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1	In-situ water-immersion experiments on amorphous silicates in the MgO–SiO ₂
2	system: implications for the onset of aqueous alteration in primitive meteorites
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16	
17	Abstract
18	Amorphous silicates, abundant in primitive carbonaceous chondrites, are among
19	the most primitive materials from the early Solar System. They show evidence of some
20	aqueous alteration in the meteorite parent bodies, but it is not clear how this highly reactive
21	material changed at an early stage after contact with water. Herein, we report in-situ
22	experiments on the aqueous alteration of amorphous silicate nanoparticles (typically 70 nm

23 in diameter); we used two different compositions that are similar to forsterite (MgO/SiO₂ = 24 2.02) and enstatite (MgO/SiO₂ = 1.15) in the simple MgO–SiO₂ system to understand basic 25 reaction principles at the onset of the aqueous alteration. The experiments were performed 26 in pure water at room temperature using X-ray diffraction (XRD), transmission electron 27 microscopy (TEM), and pH measurements. The in-situ TEM images of the 28 nanoparticles-in particular those with the forsterite composition-gradually became 29 difficult to recognize in water. The pH value of the water also increased with time, suggesting that preferential Mg²⁺ dissolution occurred from the amorphous silicates right 30 31 after mixing with water. The *in-situ* XRD patterns showed that magnesium silicate hydrate 32 (M-S-H), which is a poorly crystalline phase like a phyllosilicate, newly appeared. The 33 M-S-H seems to have been formed *via* a dissolution-precipitation process. Its formation 34 rate from amorphous silicates was considerably higher than from crystalline silicates, 35 because amorphous silicates are highly metastable and have high solubility in water. M-S-H 36 formation from the forsterite composition, which has a highly unstable amorphous structure, 37 is ten times faster than from the enstatite composition. The M-S-Hs show string-like or tiny fragmental textures in the final dried products that are very similar to those observed in the 38 39 matrices of some primitive carbonaceous chondrites. M-S-H would have been the initial 40 product formed in the aqueous alteration of amorphous silicates in the meteorites; thus, it is 41 an important tracer of early aqueous activity at low temperatures in the early Solar System. 42 By comparing the *in-situ* observations with those obtained after drying the experimental 43 samples, we found two types of M-S-Hs: epigenetic M-S-Hs-which have a slightly Si-rich 44 composition—formed during drying, and syngenetic M-S-Hs formed by in-situ alteration.

Carbonaceous chondrites may also contain these two types of hydrous silicates, and this should be investigated to understand the conditions for aqueous alteration in the early Solar System in more detail. The present study clearly showed the importance of Mg/Si ratio in the precursor materials, although the actual chondrites are in more complicated multi-component system. Future experiments based on the present results can extend the investigation to the system containing Fe, S, and other components as in carbonaceous chondrites.

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53 Keywords: amorphous silicate, magnesium silicate hydrate (M-S-H), aqueous alteration,

54 carbonaceous chondrite, in-situ experiment

1. Introduction

56 Based on infrared astronomical observations, most silicate dust is considered to be 57 amorphous in the interstellar medium (Kemper 2004) and in protoplanetary disks (van 58 Boekel et al. 2004). Therefore, amorphous silicates are believed to be a major precursor of 59 solid materials in the Solar System. Moreover, amorphous silicates are abundantly observed 60 in cometary dust as glass with embedded metal and sulfide (GEMS; e.g., Keller and 61 Messenger 2011) and in some carbonaceous chondrites (e.g., Brearley 1993, Greshake 62 1997, Leroux et al. 2015) that experienced less aqueous alteration. The amorphous silicates 63 in carbonaceous chondrites, even though they are mostly primitive, nevertheless show some 64 evidence of aqueous alteration, which occurred in the parent bodies of these meteorites due 65 to reactions between minerals—including amorphous silicates—with melted ice (e.g.,66 Abreu and Brearley 2010, Le Guillou et al. 2015a, Matsumoto et al. 2019). Therefore, the 67 aqueous alteration of amorphous silicates is important for understanding the evolution of 68 small bodies driven by aqueous fluids in the early Solar System. In addition, there is 69 increasing interest in the process of aqueous alteration of amorphous silicates in various 70 research fields, as well as in planetary science; for example, the geochemical interest in 71 basalt weathering (e.g., Berger et al. 1987, Oelkers 2001, Oelkers et al. 2001, Schindler et 72 al. 2019) and the industrial interest in the alteration of nuclear-waste glasses (Frugier et al. 73 2008, Valle et al. 2010).

Aqueous alteration of silicates in the early Solar System has been explored through experimental studies as well as by examinations of carbonaceous chondrites (e.g., Le Guillou and Brearley 2014). Although most experimental studies have focused on the

77 alteration of crystalline silicates (Nomura and Miyamoto 1998, Jones and Brearley 2006, 78 Ohnishi and Tomeoka 2007), a few studies using amorphous silicates as starting materials 79 have been reported recently. Nakamura-Messenger et al. (2011) conducted hydrothermal 80 experiments on cometary dust containing pristine amorphous silicates. Using aqueous 81 solutions with different pH values, they observed the formation of phyllosilicates similar to 82 those found in carbonaceous chondrites. Noguchi (2012) has observed similar 83 phyllosilicates in hydrothermal experiments on amorphous silicates in a CI composition 84 synthesized using the sol-gel method.

85 However, it is still unclear how these phyllosilicates formed, particularly at the low 86 temperature (e.g., room temperature) at which the aqueous alteration of most carbonaceous 87 chondrites occurred (Brearley 2006). For example, it has not yet been demonstrated 88 whether the first step toward forming phyllosilicates via aqueous alteration is the 89 dissolution of the amorphous silicates in water, hydration of the amorphous silicates, and/or 90 some other process. It is also unclear how rapidly each process progresses (whether it 91 occurs immediately or gradually) after the silicate has been immersed in water. Recently, 92 Le Guillou et al. (2015b) conducted aqueous alteration experiments with amorphous silicate 93 with olivine composition at relatively low temperatures—90 °C and 190 °C—and they 94 found some complex alteration textures in spite of the low temperature condition and short 95 duration of the experiments (two weeks). This implies that further investigation with much 96 higher time resolution is required.

97 In addition, the samples used in previous experiments experienced not only a98 hydrothermal process but also a subsequent drying process, because the run products were

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99 observed after drying of the samples (e.g., Nakamura-Messenger et al. 2011, Noguchi 2012, 100 Le Guillou et al. 2015b). During the drying process, it is reasonable to expect some phases 101 to be modified or additional phases to be formed. Any additional new phase is probably 102 similar to, but not exactly the same as, the phases formed during the hydrothermal process. 103 If this is the case, it is necessary to distinguish the original run products formed through 104 aqueous alteration from those arising during the drying process. By extension, 105 carbonaceous chondrites also may have two types of aqueous alteration products, which 106 must be distinguished in order to understand the exact conditions of their aqueous alteration. 107 This seems to have been overlooked in many cases until now.

In this study, we have therefore conducted *in-situ* observations of the aqueous alteration of amorphous silicates using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). We also analyzed the run products after drying. *In-situ* pH measurement of water with amorphous silicates was also made. Based on these results, we discuss the processes that occur in the very early stages of aqueous alteration and evaluate the effect of the subsequent drying process in order to facilitate the decoding of the carbonaceous chondrites.

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2. Experimental methods

119 2.1. Starting materials

120 The samples used in the current experiments were amorphous silicates in the 121 MgO-SiO₂ system. We used two different chemical compositions that are similar to 122 forsterite (MgO/SiO₂ = 2.02; sample name, am-Fo) and enstatite (MgO/SiO₂ = 1.15; sample 123 name, am-En). We used the MgO-SiO₂ system as it is the simplest system representing 124 amorphous silicates in carbonaceous chondrites. For simplicity we excluded FeO, which is 125 another important component, because it is difficult to control the redox state of Fe in 126 *in-situ* aqueous alteration experiments. If Fe is present as FeO, some MgO in phyllosilicates 127 is replaced by FeO. In addition, amorphous silicates in GEMS are poor in FeO, and most of 128 the Fe is included as nanoparticles of metallic iron and iron sulfide.

129 The present amorphous silicate samples were synthesized in an induction thermal 130 plasma (ITP) furnace at Nisshin Flour Milling Inc. (Koike et al. 2010, Imai 2012, 131 Yamamoto and Tachibana 2018, Takigawa et al. 2019a). In this furnace, a mixture of Mg(OH)₂ and SiO₂ powder was evaporated in a high temperature plasma ($\sim 10^4$ K), and 132 133 spherical nanoparticles ~20-200 nm (~70 nm on average) in diameter (Figs. 1a and d) were condensed from the gas by quenching at an ultra-high cooling rate ($\sim 1-10 \times 10^4$ K/s). Their 134 135 bulk chemical compositions, noted above, were determined with an electron probe 136 microanalyzer after the powders had been compressed. Scanning transmission electron 137 microscopy with energy-dispersive X-ray spectroscopy (STEM-EDS) analysis yielded 138 consistent Mg/Si ratios of 2.00(4) for am-Fo and 1.10(2) for am-En, and they displayed 139 spatial homogeneity on the nanometer scale (Figs. 1b and e). Each XRD pattern showed a 140 very broad peak corresponding to amorphous silicates, and there are no obvious peaks of 141 crystalline silicates or hydrates (Figs. 1c and f). The widths of the broad peaks were similar

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to those of amorphous silicates used in other previous experiments (*e.g.*, Roskosz et al. 2011). The peak positions for am-Fo and am-En were different (~31° and ~26° in 20 CuK α , respectively), indicating a difference in their average structures in the amorphous state. The TEM-detected electron-diffraction patterns showed that almost all the observed particles were amorphous (Figs.1 a and d).

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148 **2.2. Experimental protocol**

149 We performed two types of *in-situ* experiments (Fig. 2) on the two samples 150 (am-Fo and am-En): aqueous-XRD experiments (aq-XRD) and aqueous-TEM experiments 151 (aq-TEM), which provide complementary information. From aq-XRD, we obtained powder 152 diffraction patterns of bulk samples immersed in water, using a specific XRD holder to 153 prevent water evaporation. From aq-TEM, we obtained TEM images of individual particles 154 immersed in water, with the sample placed in a TEM holder specifically designed for liquid 155 observations. After each of the two experiments, the run product was dried, and additional 156 analyses were performed on the dried products. In addition, pH measurements of water 157 mixed with amorphous silicates were also performed. All measurements were made at 158 room temperature.

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160 2.3. Aqueous-XRD experiment

161 Each starting material (~0.3 g) was mixed with deionized water (~ 0.3 mL), with a
162 water/rock (W/R) ratio of approximately 1 by mass. For carbonaceous chondrites, a W/R
163 ratio as large as ~1 is estimated for the CI group, which shows advanced aqueous alteration

164 features (Clayton and Mayeda 1999). The sample mixture was placed in an airtight sample 165 holder (Rigaku, 2392B101) consisting of a stainless-steel stage sealed with a Viton O-ring 166 and a polyimide film to prevent evaporation. The XRD measurement was performed using 167 a powder X-ray diffractometer (Rigaku Smart Lab., Kyoto University) with Ni-filtered 168 CuKa radiation (40 kV, 40 mA). The step interval for scanning was 0.05° , and the diffraction angles (2 θ) ranged from 4° to 80°. The first measurement was made a few 169 170 minutes after the sample had been mixed with water, and the time required for one 171 measurement was about 30 min. Measurements were conducted repeatedly for ~48 h.

After the *in-situ* measurements, the seal was removed, and the sample in the holder was dried overnight at room temperature in a vacuum maintained with a diaphragm pump. Two types of XRD patterns were obtained for the dried sample: one included the polyimide film in order to facilitate comparison with the patterns obtained from the aqueous experiments, and the other did not include the film in order to obtain a clearer profile. Finally, the run products were transferred onto a normal C-grid and analyzed using 200-keV TEM with an EDS detector (JEOL JEM-2100F, JED-2300T, Kyoto University).

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180 **2.4.** Aqueous-TEM experiment

181 Each starting material was mixed with deionized, ultra-pure water. Ultrasonic 182 vibration was applied to achieve a high degree of dispersion of the amorphous silicate 183 particles in the water. A drop of the sample mixture (<1 μ L) was placed into a liquid cell in 184 a TEM holder specifically designed for *in-situ* observations (Poseidon, Protochips Inc.) and 185 was cautiously sealed with an ultrathin film of amorphous SiN_x, using the same procedure 186 as Satoh et al. (2018). (A sketch of the cell system is shown in Fig. S1 of Holtz et al. 2013 187 or Fig. S1 of Yamazaki et al. 2017, although the present experiment did not use a 188 liquid-flow system). While this was ideal for performing experiments with a W/R ratio 189 similar to those used for aq-XRD, this was impossible for the TEM holder. Thus, we 190 adopted W/R ratios of ~10–100 by mass. The holder containing the sample was then placed 191 in a TEM (JEOL JEM-2100F, Hokkaido University). We observed the time evolution of 192 the samples through bright-field imaging at 200 keV for ~24 h. The electron flux was ~ 10^2 193 electrons/ $(s \cdot nm^2)$ or less, at which no significant effects were found in previous *in-situ* 194 liquid experiments for protein crystallization (Yamazaki et al. 2017). To suppress 195 electron-irradiation effects on the reactions further, we sequentially and repeatedly 196 observed several regions, avoiding continuous illumination of any one specific region. 197 Scattering of the electron beams by water sealed with a couple of 50-nm-thick SiN_x films 198 was so extremely large that no electron-diffraction patterns or characteristic X-ray spectra 199 were measured. Due to unavoidable timing constraints imposed by procedures such as 200 sample setting and sealing, the observation started approximately 30 min after the sample 201 had been mixed with water. After the in-situ TEM experiment, which lasted for ~24 h, the 202 seal was removed, and the sample in the cell was dried overnight at room temperature in a 203 vacuum maintained with a diaphragm pump. The dried sample on the amorphous SiN_x film 204 was then observed via TEM (JEOL JEM-2100F, Kyoto University).

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206 2.5. pH measurements

Each starting material (~20 mg) was mixed with deionized water (~20 mL) at a W/R ratio of ~100 by mass, which is similar to that of the aq-TEM sample. The pH of the liquid in the mixture was repeatedly measured with a pH meter (HORIBA, LAQUAact D-75) during the two days after the moment of mixing. The samples were always covered with a plastic film to prevent water evaporation, except during the pH measurements (~1 min). We did not measure the chemical composition of the liquid, because the liquid and nanoparticles cannot be separated.

3. Results

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3.1. Aqueous-XRD experiment

216 The time evolution of the XRD patterns obtained in the aqueous alteration 217 experiments are shown in Figs. 3a and b. The patterns of the starting materials without 218 water and of the dried products at the end of the experiment are shown respectively at the 219 bottom and top of each plot. These patterns were taken in dry conditions for samples 220 covered with a polyimide film to enable robust comparison with the *in-situ* aq-XRD results. The diffraction peaks at around 43° and 51° (open triangles) correspond to the 221 stainless-steel used in the sample holder, and the broad peaks at approximately 6° , 11°, and 222 223 15° (open diamonds) correspond to the polyimide film used to seal the sample (Fig. 3d). 224 They do not present any significant problems for the analysis of the results. In addition, we 225 detected tiny, sharp peaks at approximately 13° (~0.68 nm) and 20° (~0.44 nm) for am-Fo and at 15° (~0.59 nm) and 20° (~0.44 nm) for am-En (open squares) that cannot be 226 227 attributed to any reasonable phases in the Mg-Si-O-H system or carbonates. We assume 228 that these tiny peaks are negligible for the following discussion. The absence of carbonates 229 indicates that dissolution of CO₂ from the air into the water is little and it did not change 230 the pH to affect chemical reactions seriously during the experiments.

As aqueous alteration progressed, broad new peaks appeared at $2\theta = -35^{\circ}$ and 60° (solid circles in Fig. 3). The broadness of these XRD peaks indicates very low crystallinity, and the asymmetry of the -35° peak indicates a nanometric size and a turbostratic lamellar texture (Warren 1941). These peaks can be attributed to a phyllosilicate-like hydrous phase with quite poor crystallinity, named M-S-H (magnesium silicate hydrate), which is 236 commonly known in the cement and concrete industry, where it is used in particular for 237 nuclear-waste encapsulation, and it also occurs in natural rocks such as clay-rich or granitic 238 rocks (e.g., Cole 1953, Zhang et al. 2011, Dauzeres et al. 2016, Mäder et al. 2017). Previous studies reported that synthesized M-S-Hs show XRD peaks at $\sim 7^{\circ}$ ($\sim 9^{\circ}$ in 239 air-dried conditions), ~20°, ~35° (asymmetric), and ~60° (e.g., Roosz et al. 2015, Bernard 240 241 et al. 2019), and similar features are also confirmed from M-S-Hs collected from interfaces 242 between cement and natural clay (Dauzeres et al. 2016). The structure of M-S-H is not well 243 known, but it has been correlated with talc, sepiolite, and/or serpentine group minerals 244 (Brew and Glasser 2005, Roosz et al. 2015, Nied et al. 2016, Bernard et al. 2017, 2019). The asymmetric peak at ~35° is also confirmed in some poorly crystalline, disordered 245 phyllosilicates as a prism reflection, and the peak at $2\theta = -60^{\circ}$ corresponds to the 060 246 247 and/or 330 reflections from phyllosilicates.

The profiles at around $25-33^{\circ}$, where amorphous silicates show broad diffraction peaks (the gray arrows in Fig. 3), changed significantly during the experiments. These changes may be contributed by water (Fig. 3c) and by the M-S-H ~20° peaks, as well as by amorphous silicates. Thus, it is difficult to identify the cause of the profile change without deconvolving the pattern, as we discuss later.

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254 **3.2. Run products after aqueous-XRD experiments**

Fig. 4 shows the XRD patterns of the dried run products without the airtight sample holder (the polyimide film and stainless-steel holder). In addition to the features already detected in the aq-XRD patterns (the ~25° broad peak, ~35° prism peak, and ~60° 258 peak), a very broad peak at $2\theta = 9^\circ$, which corresponds to the basal-plane reflection of 259 M-S-H, was detected in am-Fo (Fig. 4a, inset). This position is similar to talc, one of the 260 Mg phyllosilicates [Mg₃Si₄O₁₀(OH)₂], although the peak is weak and very broad, indicating 261 disordered stacking. In contrast, no clear signature of basal-plane reflection was observed in am-En, but a very broad increase in intensity around $2\theta = 5-11^{\circ}$ can be recognized by 262 263 comparison with the blank measurement pattern (Fig. 4b, dotted line in the inset panel). 264 This highly-diffused basal diffraction indicates that the degree of the stacking order is 265 extremely low.

266 TEM images of dried aq-XRD samples are shown in Fig. 5. The am-Fo particles 267 have almost lost their original spherical shapes and have formed aggregates of string-like 268 materials (Fig. 5a). In contrast, the am-En particles more-or-less maintained their original 269 spherical shapes (Fig. 5d), and fine objects rather than string-like materials were found 270 around the particles. Both may correspond to M-S-H. High-resolution TEM images of the 271 M-S-Hs (lower right images in Figs. 5a and d) show no clear lattice fringes, indicating 272 extremely poor crystallinity, which corresponds to the very broad XRD pattern (Fig. 4). 273 The selected-area electron-diffraction (SAED) patterns of both samples feature rings (Figs. 274 5b and e). They show peaks suggesting ~ 0.25 nm and ~ 0.15 nm in *d*-spacing, 275 corresponding to the XRD peaks at 35° and 60° in Fig. 4, respectively.

STEM-EDS analysis of the products yields the average Mg/Si ratios of 2.04(3) for
am-Fo and 1.04(3) for am-En, suggesting that the average compositions changed very little,
if at all, from the starting materials. However, the STEM-EDS imaging exhibits spatial
heterogeneity of the Si/ (Si + Mg) ratio at the nanometer scale (Figs. 5c and f). In both

samples, the particle surfaces seem to be enriched in Si. This seems to correspond to the
string-like materials or fine objects and probably precipitated from liquid during drying, as
also described later.

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284 **3.3. Aqueous-TEM experiment**

285 To obtain nanometer scale images of particles during aqueous alteration, we 286 performed *in-situ* TEM observations for water-immersed silicate particles (Fig. 6). As time 287 passed, the aq-TEM images gradually became blurred throughout the whole image, and 288 thus particles became difficult to recognize clearly in the liquid. This is probably due to an 289 increase in the electron-scattering power of the aqueous solution caused by cation 290 dissolution from the silicates into the water. Although the particle sizes in the aq-TEM 291 images appear to be larger than those of the starting material (particularly for am-Fo, Fig. 292 6a), this is probably only an apparent expansion caused by a combination of particle 293 clustering and image blurring. The expansion may also reflect hydration of individual 294 particles, but it is difficult to determine whether it really occurs from the aq-TEM images 295 alone. The blurring seems to progress faster for am-Fo (Fig. 6a) than for am-En (Fig. 6b). 296 The change in particle appearance is recognized more easily for am-En. Final in-situ 297 aq-TEM images after the elapse of almost a day are shown at the bottom of Fig. 6 and in 298 Figs. 7a and c. These images show that the boundaries between particles and liquids are 299 barely recognizable for both am-Fo and am-En.

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302 3.4. Run products after the aqueous-TEM experiments

303 Figs. 7b and d show TEM images and SAED patterns of the two run products after 304 drying. The dark objects observed in Figs. 7a and c likely correspond to particles that are 305 seen clearly in Figs. 7b and d. The textures of the dried products from am-Fo (Fig. 7b) are 306 almost the same as those of the aq-XRD products (Fig. 5a), whereas the am-En particles 307 (Fig. 7d) maintained their sphericity to a higher degree than those of aq-XRD (Fig. 5d). On 308 the SiN_x film, aggregates of string-like materials for am-Fo (Fig. 7b lower right) and small 309 irregular objects a few tens of nm in size for am-En (Fig. 7d lower right) were observed. 310 They were likely the same materials as those attached around the particles and were likely 311 precipitated from the liquid. High-resolution TEM images of the aq-TEM products were 312 not obtained, because they were less clear due to the background caused by the 50-nm-thick 313 amorphous SiN_x film used as the bottom floor of the sample holder for aq-TEM.

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316 **3.5. pH measurements**

Fig. 8 shows the results of the pH measurements. This clearly shows that the pH value of the liquid became high in the beginning, suggesting preferential Mg^{2+} dissolution from the silicates into the water. This is consistent with previous studies (Chizmadia and Lebrón-Rivera 2010, Hellmann et al. 2012, Ruiz-Agudo et al. 2014, Gin et al. 2015) and indicates that the blurring observed in aq-TEM was mainly caused by this dissolution. The pH value reached a maximum right after mixing for am-Fo and in ~2 hours after mixing for am-En (Fig. 8, inset). The pH value then decreased gradually, probably due to subsequent Si^{4+} (SiO₄⁴⁻) dissolution and the precipitation of M-S-H, consuming the Mg²⁺ in the 325 solution. After two days, the pH value still remained higher than 9.

4. Discussion

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328 4.1. XRD peak deconvolution

329 For quantitative evaluation, peak-fitting was conducted for the series of aq-XRD 330 profiles (a typical fitting result is shown in Fig. 9). The profiles in the range $2\theta = 10-55^{\circ}$ 331 were fitted by a combination of diffraction peaks due to the polyimide film, amorphous 332 silicates, M-S-H, and liquid, with a background assumed to be linear (Fig. 9a). The 333 polyimide diffraction peak (10°) and the amorphous peak ($\sim 25^{\circ}$) were fitted with Voigt 334 functions, and the M-S-H prism peak (~35°) was fitted with an asymmetric split Voigt 335 function. The diffraction profile of the liquid was assumed to be the same as that of water 336 (Fig. 3c). Because the water diffraction profile was well fitted with two Voigt functions, the 337 liquid diffraction was fitted with the same two Voigt functions, with only the scale factor adjusted. The polyimide peak at ~6° and the M-S-H peak at ~60° are out of the range $2\theta =$ 338 339 10-55° and do not overlap with any other peaks. Thus, they were fitted individually after 340 subtracting a linear background (Figs. 9b and c).

341 All the aq-XRD patterns were well fitted with a superposition of the above 342 functions, yielding respective peak intensities from all the patterns. Fig. 10 shows the time 343 evolution of the integrated peak intensities of the liquid, M-S-H (prism and $\sim 60^{\circ}$), and 344 amorphous silicates after normalization to the intensity of the polyimide $\sim 6^{\circ}$ peak, which 345 should be constant during each experiment. The peak intensities of the M-S-H prism (Figs. 346 10b and f) and $\sim 60^{\circ}$ peaks (Figs. 10c and g) increase with time in a similar way for both 347 am-Fo and am-En, and the curves for these intensity increases are roughly complementary 348 to those of the liquid (Figs. 10a and e) and the amorphous silicates (Figs. 10d and h). The peak intensity of the liquid did not drop to zero until the samples were vacuum dried. It
should be noted that the intensity of the amorphous silicates may not be accurate, because
several peaks overlap in the 2θ region around 25–33°, and some other peaks which were
not used in the present fitting—such as the M-S-H ~20° peak (e.g., Roosz et al. 2015,
Bernard et al. 2019)—may exist in this region as well.

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4.2. Aqueous alteration processes in the earliest stage

357 4.2.1 The process controlling M-S-H formation

The selective dissolution of Mg²⁺ followed by Si⁴⁺ (SiO₄⁴⁻) dissolution, as 358 indicated by the pH measurement (Fig. 8), is consistent with the Si-O bond energy being 359 significantly higher than the Mg–O bond energy (Huggins and Sun 1946). This would make 360 the diffusion coefficient of Mg^{2+} higher than that of Si^{4+} in the amorphous silicates. 361 362 Moreover, the amorphous silicates are in a highly metastable state, and thus their 363 solubilities should be larger than that of M-S-H, which is comparable with the solubilities of Mg phyllosilicates (Bernard et al. 2017). This should cause overshoot of the Mg²⁺ and 364 Si⁴⁺ dissolution, to the extent that their solubility product becomes much higher than that 365 366 for phyllosilicates and M-S-H. From the highly supersaturated solution, highly disordered 367 M-S-Hs should be formed, rather than the more-stable crystalline phases. A similar 368 dissolution-precipitation process has been proposed to be mostly dominant for general 369 mineral-fluid reactions as well (Hellmann et al. 2012, Ruiz-Agudo et al. 2014, Gin et al. 370 2015), but there may be great differences in the dissolution rates. In altering amorphous 371 silicates, very rapid dissolution produces a supersaturated solution and the formation of a372 characteristic M-S-H with a highly disordered structure.

373 We observe some diffraction intensity from amorphous silicates even at the end of 374 the experiments (Figs. 10d and h). This suggests the existence of amorphous silicate 375 remnants, which should be more-or-less hydrated. Assuming that the hydration rate is 376 controlled primarily by the diffusion of water molecules into the amorphous silicates, we 377 roughly estimated the degree of hydration. By extrapolating experimental results of the 378 diffusion coefficient of water (D_{H_2O}) in amorphous silica (Wakabayashi and Tomozawa 379 1989) to room temperature, a diffusion distance in 1 hour (t = 1 h) is estimated to be ~15 380 nm, which corresponds to a volume fraction of ~80% for spherical particles with the 381 diameter of 70 nm. Because D_{H_2O} in am-Fo and am-En should be larger than that in amorphous silica, it is reasonable that hydration would have occurred in a few hours or less 382 383 after contact with water in the current experiments. Figs. 10a shows that the water intensity 384 decreases before the formation of M-S-H in am-Fo. This also suggests that amorphous 385 silicate particles not only were dissolved into the water to form M-S-H but also were 386 hydrated.

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389 4.2.2 Rate equation for M-S-H formation

We have estimated the M-S-H formation rate using the deconvolved XRD peakintensities of the M-S-H peaks (shown in Figs. 10b, c, f, and g). We adopted a simple

392 first-order equation as an empirical model, expressing the M-S-H peak intensity as a393 function of time *t* as

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$$I(t) = I_0 [1 - \exp\{k(t - t_0)\}], \tag{1}$$

395 where I_0 is the final intensity, k is the rate constant, and t_0 is the time delay to the start 396 of M-S-H formation.

397 Using this empirical equation, good fits were obtained, as shown in Figs. 10b, c, f, 398 and g (solid lines), yielding the fitting parameters shown in the figures. The fitted results for the prism peak and the ~60° peak are almost the same. The delay time $t_0 \sim 1$ h for 399 am-Fo is clearly smaller than $t_0 \sim 4-8$ h for am-En. This difference is comparable to the 400 401 difference in the time for the water solution to reach the highest pH values: ~10 min for 402 am-Fo and ~2 hours for am-En (Fig. 8). The highest pH value represents the high Mg^{2+} -dissolved state, and subsequent $Si^{4+}(SiO_4^{4-})$ dissolution should be delayed. The delay 403 404 time t_0 therefore can be interpreted roughly as the time for the water solution to reach a 405 sufficiently high degree of supersaturation for M-S-H formation (e.g., the maximum 406 solubility product).

The rate constant k for am-Fo (~0.3–0.4 h⁻¹) is about 10 times higher than for am-En (~0.01–0.02 h⁻¹). Therefore, the degree of M-S-H formation (I/I_0), reaches ~90 % after only 7–9 hours for am-Fo, whereas for am-En the time for a 90% of the M-S-H to form requires ~140–230 h (5–10 days). The difference in k is likely related to the difference in the degree of supersaturation, which is the driving force for precipitation. The shorter t_0 and larger k for am-Fo than for am-En are both related to its more rapid

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dissolution, which is probably due to the unstable structure of am-Fo, where polymerization of the SiO₄ tetrahedron is essentially absent (Kohara et al. 2004).

415 This equation is applicable only for conditions with a sufficient amount of water 416 and with a W/R ratio roughly larger than 1. This may be reasonable if we consider the water 417 content in Mg phyllosilicates (e.g., 18.8, 17.9, 13.0, and 4.8 wt.% H₂O in saponite, 418 vermiculite, serpentine, and talc, respectively). The peak-fitting results (Figs. 10a and d) 419 also indicate that water is actually present even in the final stage of the experiments. Thus, 420 assuming that the function I(t) is adequate for a W/R ratio of ~1 and higher, it can be applied to the results from aq-TEM as well as to those from aq-XRD. The degree of M-S-H 421 422 formation in the products of am-Fo after aq-XRD (~48 h) and aq-TEM (~24 h) are both estimated to be $I/I_0 > 99.9$ %. On the other hand, the values of I/I_0 for the am-En 423 products are estimated to be much lower. For am-En, the I/I_0 values from the aq-TEM 424 425 and aq-XRD products estimated from eq.(1) are ~17% at $t \sim 19$ h and ~43% at $t \sim 40$ h, 426 respectively. These values are consistent with the textures observed by TEM. The TEM 427 images of the am-Fo products showed that they have almost lost their original spherical 428 shapes, whereas the am-En products have not. Moreover, for am-En the sphericity is almost 429 preserved in aq-TEM (Fig. 7d) compared to aq-XRD (Fig. 5d).

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432 4.3. Structural variation of the M-S-H

433 To detect changes in the M-S-H structure in detail, we focused on the M-S-H peak 434 at $\sim 60^{\circ}$, which does not overlap with other peaks. Fig. 11 shows the time evolution of the 435 peak-top position, with the FWHM determined by the split Voigt function. There are clear 436 differences between am-Fo and am-En. The FWHM of am-En is larger than that of am-Fo, 437 indicating that the M-S-H from am-En has poorer crystallinity than that from am-Fo. 438 Moreover, the difference in the 2θ positions of am-Fo and am-En reflects a difference in the 439 M-S-H structures. Similarly to Mg phyllosilicates, M-S-H is expected to be composed of 440 two basic components in the crystal structure: a sheet of triple-edge-sharing MgO₆ octahedra (Mg^O sheet) and a sheet of corner-sharing SiO₄ tetrahedra (Si^T sheet). The *b*-axis 441 length of the single Mg^{O} sheet is assumed to be ~0.944 nm by reference to that of brucite 442 $[Mg(OH)_2]$, which consists of Mg^O sheets alone (Ma et al. 2013), whereas the *b*-axis length 443 of the single Si^T sheet is assumed to be ~0.916 nm, based on the mean Si–O bond distance 444 of 0.162 nm (e.g., Jones 1968). These two *b*-axis lengths (~0.944 and ~0.916 nm) 445 correspond to 060 reflection peaks at 2 θ values of ~58.7° and ~60.7°, respectively (Fig. 11, 446 447 red and blue lines). Our XRD results show that the M-S-H peaks are located at about 59- 60° , between those of the Mg^O and Si^T sheets. The difference in the *b*-axis lengths of the 448 M-S-H may correspond to different proportions of randomly stacked Mg^O and Si^T sheets. 449 The XRD patterns of M-S-H in a recent study (Bernard et al. 2019) also shows a consistent 450 451 trend in the peak position change with variations in the Mg/Si ratio. Although there should 452 be large number of in-sheet defects in M-S-H as well as stacking disorder, the assumption 453 seems roughly available. In contrast, such variations do not occur in crystalline Mg 454 phyllosilicates; they have almost constant b-axis lengths of ~0.92 nm and 060/330 reflections at ~60-61°, regardless of the Mg/Si ratio. This is because crystalline Mg 455 phyllosilicates require almost the same mesh size (a- and b-axis lengths) for Si^{T} and Mg^{O} 456

457 sheets; this size is close to that of the Si^{T} sheet, which is stiffer than the Mg^O sheet. The 458 length of the M-S-H *b*-axis varies, probably due to its very low crystallinity and structural 459 flexibility. The present results (Fig. 11) implies that the M-S-H in the am-Fo experiment has 460 a more Mg-rich composition (more abundant in the Mg^O sheet) than that in the am-En 461 experiment and that the structure of M-S-H in am-Fo may be more similar to brucite than to 462 silicates.

463 The 2 θ peak position changed slightly during the experiments, particularly in the 464 early stage of M-S-H formation (~3 h) for am-Fo and after drying. Assuming that the 465 structural changes did not occur after precipitation, the peak position change can be 466 attributed to changes in the structure of the precipitating M-S-H. The lower peak position of 467 the first M-S-H implies that the supersaturated solution has a high Mg content, which is 468 consistent with the selective dissolution of Mg into the water during the first stage. The 469 peak shifts to higher 20 during drying of both samples, indicating that the M-S-H that 470 precipitated during drying has a more Si-rich composition than that formed during aqueous alteration. The Si⁴⁺ dissolved in water may have precipitated in larger quantities during the 471 472 drying process. This compositional change is recorded as the Si-rich rims on the M-S-H 473 particles in the STEM-EDS images (Figs. 5c and f). The present results indicate that there 474 exist two types of M-S-H: syngenetic M-S-H, which appears during the aqueous alteration 475 process, and *epigenetic M-S-H* that arises during the drying process. There is a high 476 possibility that the *c*-axis length (basal-plane spacing) may also be different between the 477 two types, although this could not be confirmed from the *in-situ* XRD patterns.

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- 482 4.4. Implications for planetary science

483 *4.4.1. M-S-H in primitive carbonaceous chondrites*

484 Carbonaceous chondrites are subdivided into multiple classes (CB, CI, CH, CK, 485 CM, CO, CR, and CV). Among them, the CI chondrites received the highest degree of 486 aqueous alteration. The CM and CR chondrites generally suffered high degrees of aqueous 487 alteration as well, with most of the water stored as hydrous phyllosilicates, mainly in the 488 matrix (e.g., Tomeoka and Buseck 1988, Bunch and Chang 1980, Weisberg et al. 1993, 489 Tomeoka and Buseck 1985, Zolensky et al. 1993). However, some CM and CR chondrites 490 contain primitive amorphous silicates that have likely survived aqueous alteration (Abreu 491 and Brearley 2010, Le Guillou and Brearley 2014, Leroux et al. 2015, Chizmadia and 492 Brearley 2008). Similar matrices of primitive nature were observed also in the ALH77307 493 CO chondrite (Brearley 1993) and in the ungrouped carbonaceous chondrite Acfer 094 494 (Greshake 1977, Matsumoto et al. 2019). These chondrites are termed "primitive 495 carbonaceous chondrites." In previous investigations of such primitive carbonaceous 496 chondrites, phases like poorly crystallized layered silicates with broad-ring SAED patterns 497 have been reported (e.g., Leroux et al. 2015; Matsumoto et al. 2019). These phases must be 498 the same as the M-S-H identified in our experimental products, and which was produced 499 from amorphous silicates by a dissolution-precipitation process in the early stage of 500 aqueous alteration. This is an important phase for indicating the earliest aqueous alteration

at low temperatures, and it should be distinguished from amorphous silicates orwell-crystallized phyllosilicates.

503 We consider the possibility that M-S-H can be a precursor material for some 504 crystalline phyllosilicates commonly observed in aqueously altered carbonaceous 505 chondrites. From the structural viewpoint, phyllosilicates can be formed by subsequent maturing of the M-S-H, if it is heated at slightly higher temperatures. The structural 506 variation in M-S-H—which corresponds to a variable ratio of Mg^O to Si^T sheets and to the 507 508 degree of order in their stacking sequence-may contribute to the fine textures or defects of 509 the phyllosilicate, because the structure of phyllosilicate is essentially characterized by the type of unit layer. Serpentine has a 1:1 unit layer (composed of 1 Si^T and 1 Mg^O sheet), 510 whereas talc/smectite/vermiculite has a 2:1 unit layer (composed of 2 Si^T and 1 Mg^O sheet). 511 512 In particular, mixed-layer phyllosilicates such as serpentine-smectite have been reported in 513 extreme aqueously altered carbonaceous chondrites (e.g., Tomeoka and Buseck 1988). The 514 M-S-H in our products has a broad and low-intensity basal-plane reflection in the XRD 515 patterns (Fig. 4). This can be interpreted as the overlap of several broad peaks from various 516 basal planes. The M-S-H may transform into mixed-layer phyllosilicates or 517 well-crystallized phyllosilicates, depending on subsequent alteration conditions.

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519 4.4.2. Significance of amorphous silicates as primary materials for carbonaceous
520 chondrites

521 As described in section 4.2.1, the disordered structure of M-S-H is attributed to the
522 highly metastable state of the precursor silicates. Therefore, the presence of M-S-H is

523 important as a tracer of early aqueous activity for primitive carbonaceous chondrites, in524 which the matrices originally consisted of amorphous silicates.

525 Moreover, the formation rate of phases aqueously altered from amorphous silicates 526 is significantly faster than that from crystalline silicates. For example, when enstatite was 527 used as a starting material, serpentine formed in pure water only at high temperature 528 (300°C) and after a long period (>168 h), and serpentine and saponite formed only at high 529 temperature (300°C) in water with a high pH value, which was obtained by artificially 530 adding NaOH (pH = 14; Ohnishi and Tomeoka 2007). In contrast, extremely rapid 531 formation of M-S-H in water with high pH values (Fig. 8), which was obtained by the 532 dissolution of amorphous silicates into pure water at room temperature, was observed in the 533 present experiments (Fig. 10). The aqueous alteration of CM and CI chondrites have been 534 suggested to have occurred at similar low temperature conditions: <100 °C for most CM 535 chondrites (e.g., Clayton and Mayeda 1999, Guo and Eiler 2007) and at ~50 °C (Leshin et 536 al. 1997) to ~150 °C (Clayton and Mayeda 1999) for CI chondrites. Therefore, a large part 537 of the hydrous phyllosilicates found in CM and CI chondrites may have been formed 538 through M-S-H from the amorphous silicates.

In the actual carbonaceous chondrites, Fe and/or S are also important for the hydrous phases such as PCP/tochilinite-cronstedtite interlayer (Tomeoka and Buseck 1985). In particular, some studies have suggested that FeO may have the effect of suppressing aqueous alteration, although the process seems not so simple (Chzmadia et al. 2006, Chizmadia and Lebrón-Rivera 2010, Chizmadia et al. 2011). Further investigation in the system containing Fe and S using the present methods is required for a morecomprehensive understanding of the aqueous alteration of carbonaceous chondrites.

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548 *4.4.3. Two different generations of hydrous phases*

549 The present results strongly suggest the presence of two different generations of 550 M-S-H: syngenetic M-S-H and epigenetic M-S-H. Similarly, two different generations may 551 exist not only for M-S-H but also for other hydrous phases, such as crystalline 552 phyllosilicates in general, and they might be preserved in carbonaceous chondrites. Because 553 the two types should have slightly different compositions and/or structures, at least at the 554 time of the formation, it may be possible to discriminate between them by careful analysis. 555 The syngenetic phases should be examined selectively to understand the exact conditions 556 for aqueous alteration. The *epigenetic* phases that arises during the drying process may 557 effectively reflect the trace-element composition of the aqueous fluid. This will be 558 important particularly to interpret the experimental products simulating the aqueous 559 alteration in future studies.

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561 4.5. Implications for cement manufacturing

M-S-H also has been a topic of interest due to its potential use in low-pH cements, *e.g.*, for nuclear-waste encapsulation (*e.g.*, Zhang et al. 2011, Dauzeres et al. 2016, Mäder et al. 2017). As shown in the present study, M-S-H phases formed by different methods and different processes may have different properties because of the diversity in their chemical 566 compositions and detailed structures, although this is still unresolved (*e.g.*, Roosz et al. 567 2015). These diversities are expected to provide the potential for designing more efficient 568 materials. The present study is the first to point out clearly that the M-S-H known in the 569 cement industry is extremely similar to the silicate ubiquitously found in primitive 570 carbonaceous chondrites, which has been called various terms such as amorphous material, 571 nanocrystalline material or very poorly crystalline material (Brealy 1993, Leroux et al. 572 2015, Chizmadia and Brearley 2008, Matsumoto et al. 2019).

This study also showed that M-S-H can be formed rapidly by aqueous alteration of amorphous silicates. In addition, the ITP method easily can be used to form amorphous silicate nanoparticles with different chemical compositions, not only in the system MgO– SiO₂ but also in multi-component systems that include a variety of cations (*e.g.*, Kim et al. 2017, Takigawa et al. 2019b). This may provide a procedure for manufacturing different varieties of silicate hydrates such as M-S-H and C-S-H (calcium silicate hydrate).

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5. Conclusions

In-situ water-immersion experiments on amorphous silicates using the MgO–SiO₂ system were conducted to elucidate the onset processes of aqueous alteration recorded in carbonaceous chondrites. The aq-TEM images showed gradual blurring probably due to cation dissolution from the silicates into the water. The supplemental pH measurements suggested that Mg^{2+} was dissolved immediately after the silicates were mixed with water and then Si⁴⁺ was dissolved, which is consistent with the aq-TEM results. After the rapid dissolution process, a phyllosilicate-like phase with extremely low crystallinity was
generated, which was identified as M-S-H (*e.g.*, Cole 1953, Zhang et al. 2011, Brew and
Glasser 2005, Roosz et al. 2015, Nied et al. 2016, Bernard et al. 2017, 2019) by
investigating the aq-XRD patterns.

The M-S-H was observed *via* TEM in the dried run products after the aqueous experiments as string-like or tiny fragmental materials. Their appearance is very similar to that of the silicates that have been observed in some primitive carbonaceous chondrites and described as slightly hydrated phases like poorly crystallized phyllosilicates (*e.g.*, Leroux et al. 2015, Matsumoto et al. 2019). These phases also must be M-S-H or related phases. The M-S-H should exist ubiquitously in primitive carbonaceous chondrites, and it is important as a tracer of the earliest aqueous activity in the early Solar System.

599 The M-S-H formation can occur within a day, even in pure water at room 600 temperature, which is significantly faster than the alteration of crystalline silicates. This is 601 due to the high metastability of the amorphous silicate. Moreover, the solubility of 602 amorphous silicates in water is much larger than that of M-S-H or phyllosilicates, causing overshoot of the dissolved Mg²⁺ and Si⁴⁺ concentrations, followed by precipitation of 603 604 highly disordered M-S-Hs that are metastable, rather than stable crystalline phases, from 605 highly supersaturated solutions with high pH. This dissolution-precipitation process may 606 be the major process of aqueous alteration for amorphous silicates.

607 The M-S-H formation rate for am-Fo is about ten times higher than that for am-En.
608 This is ascribed to the difference in solubility in water, which is caused in turn by the
609 difference in thermodynamic stability of their original amorphous structure. This indicates

610 that the aqueous alteration rate depends largely on the composition/structure of the original611 amorphous silicate, particularly at the W/R ratio of ~1.

612 Finally, the present results strongly suggest the presence of two different 613 generations of M-S-H: syngenetic M-S-H and epigenetic M-S-H. The epigenetic M-S-H is 614 generated by the drying process. The two types of aqueous alteration products-not only of 615 M-S-H but also of other hydrous phases—may coexist in carbonaceous chondrites. Thus, 616 they must be distinguished in order to understand their formation histories accurately. In 617 this study, the epigenetic M-S-H has a slightly more Si-rich composition than the 618 syngenetic one. It may also be possible to evaluate them selectively in carbonaceous 619 chondrites by future careful analyses.

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Figure captions





Amorphous silicate particles used as starting materials for am-Fo (MgO/SiO₂ = 2.02). (a)
TEM image and SAED pattern, (b) Annular dark-field (ADF)-STEM image and EDS map,
and (c) XRD pattern. For am-En (MgO/SiO₂ = 1.15), (d) TEM image and SAED pattern,
(e) ADF-STEM image and EDS map, and (f) XRD pattern. The EDS maps show the count
ratio for Si-K / (Si-K + Mg-K).



- 825 Figure 2.
- 826 Schematic of the experimental protocol.



Figure 3.

Time evolution of the XRD patterns obtained successively in the aq-XRD experiments. (a) XRD patterns of am-Fo. (b) XRD patterns of am-En. (c) XRD pattern of water for reference. (d) XRD pattern of the airtight sample holder for reference. In (a) and (b), *in-situ* XRD patterns are shown in order of elapsed time from bottom to top. The plots are offset for convenient analysis. The patterns of the starting materials and of the final run

842 products after drying are also shown at the very bottom and the top of each plot, 843 respectively. These were obtained in dry conditions but covered with a polyimide film and a 844 stainless-steel stage. The *in-situ* patterns are labeled with the time elapsed since the starting 845 material was mixed with water. Peaks in the XRD patterns are marked with the following 846 symbols: polyimide, open diamonds; stainless-steel, open triangles; unknown, open 847 squares; amorphous silicate, arrows; and newly appeared phase (M-S-H), solid circles.

848





851 Figure 4.

852 XRD patterns of the dried run products without the airtight sample holder (polyimide film 853 and stainless-steel holder). (a) am-Fo and (b) am-En. Peaks related to amorphous silicates 854 and M-S-H are indicated by arrows and solid circles, respectively. Each inset is an 855 enlargement of the low- 2θ -angle region, where the XRD pattern of a blank measurement 856 that was performed under the same conditions but without a sample is represented by a 857 dotted line. Vertical dotted lines indicate the 2θ positions of the basal reflections of Mg 858 phyllosilicates: Sme, smectite; Vrm, vermiculite; Tlc, talc; and Srp, serpentine.



860 **Figure 5.**

TEM images and SAED patterns of am-Fo (a–c) and am-En (d–f) after aq-XRD. (a) and (d) TEM images of dried run products. (b) and (e) SAED patterns and their angular-integrated profiles. The broad intensity increases at ~0.25 and ~0.15 nm in d-spacing are derived from M-S-H and correspond to the XRD peaks at 35° and 60°, respectively. (c) and (e) ADF-STEM images and EDS maps. The EDS maps show the count ratio of Si-K / (Si-K + Mg-K).



TEM images of (a) am-Fo and(b) am-En in the aq-TEM experiment. The upper-right panels show the dry starting materials. All other images are *in-situ* images of materials immersed in water. The images in each left column are labeled with the time elapsed (in hours and minutes) since the starting material was mixed with water. The images in each right column are enlargements of the dotted squares in the left images. The magnifications of the images are the same within each column.



876

877 Figure 7.

TEM images of am-Fo (a–b) and am-En (c–d) at the end of the aq-TEM experiments. (a) and (c) *In-situ* images at the end of the aq-TEM experiments before removing the sealing. (b) and (d) TEM images and SAED patterns of dried run products after removing the sealing. The upper-right panel shows the SAED pattern obtained from the particles. The lower-left panel is an enlarged image of the particles, and the lower right panels are enlarged images of the SiN_x film floor.





886 Figure 8.

Time evolution of the measured pH values of the water solutions of am-Fo (solid circles) and am-En (open circles). The horizontal axis indicates the time elapsed since the starting material was mixed with water. The inset is an enlargement for the elapsed time period 0–5 h and the pH values 9–11. An increase in the pH value is interpreted as resulting from selective dissolution of Mg^{2+} ions from the amorphous silicates, whereas a decrease is interpreted as resulting from subsequent Si⁴⁺ dissolution and/or M-S-H formation.

893

894



Figure 9.

typical peak-fitting Α the for aq-XRD result pattern of am-Fo at 45.0 h after mixing with water. The experimental profile and the fit are shown by crosses and by a black line, respectively. (a) For the 2θ region $10-55^{\circ}$, polyimide film, amorphous silicate, M-S-H, liquid, and smoothly varying а background intensity were assumed (gray lines). The

911 background was assumed to be a linear function. The polyimide intensity (~10°), 912 amorphous peak (~25°), and M-S-H peak (~60°) were fitted with Voigt functions, and the 913 M-S-H prism peak (~35°) was fitted with a split Voigt function. The liquid diffraction 914 profile was assumed to be composed of two Voigt functions, which we determined by 915 fitting to the water diffraction pattern (Fig. 3c). (b) and (c) The polyimide peak at ~6° and 916 the M-S-H peak at ~60° that are out of the range $2\theta = 10-55^\circ$ were fitted individually after 917 subtraction of a linear background.



Figure 10.

Time evolution of the intensities of the liquid, M-S-H, and amorphous materials from the in-situ XRD patterns of am-Fo (a-d)and am-En (e-h). The intensities are normalized the to polyimide peak intensity at $\sim 6^{\circ}$, which should be independent of the elapsed time.

932 The intensities of the starting materials and the final run products after drying are also 933 shown (diamonds). The horizontal axis indicates the time elapsed since the starting material 934 was mixed with water. (a) and (e) The peak intensity of liquid. (b) and (f) The intensity of 935 the M-S-H prism peak. (c) and (g) The intensity of the M-S-H $\sim 60^{\circ}$ peak. (d) and (h) The peak intensity of amorphous material. The solid lines in (b), (c), (f), and (g) are results 936 937 obtained by fitting with the empirical expression for I(t) given by eq. (1). The optimized parameters t_0 and k and the coefficient of determination R^2 for each fit are also shown in 938 939 each panel.







942 Time evolution of the peak-top position of the M-S-H ~60° peak, with its FWHM
943 determined by fitting with a split Voigt function for am-Fo (a) and am-En (b). Those of the
944 final run products after drying are also shown by diamonds. The horizontal axis indicates
945 the time elapsed since the starting material was mixed with water.