$_2$O | H$_2$O | H$_2$O (liquid)$^a$
|------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------------|-------|-------|-------|
| t (days)   | 60    | 120         | 60    | 120         | 60    | 120         | 60    | 120         | 10    | 10          | 10    | 10          | 10    | 10    | 10    |
| sample     | S1    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | …     | …           | ✓✓    | ✓✓           | ✓✓    | ✓✓    | ✓✓    |
|            | S2    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | …     | …           | ✓✓    | ✓✓           | ✓✓    | ✓✓    | ✓✓    |
|            | S3    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | …     | …           | ✓✓    | ✓✓           | ✓✓    | ✓✓    | ✓✓    |
| glycine    | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | …     | …           | ✓✓    | ✓✓           | ✓✓    | ✓✓    | ✓✓    |
| ribose     | …     | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | ✓✓    | ✓✓           | …     | …           | ✓✓    | ✓✓           | ✓✓    | ✓✓    | ✓✓    |

Note.

$^a$ Experiments in liquid H$_2$O.
spectra shown in Figure 3, the samples embedded within KBr pellets were heated to 150°C for 40 minutes to reduce the adsorbed H₂O in the samples. Figure 4 shows heated samples after 120 day experiments at −17°C and those exposed to H₂O vapor at 50°C. While SiO–H peaks due to hydration are clearly visible in spectra of samples after the 10 day experiments at 50°C, peaks associated with adsorbed D₂O and SiO–D bonds formed by reaction between D₂O vapor and amorphous silicates are not apparent after low-temperature experiments. Thus, the hydration of amorphous silicates seems not to have occurred during the low-temperature experiments.

Recoveries of glycine and ribose exposed to D₂O ice and NH₃-containing D₂O ice are shown in Figure 5 for experiments involving up to 120 days at −27°C and −17°C (glycine and ribose), and 10 days at −2°C (glycine). No detectable loss of glycine or ribose was observed.

4. Discussion

The exposure experiments show no alteration of silicates S1, S2, and S3 exposed to saturated water vapor with or without 0.15% NH₃ at −17°C for 120 days. The chemical compositions of silicates used in this study cover a wide range of Mg/Si ratios (<1.5) of chondritic porous (CP) IDPs (Keller & Messenger 2011). Elemental ratios of Mg, Fe, Al, Ca, Na, and Ni to Si of S3 are within the range of GEMS in IDPs, and the textures of nano-metals in the amorphous silicates are very similar to those of GEMS (Keller & Messenger 2011; Kim et al. 2017). Samples S1, S2, and S3 also have higher reaction surface-area to volume ratios than most GEMS grains in CP-IDPs, which are typically ~300 nm in diameter (Keller & Messenger 2011). The hydration rates of crystalline silicates such as olivine and pyroxene in comets are orders of magnitude lower than those of amorphous silicate nanoparticles. The present results thus indicate that alteration of amorphous (including glassy) and crystalline silicates in comets is not expected to occur at temperatures of −20°C or lower within 120 days.

Alteration was not detected for either glycine or ribose exposed to ice or saturated D₂O vapor with or without 0.15% NH₃ at −17°C within 120 days. The variation of organic molecules in comets remains unclear but it would be far greater than that of minerals because carbonaceous chondrites contain millions of organic molecules (Schmitt-Kopplin et al. 2010). The results indicate that organic compounds less labile than ribose and glycine are not altered in comets at temperatures of −20°C or lower within 120 days.

Surface temperatures of comets change dramatically with distance from the Sun and the presence or absence of ice on their surfaces. The thermal histories of two locations on the nucleus of comet 67P during a full orbit are shown in Figure 6.
Temperatures were calculated using the model of Davidsson & Rickman (2014). In brief, local illumination conditions were calculated during nucleus rotation and orbital motion, taking into account the direct solar flux as well as shadowing and self-heating (diffuse radiation scattered or emitted from other parts of the surface) of the irregularly shaped nucleus. The one-dimensional heat conservation equation was solved with an upper boundary condition balancing absorbed radiation flux...
with thermal emission losses, consumption by sublimation of near-surface water ice, and heat conduction to or from the interior, assuming a 20 vol.% water–ice content and a thermal inertia of $50 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ (B. J. R. Davidsson 2019, in preparation).

Figure 6(a) shows conditions on the eastern part of the Ash region of 67P and exemplifies the thermal history of a location that experiences polar night during the perihelion passage. In this case, the temperature does not exceed $-70 \degree C$ at any time. Conditions at the central part of the Imhotep region, where solar illumination is fairly strong during the perihelion passage, are shown in Figure 6(b). There the surface temperature does not exceed $-45 \degree C$ because of cooling due to the sublimation of ice. Even if ice is absent from the surface, the temperature of the ice-sublimation front (a few millimeters below the surface) is about $-70 \degree C$ (Kömle & Steiner 1992; Grün et al. 1993). In that case, the surface temperature can reach 30$\degree C$–100$\degree C$ but decreases rapidly toward the ice-front temperature within the thin, dry mantle dust. The absence of hydrated silicates on 67P indicates that a very limited amount of the dust has experienced such high temperatures, or that silicate grains in high-temperature areas are not hydrated because of the low H$_2$O pressure at the surface.

The rate of reaction between dust grains and ice and ice vapor depends on the activation energy of the reaction, temperature, and vapor pressures of the volatiles. The activation energy was not determined in our low-temperature experiments because there was no significant change in XRD or FT-IR spectra, even in the longest-duration experiments. The experiments were performed under saturated vapor-pressure conditions for D$_2$O, whereas the partial pressure of H$_2$O on the surface or in the subsurface of comets is lower than the equilibrium vapor pressure. The hydration reactions might be controlled by dust–H$_2$O collision frequency because the grains are very small and H$_2$O easily adsorbed on silicates. Exposure durations required for hydration on the actual comet would therefore be longer than in our experiments, which thus indicates that the experiments provide the minimum number of water molecules colliding with amorphous silicates for hydration to or not to occur. Assuming a grain diameter of 100 nm, the number of H$_2$O molecules colliding with a single grain during 10 days at 25$\degree C$ is estimated to be $2.6 \times 10^{-6}$.
molecules from the Hertz–Knudsen equation. Even on a dry surface, amorphous silicates can be hydrated if enough H$_2$O molecules diffuse from the ice-sublimation front and collide with each grain. The same calculation for 120 days at $-17^\circ$C indicates that alteration might not occur at that temperature even if $4.2 \times 10^{-6}$ moles of H$_2$O molecules collide with dust. The partial pressure of H$_2$O on comet 67P at $-17^\circ$C was 0.01–0.20 Pa (B. J. R. Davidsson 2019, in preparation), which is ($0.1$–$2.0) \times 10^{-3}$ times the experimental pressure of D$_2$O in our experiments. This indicates that comet dust would not alter for 25–510 comet periods ($164$–$3290$ yr) under the assumption that the hydration is controlled by the collision frequency between dust and H$_2$O molecules. This is a minimum estimate because 120 days was the maximum duration in this study, temperatures are much lower than $-17^\circ$C except for the thin layer on the surface without ice, and the number density of adsorbed H$_2$O molecules on the surface of amorphous silicate is lower due to the low partial pressure of water on the comet. This is consistent with the absence of a phyllosilicate signature on 67P, and suggests that amino acids and sugars have not been altered by thermal radiation from the Sun.

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