Lawrence Berkeley National Laboratory

Recent Work

Title

STXM-XANES analyses of Murchison meteorite samples captured by aerogel after hypervelocity impacts: A potential implication of organic matter degradation for micrometeoroid collection experiments

Permalink

<https://escholarship.org/uc/item/1hn0753g>

Journal

Geochemical Journal, 53(1)

ISSN

0016-7002

Authors

Kebukawa, Y
Okudaira, K
Yabuta, H
et al.

Publication Date

2019

DOI

10.2343/geochemj.2.0549

Peer reviewed

1STXM-XANES analyses of Murchison meteorite samples captured
2by aerogel after hypervelocity impacts: A potential implication of
3organic matter degradation for micrometeoroid collection
4experiments

5

6Yoko Kebukawa^{1*}, Kyoko Okudaira², Hikaru Yabuta³, Sunao Hasegawa⁴,
7Makoto Tabata⁵, Yoshihiro Furukawa⁶, Motoo Ito⁷, Aiko Nakato⁴, A. L. David
8Kilcoyne⁸, Kensei Kobayashi¹, Shin-ichi Yokobori⁹, Eiichi Imai¹⁰, Yuko
9Kawaguchi⁹, Hajime Yano⁴, and Akihiko Yamagishi⁹

10

11¹Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai,
12Hodogaya-ku, Yokohama 240-8501, Japan

13²Research Center for Advanced Information Science and Technology,
14University of Aizu, Tsuruga, Ikki-machi, Aizu-Wakamatsu, Fukushima, 965-
158580, Japan

16³Department of Earth and Planetary Systems Science, Hiroshima
17University, 1-3-1 Kagamiyama, Hiroshima 739-8526, Japan

18⁴Institute of Space and Astronautical Science (ISAS), Japan Aerospace
19Exploration Agency (JAXA), 3-1-1 Yoshinodai, Sagamihara, Kanagawa 252-
205210, Japan

21⁵Department of Physics, Chiba University, 1-33 Yayoicho, Inage-ku, Chiba
22263-8522, Japan

23⁶Department of Earth Science, Tohoku University, 6-3 Aramaki Aza Aoba,
24Aoba-ku, Sendai 980-8578, Japan

25⁷Kochi Institute for Core Sample Research, JAMSTEC, B200 Monobe,
26Nankoku, Kochi 783-8502, Japan

27⁸Advanced Light Source, Lawrence Berkeley National Laboratory, 1
28Cyclotron Road, Berkeley, CA 94720, USA

29⁹Department of Applied Life Sciences, Tokyo University of Pharmacy and
30Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo, 192-0392, Japan

31¹⁰Nagaoka University of Technology, 1603-1 Kamitomiokamachi, Nagaoka,
32Niigata, 940-2188, Japan

33

34*Corresponding author: Y. Kebukawa, E-mail: kebukawa@ynu.ac.jp

35TEL/ FAX: +81-45-339-3937

36

37

38Keywords: micrometeoroid; meteorite; impact; organic matter; Tanpopo
39mission

40

41**Abstract**

42 The Tanpopo mission is an astrobiology space experiment at the
43 Japanese Experiment Module (JEM) 'Kibo' on the International Space
44 Station (ISS). One of the sub-divided themes of the Tanpopo mission is for
45 the intact capture of organic bearing micrometeoroids in low Earth orbit
46 using ultralow density silica aerogel (0.01 g/cm^3). In order to evaluate
47 damage to organic matter in micrometeoroids during hyper velocity
48 impacts into the aerogel, Murchison meteorite powdered samples, analogs
49 of organic bearing micrometeoroids, were fired into flight-grade silica
50 aerogel (0.01 g/cm^3) using a two-stage light-gas gun with velocities of 4.4
51 and 5.9 km/s. The recovered Murchison grains were analyzed using
52 scanning transmission X-ray microscopy/X-ray absorption near edge
53 structure (STXM/XANES), transmission electron microscopy (TEM) and
54 nanoscale secondary ion mass spectrometry (NanoSIMS). TEM observation
55 did not show significant modifications of the recovered Murchison grains.
56 Carbon-XANES spectra, however, showed a large depletion of the organic
57 matter after the 5.9 km/s impact, but no such effects nor any significant
58 hydrogen isotopic fractionation were observed after the 4.4 km/s impact.

59

60**INTRODUCTION**

61 Low-density silica aerogels have been used to capture small
62 particles traveling at high velocities in several space missions, such as the
63 cometary dust particles from the Comet 81P/Wild 2 on the Stardust
64 mission (Brownlee *et al.*, 2006). An ultralow-density silica aerogel (0.01 g/
65 cm^3) has been developed at Chiba University (Tabata *et al.*, 2016) for the
66 Tanpopo mission which has an astrobiology space experiment at the

67Japanese Experiment Module (JEM) 'Kibo' on the International Space
68Station (ISS) (Cottin *et al.*, 2017; Kawaguchi *et al.*, 2016; Yamagishi *et al.*,
692009). One of the sub-divided themes of the Tanpopo mission is the
70capture of intact organic bearing micrometeoroids in low Earth orbit. The
71micrometeoroids impact the ISS at several kilometers per second, and
72therefore a low-density silica aerogel would be suitable for capturing
73relatively intact micrometeoroids. However, the highly insulative nature of
74aerogel may cause heating of captured materials by the friction generated
75as a result of the high velocity impact (e.g., Noguchi *et al.*, 2007).

76 Some earlier studies showed that phyllosilicates, within the few
77micrometer alteration rims of serpentine, cronstedtite, and the Murchison
78meteorite particles, were intact after 2-6 km/s impact into 0.03 g/cm³
79density aerogel, despite the significant volume loss from the particle's
80outside surface during the penetration processes (Noguchi *et al.*, 2007;
81Okudaira *et al.*, 2004). For example, detailed examination of the
82"keystone" samples from the Stardust mission, showed that the upper
83parts of the entrant hollow tracks are lined with relatively large amounts
84of melted aerogel and dissolved projectile, but the track ends contain
85largely un-melted cometary fragments (Brownlee *et al.*, 2006). Although,
86some organic matter in the cometary dust particles survived
87approximately 6.1 km/s impact into the aerogel tiles (e.g., Cody *et al.*,
882008a; Sandford *et al.*, 2006), one cannot exclude the possibility that they
89could be chemically altered by the impact (Sandford *et al.*, 2010).

90 Modification of the organic matter (OM) have been examined using
91several analogue materials fired into Stardust-like aerogels at velocities

92 around 6 km/s. This suggested that the degree of alteration of organic
93 compounds significantly depends on the nature of the organic compounds
94 and the matrix materials (Sandford *et al.*, 2006). Cocoa powder mixed
95 with small soda-lime glass spheres underwent extensive alteration
96 including both bond-breaking and bond-creation, with the OM found
97 distributed along the bulb-shaped track, while Allende meteorites that
98 evidence polycyclic aromatic hydrocarbons (PAHs), were not greatly
99 altered (Sandford *et al.*, 2006). Particles of poly(methyl methacrylate) and
100 poly(ethyl methacrylate) that were fired into aerogel (density 0.06 g/cm³)
101 at ~5 km/s showed no distinct chemical modification based on Raman
102 spectroscopy (Burchell *et al.*, 2004). However, coal samples fired into
103 aerogel targets (0.03 g/cm³) at velocities of around 6 km/s showed that
104 particle surfaces are largely homogenized during capture, apparently
105 indicating a devolatilization step during capture processing, with both
106 graphitization and amorphization found in the coal samples (Fries *et al.*,
107 2009).

108 To evaluate the effect of hyper-velocity capture of micrometeoroids,
109 laboratory experiments with flight-grade ultralow-density aerogel (0.01 g/
110 cm³) have been conducted for the Murchison meteorite powder as an
111 analogue of micrometeoroids that contain OM, using a two-stage light gas
112 gun (Ogata *et al.*, 2013). Ogata *et al.* (2013) reported that infrared and
113 Raman spectroscopic measurements of Murchison recovered from 4 km/s
114 impact, showed that a major part of the OM survived. Accordingly, we
115 evaluate the modification of Murchison recovered from 4.4 km/s and 5.9
116 km/s impacts using scanning transmission X-ray microscopy (STXM),

117transmission electron microscopy (TEM), and high-resolution secondary
118ion mass spectrometry (NanoSIMS). In the following, we present a
119summary of the experimental techniques used to investigate the possible
120changes to the OM in the meteorites, followed by a discussion and
121conclusion.

122

123**EXPERIMENTAL**

124 **Two-Stage Light-Gas Gun Experiments**

125 The Murchison powder samples (micron-sized grains) were placed in
126sabots and fired into silica aerogels (0.01 g/cm^3) by a two-stage light-gas
127gun at ISAS, JAXA. Experimental conditions are summarized in Table 1
128with details of the experimental methods described in [Okudaira et al.](#)
129[\(2004\)](#). We used the flight-grade ultralow-density (0.01 g/cm^3) aerogel
130developed to capture cosmic dust particles. The details of the aerogel are
131provided in [Tabata et al. \(2016\)](#).

132

133 **Sample Preparation**

134 Several Murchison grains were extracted from the aerogel. Since the
135 Murchison meteorite has an inhomogeneous composition, “black” (matrix
136 where OM is typically present) terminal grains were selected for
137 subsequent analyses. The extraction was manually conducted under an
138 optical microscope. After the impact experiment, each aerogel was
139 trimmed into smaller blocks using a clean surgical knife. Then, two grains
140 from #399 (grain 1: 20-25 μm , grain 2: 10-15 μm and two grains from
141 #1473, (grain 1: 30-40 μm , grain 2: 10-15 μm) after the shots,

142 respectively were manually extracted from the aerogel with tungsten and
143 glass needles.

144 The STXM analysis requires ~100 nm-thick sections to transmit the
145 soft X-rays for chemical analysis. We prepared ultramicrotomed thin
146 sections using a sulfur-embedding method following [Nakamura-Messenger](#)
147 [et al. \(2006\)](#). A grain of the Murchison meteorite recovered from aerogel
148 was embedded in a molten (115 °C) then supercooled sulfur droplet with a
149 glass needle. After solidification, the sulfur droplet was attached onto an
150 epoxy stub using “Super Glue” for slicing into 100 nm-thick sections with
151 a LEICA ultramicrotome using a DIATOME diamond knife. The sections
152 were floated onto deionized water and transferred to silicon oxide-coated
153 copper TEM grids (3 mm in diameter). Before analysis, the sections were
154 mildly heated (<100°C, <15 min) until the sulfur sublimated off the grids,
155 leaving the microtomed samples essentially intact (Bassim *et al.*, 2012).

156

157 **STXM-XANES**

158 X-ray absorption near edge structure (XANES) analyses for the
159 carbon and nitrogen *K*-edges were performed using the STXM at beam line
160 5.3.2.2 of the Advanced Light Source, Lawrence Berkeley National
161 Laboratory (Kilcoyne *et al.*, 2003). Details of the experimental methods
162 have been described in [Kebukawa et al. \(2017\)](#). Beam focusing utilized
163 Fresnel zone plate optics for a theoretical spot size of ~31 nm. The C, N-
164 XANES spectra were acquired using a multi-spectral imaging method
165 (“Stacks” method; Jacobsen *et al.*, 2000). The energy step size (ΔE)
166 employed was 0.1 to 0.2 eV in the fine structure portions of the near-edge

167region (283–296 eV), and 0.5 to 1 eV in the pre-edge and post-edge
168regions (278–283 and 296–301 eV for C). The acquisition time per energy
169step (dwell time) varied from 2 to 4 ms (up to 9 ms). An X-ray absorption
170spectrum was acquired by using the Beer-Lambert law, $-\ln(I/I_0)$, where I is
171the intensity of the photons from the sample region and I_0 is the intensity
172of the photons from a blank area next to the sample region.

173

174 **TEM**

175 In order to examine heating effects due to the capture of the
176particles by the aerogel, we conducted transmission electron microscopy
177(TEM) analysis on the recovered grains after 4.4 km/s impact (#399) and
1785.9 km/s impact (#1473). TEM analysis was performed using a JEOL JEM-
1792100F microscope equipped with an energy dispersive X-ray spectrometer
180(EDX) at Tohoku University. The acceleration voltage was 200 kV.

181

182 **NanoSIMS**

183 Hydrogen isotope analysis of recovered grains after 4.4 km/s impact
184(#399) and an intact Murchison grain were carried out with the JAMSTEC
185NanoSIMS 50L ion microprobe. Detailed measurement conditions are
186described elsewhere (Ito *et al.*, 2014). In brief, a focused primary Cs^+ ion
187beam of approximately ~ 2.5 pA (spatial resolution ~ 200 nm) was
188rastered over areas of $18 \times 18 \mu\text{m}^2$ for grain 1 and $30 \times 30 \mu\text{m}^2$ for grain
1892 of the samples. Images of $^1\text{H}^-$, $^2\text{D}^-$, $^{12}\text{C}^-$ and secondary electrons were
190acquired simultaneously. Each run was repeatedly scanned (20 times)
191over the same area, with individual images consisting of 256×256 pixels.

The dwell time was 10 ms/pixel for the measurements, and total acquisition time was about 3.6 hours. We carefully checked surface changes during analysis, and obvious changes were not observed during the analysis. δD images were generated from 1H and 2D images using the software “NASA JSC imaging software for NanoSIMS” developed in the Interactive Data Language (IDL) program (Ito and Messenger, 2008). 1-hydroxybenzotriazole hydrate was used for the H isotopic standard measurements (Ito et al., 2014). Note that we could not conduct NanoSIMS analysis for the grains recovered from 5.9 km/s impact (#1473), since all #1473 samples have been exposed to electron irradiations by TEM analysis that would induce large D-H fractionations (De Gregorio et al., 2010).

204

205 RESULTS

206 STXM-XANES

Fig. 1 shows the STXM images of the Murchison meteorite shots #399 grains 1 and 2, and #1473 grains 1 and 2. C-XANES spectra (Fig. 2) were obtained from the location indicated by the red rectangles. The matrix of Murchison is heterogeneous, thus we analyzed several different areas for each grain, except shot #1473 grain 2, where we could not recover enough ultramicrotomed sections. The C-XANES of a pristine Murchison meteorite showed peaks at 285.2 eV assigned to aromatic C, 286.5 eV assigned to C=O, 287.7 eV assigned to aliphatic C, 288.6 eV assigned to carboxyl/ester and 289.7 eV assigned to alcohol/ether. The peak assignments are based on [Cody et al. \(2008a\)](#) and [Vinogradoff et al.](#)

217(2018), and are summarized in Table 2. These features are typical to the
218Murchison insoluble organic matter (IOM), although the 287.7 eV peak is
219not always present in the Murchison IOM (Cody *et al.*, 2008b; De Gregorio
220*et al.*, 2013; Vinogradoff *et al.*, 2017). Indeed, the relative peak intensities
221of our C-XANES of Murchison are not always consistent with the Murchison
222IOM. In particular, aromatic C and C=O relative to carboxyl in our
223Murchison are smaller than those in the Murchison IOM. However, it is
224expected that the C-XANES spectra of untreated (not demineralized)
225Murchison are somewhat different from those of the IOM samples and
226show local variations in the peak intensities (Le Guillou *et al.*, 2014). The
227N-XANES were mostly featureless, indicating that there were no distinct
228nitrogen-bearing functional groups (data not shown).

229 The C-XANES spectra of the Murchison samples from shot #399 (4.4 km/
230s), mostly preserved these organic features, although peak intensities had
231some variations mostly due to sample heterogeneity. In the case of
232sample shot #1473 (5.9 km/s), most of these features were substantially
233reduced in intensity. Little or no absorption at the ionization potential
234regions (at around 291 eV) indicates a loss of OM. Only a peak at ~289 eV
235was observed in the C-XANES of shot #1473 grain 1 (C1 to C3 in Fig. 2c).
236The peak at ~289 eV can be attributed to a σ^* transition of sp^3 bonded
237carbon (Stöhr, 1992), and indicates dearomatization of organic matter
238accompanied with significant carbon loss in the Murchison meteorite after
239impact at this higher velocity. While, the C-XANES spectrum of shot
240#1473 grain 2 (Fig. 2c) showed no substantive carbon signatures. It
241should be noted that we have analyzed several different fragments of

242 Murchison matrix in several different occasions, but we have never
243 observed C-XANES feature shown in the 5.9 km/s samples, thus it should
244 not be due to original sample characteristics, i.e., these Murchison grains
245 originally contains little OM.

246 Fig. 3 shows image contrast maps of the Murchison shots #399 area
247 A3 and B5, and #1473 area C1a at energies indicated in the figure. A
248 normalization of a STXM image taken at a peak energy to an image below
249 the pre-edge in the measurements, enables contrast image maps to be
250 obtained. The images emphasize the component and density of
251 distribution of the functional groups in the samples. The variation in
252 intensity within the contrast images at 285.0 eV (aromatic), 287.5
253 (aliphatic), and 288.5 eV (O-C=O) (normalized to an image at 283.0 eV)
254 show some heterogeneities. The heterogeneities in contrast could be due
255 to both difference of thickness and actual heterogeneous distribution of
256 OM. However, no zoning or gradients were observed in the sample grains.

257

258 **TEM ANALYSIS**

259 The same sample sections were analyzed with TEM after STXM
260 measurements to search for minerals that can be used as indicators of
261 heating/shock processes. Fig. 4 shows TEM images of the shot #399 (4.4
262 km/s) samples with corresponding energy dispersive X-ray (EDS) spectra.
263 The outer surfaces of minerals are mostly covered with amorphous
264 carbonaceous matter (Fig. 4A and 4B). Part of the carbonaceous matter
265 form bridging structure between mineral particles (Fig. 4A and 4B). These
266 observations were consistent with C-XANES spectra of the organic matter

267in the Murchison that did not show significant changes after the impact,
268although TEM cannot analyze changes in molecular structures.

269 For shot #1473 (5.9 km/s) samples, TEM measurements on the “C1”
270fragments (Figs. 1C, 5 and 6) indicated some carbonaceous material in
271the inner part of the recovered aggregate grain (Figs. 5A and 6A). An
272examination of the “outer” surface part of the grain obtained from the
273edge of the ultramicrotomed section, “C1a”, where C-XANES analysis was
274performed before TEM, shows serpentine covered with some carbon
275membranes (Figs. 5B and 6B). The TEM measurements also confirmed the
276presence of many phyllosilicate grains (i.e., serpentine or cronstedtite) in
277the C1 grain (Figs. 5C and 5D).

278 No shock features were recognized in the recovered Murchison
279grains in shot #399 and #1473. However, the possibility of a shock
280process cannot be excluded since the analyzed area by TEM were limited.

281

282 **NanoSIMS ANALYSIS**

283 In order to examine isotope fractionation in the captured particles
284by aerogel, hydrogen isotopic composition of the ultramicrotomed
285fragments of the Murchison shot #399 sample recovered after 4.4 km/s
286impact was obtained using NanoSIMS (Fig. 7). The hydrogen isotopic
287composition were analyzed on fragments that were not subjected to TEM
288analysis, to avoid any isotope fractionation due to electron beam damage
289(De Gregorio *et al.*, 2010). The average δD values of the #399 grain 1 and
2902 are -22 ± 20 ‰ and -39 ± 25 ‰, respectively. These values are
291consistent with δD values of a pristine Murchison which is -42 ± 15 ‰,

accounting for analytical errors. Reported bulk δD values of the Murchison meteorite are -61.7 ± 3.1 ‰ (Alexander *et al.*, 2012) and -53.25 ± 2.63 ‰ (Pearson *et al.*, 2001), and are slightly higher than the values in this study. This difference is probably due to sample bias related to the amount of OM, and hydrous and anhydrous minerals present in the samples.

IMPACT AND SHOCK ANALYSIS

Using an impedance matching method to estimate maximum shock pressures of particles when they impact aerogel targets, the shock pressure P was calculated using the relation $P = \rho v U$, where ρ is the target density, v is the particle velocity, and U is the shock velocity ($= C + Sv$). Two coefficients (C and S) necessary to determine Hugoniot curves are unknown for unique materials such as ultralow-density silica aerogel used in this study. Therefore, we extrapolated coefficients and determined Hugoniot curve by using values of higher density silica aerogels (0.06, 0.128, 0.172, 0.295, 0.4 and 0.55 g/cm³) whose coefficients (C and S) are available in order to estimate the C and S values of 0.03 g/cm³ silica aerogel. C (sound velocity) and S are intrinsic values of targets. The S coefficient of silica aerogels in several studies (Ahrens, 1995; Grover *et al.*, 1992) are approximately 1, thus $S = 1$ is used in this estimation. Projectiles used in the plots are glass (2.31 g/cm³), serpentine (2.62 g/cm³) and iron (7.85 g/cm³). The results are shown in Fig. 8. The shock pressures were estimated as ~ 0.5 GPa and ~ 1 GPa for 4 km/s and 6 km/s impact velocities, respectively, in the case of serpentine projectiles and

3170.03 g/cm³ aerogel targets. The result is consistent with Fig. 21 in
318[Kitazawa et al. \(1999\)](#). Since the density of the Murchison meteorite is
3192.15-2.40 g/cm³ (Macke et al., 2011; McCausland et al., 2011), the shock
320pressures of Murchison meteorite projectiles into 0.01 g/cm³ aerogel
321projectiles collectors should not exceed 1 GPa as in our experiments.

322

323 **DISCUSSION**

324 TEM observation showed no clear evidence for alteration of the
325grains recovered after both 4.4 km/s impact (shot #399) and 5.9 km/s
326impact (shot #1473) into the 0.01 g/cm³ aerogel. In addition, the TEM
327measurements showed that cronstedtite and serpentine did not
328decompose after impact into the aerogel. Since the reported
329decomposition temperature of cronstedtite is 470 °C (Caillère and Hénin,
3301957), and that of serpentine is 600-660 °C (Akai, 1992), the temperature
331of the remaining part of the grains could not have exceeded 470 °C.
332However, one cannot exclude the possibility that the Murchison grains
333experienced a higher temperature for a short duration that did not allow
334dehydration of cronstedtite. The decomposition of phyllosilicates is a time-
335temperature sensitive process, i.e., the decomposition occurs more
336rapidly at a higher temperature, generally following the Arrhenius law. The
337phyllosilicates can survive for short periods of time at temperatures well
338above the published laboratory decomposition temperature that is
339expected in our experiments. Thus, we calculated how decomposition rate
340could change depends on the temperatures using reported activation
341energies for dehydration of serpentine. Fig. 9 shows the reaction rate k

relative to the reaction rate at 630 °C (reported decomposition temperature of serpentine) calculated as a function of temperature T , using the Arrhenius equation: $k = A\exp(-E_a/RT)$ where A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant. The reported activation energies for dehydration of serpentine vary; 284 kJ/mol (Alizadehhesari *et al.*, 2012), 429 ± 200 kJ/mol and 528 ± 34 kJ/mol (Llana-Fúnez *et al.*, 2007). Thus we calculated for each reported activation energy. The calculation indicated that decomposition rates are 10^3 to 10^6 times faster at 800 °C compared to at 630 °C, and 10^6 to 10^9 times faster at 1000 °C. Considering that the apparent equilibration time of serpentine decomposition is within hours ($\sim 10^4$ sec) (Akai, 1992), serpentine could survive for 10^{-2} to 10 sec at 800 °C and 10^{-5} to 10^{-2} sec at 1000 °C. It also indicates that it is unlikely to survive over 1000 °C even for a short period of time. Note that we only calculate the decomposition rates for serpentine, since we could not find activation energies for cronstedtite and tochilinite.

Previous experiments using serpentine and cronstedtite reported that the maximum surface temperature reached 2000 ± 200 K (2273 ± 200 °C) but noted that several-micrometers into the interior of the sample, grains were left intact after 2-4 km/s impact into 0.03 g/cm³ aerogel (Okudaira *et al.*, 2004). Additional higher velocity (>6 km/s) impact experiments indicate that the impact of the grains (<2 μm thick) had steep thermal gradients ~ 2500 °C/μm from the surface to the interior, with the center below 300 °C (Noguchi *et al.*, 2007). Significant volume loss (~ 90 %) by evaporation due to internal friction (ablation)

during penetration was reported by Okudaira et al. (2004). We did not find an altered surface on the Murchison grains, but the volume of the grain was reduced, since the starting grain sizes were roughly 30-100 μm for the 4.4 km/s impact (shot #399) and 37-60 μm for the 5.9 km/s impact (shot #1473), whereas the recovered samples were $\sim 20\text{-}25$ μm (grain 1) and 10-15 μm (grain 2) in size for 4.4 km/s impact, and 30-40 μm (grain 1) and 10-15 μm (grain 2) in size for 5.9 km/s impact. In addition, terminal grains could have fragmented during and/or after penetration into the aerogel, but we did not find clear evidence of fragmentation by optical-microscopy observations of impact tracks. Alternatively, there is a possibility that fragmentation of samples occurred during preparation using the ultramicrotome. It should be noted that there are large uncertainties in the grain sizes, thus we could not lead conclusive implications for grain size effects from our experiments. Since the starting grain sizes were about the same range for both 4.4 km/s and 5.9 km/s impact samples, the grain size effects should be lower than the impact velocity effects.

384 The organic matter observed by C-XANES from the Murchison grains
385 recovered after 4.4 km/s impact (shot #399) seem generally intact, but
386 the grains recovered after 5.9 km/s impact (shot #1473), into the 0.01 g/
387 cm^3 aerogel, show drastic changes in organic structure. We did not find
388 an alteration of the surface or gradual changes of organic molecular
389 structures by STXM-XANES within ~ 100 nm spatial sizes of the sample
390 areas (Fig. 3). In our experiments, the threshold impact velocity for
391 changes in C-XANES spectra are between 4.4 and 5.9 km/s.

392 Macromolecular organic matter with entry velocities of ~ 4.4 km/s or less
393 can survive from the impact into the 0.01 g/cm^3 aerogel as reflected in
394 the C-XANES and TEM measurements in micrometeoroids. However, as
395 mentioned previously, we cannot exclude the possibility of grain size
396 effects, which are smaller than impact velocity effects for organic matter
397 content and survivability. The majority of meteoroids at the ISS orbit
398 were reported to have impact velocities of 10 to 20 km/s, but some
399 meteoroids could have lower velocities (Drolshagen and ESA, 2009). This
400 indicates that OM in most of the meteoroids would be modified, but some
401 low-velocity meteoroids could preserve pristine OM.

402 [Ogata et al. \(2013\)](#) carried out a hyper-velocity impact experiment of
403 Murchison meteorite powder into 0.01 g/cm^3 silica aerogel at 4 km/s
404 using a two-stage light gas gun and analyzed the shocked meteorite
405 samples by micro-FTIR and micro-Raman spectroscopy. They revealed
406 that aromatic structures of organic materials in the meteorite were not
407 adversely changed before and after the shock, while the abundances of
408 organics were slightly decreased and aliphatic carbon chain length were
409 changed after the aerogel capture. Significant change in aliphatic
410 moieties was not observed by C-XANES in our experiments, since C-
411 XANES is less sensitive to aliphatics compared to FTIR. It is consistent
412 with our results for C-XANES showing that 4.4 km/s impact do not induce
413 significant changes of OM characteristics.

414 In the case of the higher velocity (5.9 km/s) impact, large amounts
415 of organic matter in the Murchison meteorite are ablated/vaporized upon
416 entry into the aerogel. A C-XANES spectrum of one of the Murchison

417 grains recovered after 5.9 km/s impact (#1473 grain 1) probably indicates
418 dearomatization of the organic matter (Fig. 2c). This conclusion is partially
419 consistent with earlier experiments using terrestrial coal samples fired
420 into aerogel targets (0.03 g/cm³) at velocities of ~6 km/s and showed that
421 both graphitization and amorphization occur, possibly due to
422 devolatilization and re-condensation within the particles (Fries *et al.*,
423 2009). We did not see any evidence of graphitization in the Murchison
424 particles recovered from the impacts. However, because the chemical
425 structure of organic matter in the Murchison is more susceptible to
426 heating, and/or the OM in Murchison is diffused in the matrix minerals it is
427 more susceptible to ablation and volatilization compared to compacted
428 organic matter such as coal grains. The majority (~70%) of the OM exists
429 in the form of insoluble organic matter (IOM) that consist of aromatic units
430 with up to four rings bridged by aliphatic carbon chain, ether, and ester
431 moieties (e.g., Derenne and Robert, 2010; Hayatsu *et al.*, 1977). Previous
432 kinetically controlled flash heating experiments indicated that the
433 likelihood of vaporized organic matter by cracking these bonds between
434 aromatic units, is faster than aromatization (Cody *et al.*, 2008b; Kebukawa
435 *et al.*, 2010). Thus, the IOM fragments could be easily vaporized even by
436 residual heat. For example, the vapor pressures of a simple form of a four
437 ring aromatic hydrocarbon, pyrene, are 17.1 Pa at 398 K and 345.3 Pa at
438 458 K (Smith *et al.*, 1980), and thus would easily vaporize under our
439 experimental conditions (<10 Pa).

440 In the case of the cometary dust particles captured by Stardust
441 mission, some particles (e.g., #2 and #3 in Fig. 1 of Cody *et al.*, 2008a)

442show a large peak at 288.7 eV with a small peak at 285 eV and these
443characteristics are similar to our C-XANES spectra of the Murchison
444recovered after 5.9 km/s impact (#1473). It might imply that some of the
445Stardust recovered particles would have been affected by the capture
446process.

447 No shock features were recognized in the recovered Murchison
448grains by TEM. However, the possibility of shock process cannot be
449excluded since the analyzed area by TEM were limited. Previous higher
450velocity (>6 km/s) experiments using higher density aerogel (0.03 g/cm³)
451showed no remarkable shock features (Noguchi *et al.*, 2007). In addition,
452little or no loss of organic matter was observed in a Murchison meteorite
453shocked to ~20 GPa, by thermal-desorption photoionization mass
454spectrometry which is sensitive to labile fragments from IOM (Tingle *et al.*,
4551992). Mimura and Toyama (2005) showed that decompositions of PAHs
456started at ~10 GPa and over 95% of PAHs were decomposed at 30 GPa
457(shock temperature was 1480 K at 30 GPa). These experiments showed
458that shock pressures less than a few tens of GPa did not affect organic
459matter significantly, which is much higher compared to our experiments.
460Thus, the alteration of the organic matter is mostly due to friction heating
461rather than shock heating. Moreover, labile fractions such as amino acids
462could have been more easily modified, e.g., a 3.5 GPa shock reduced ~50
463% amino acids that were embedded in a mineral matrix (Peterson *et al.*,
4641997). Thus, modification of labile functional groups evident in C-XANES
465(in pristine samples) would be possible at a few GPa shock, but aromatic

skeletons would not be affected significantly by 1 GPa or less impacts as in the case of our experiments (Fig. 8).

The δD values observed by NanoSIMS from the Murchison grains recovered after 4.4 km/s impact (shot #399) seem to be preserved (recovered grain 1 and 2 are $-22 \pm 20 \text{ ‰}$ and $-39 \pm 25 \text{ ‰}$, respectively while pristine Murchison is $-42 \pm 15 \text{ ‰}$). However, it cannot be ruled out that the mixing between aerogel and a Murchison grain during the impact process causes isotopic fractionation. Nevertheless, our experiment for the sample with 4.4 km/s impact does not show resolvable difference in terms of hydrogen isotopic ratio compared to intact Murchison. Note that NanoSIMS images of the #399 samples show typical characteristics of micron-sized isotopic anomalous regions (hotspots) and heterogeneous distributions of hydrogen isotopes (Fig. 7). These features have been observed in the previous hydrogen isotope measurements on extraterrestrial materials with NanoSIMS (e.g., Piani *et al.*, 2015). Thus, the effect of the 4.4 km/s impact for hydrogen isotopic characteristics would be minimum. In addition, [Mimura *et al.* \(2007\)](#) reported that the selective release of D from IOM of Murchison by impact shock occurs at values of 1-37 GPa. Based on their results, δD of shot #399 (4.4km/s) should be lower than initial value if the H isotopic composition is affected by the shock process ($> 1 \text{ GPa}$), but our δD trend was opposite. Thus, it also supports that the effect of the 4.4km/s impact for H isotopic characteristics is minimal.

CONCLUSIONS

491 We evaluated the degradation of the Murchison meteorite with
492 impact velocities of 4.4 km/s and 5.9 km/s captured by 0.01 g/cm³ aerogel
493 which was developed for the Tanpopo mission. No significant degradation
494 of the recovered Murchison grains was observed by TEM. However,
495 significant spectral changes were observed in C-XANES spectra of the
496 Murchison grains recovered from the 5.9 km/s impact. While no significant
497 changes in the recovered samples in C-XANES spectra and hydrogen
498 isotopic ratio and mineralogical composition were observed for the 4.4
499 km/s impact.

500 For 5.9 km/s impact, the majority of carbonaceous matter in the
501 Murchison grain was ablated and some dearomatization was observed.
502 The loss and change are likely due to flash heating and possibly partial re-
503 condensation during the penetration process into the aerogel. The
504 degradation in organic matter does not depend on the grain size, but on
505 the impact velocities. The Tanpopo mission first year aerogel samples
506 have been allocated to each research group, after the initial analysis at
507 ISAS/JAXA. A detailed analysis on the particles collected from the low
508 Earth orbit of the ISS will be reported in forthcoming articles.

509

510 **Acknowledgments**

511 The authors thank Dr. Keiko Nakamura-Messenger (JSC/NASA) for
512 her instructions in the sample sulfur-embedding method. We thank
513 anonymous reviewers for helpful comments. The two-stage light-gas gun
514 experiments were supported by ISAS/JAXA as a collaborative program with
515 the Hypervelocity Impact Facility (former name: Space Plasma

Laboratory). STXM-XANES data were acquired at beamline 5.3.2.2 at the ALS, which is supported by the Director of the Office of Science, Department of Energy, under Contract No. DE-AC02-05CH11231. This work is supported by Japan Society for the Promotion of Science KAKENHI (grant number JP15K17794, JP17H02991, JP17H06458, JP18K03722, 126287142), the Astrobiology Project of the Center for Novel Science Initiatives (CNSI), National Institutes of Natural Sciences (NINS) (Grant Number: AB271015, AB281004, AB291005, AB301020), and the Shimadzu Science Foundation (2016).

References

- Ahrens, T.J., Johnson, M.L. (1995) Shock wave data for rocks. In: Ahrens, T.J. (Ed.), *A Handbook of Physical Constants: Rock Physics and Phase Relations*. American Geophysical Union, Washington, DC, 35-44.
- Ahrens, T. J. (1995) *Mineral physics and crystallography: a handbook of physical constants*. American Geophysical Union
- Akai, J. (1992) TTT diagram of serpentine and saponite, and estimation of metamorphic heating degree of Antarctic carbonaceous chondrites. *Antarctic Meteorite Research*. **5**, 120.
- Alexander, C. M., Bowden, R., Fogel, M. L., Howard, K. T., Herd, C. D. and Nittler, L. R. (2012) The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. *Science*. **337**, 721-723.

540 Alizadehhesari, K., Golding, S. D. and Bhatia, S. K. (2012) Kinetics of the
541 dehydroxylation of serpentine. *Energy & Fuels*. **26**, 783-790.

542 Bassim, N. D., De Gregorio, B. T., Kilcoyne, A. L. D., Scott, K., Chou, T.,
543 Wirick, S., Cody, G. and Stroud, R. M. (2012) Minimizing damage
544 during FIB sample preparation of soft materials. *Journal of*
545 *Microscopy*. **245**, 288-301.

546 Brownlee, D., Tsou, P., Aléon, J., Alexander, C. M. O. D., Araki, T., Bajt, S.,
547 Baratta, G. A., Bastien, R., Bland, P., Bleuet, P., Borg, J., Bradley, J.
548 P., Brearley, A., Brenker, F., Brennan, S., Bridges, J. C., Browning, N.
549 D., Brucato, J. R., Bullock, E., Burchell, M. J., Busemann, H.,
550 Butterworth, A., Chaussidon, M., Cheuvront, A., Chi, M., Cintala, M.
551 J., Clark, B. C., Clemett, S. J., Cody, G., Colangeli, L., Cooper, G.,
552 Cordier, P., Daghljan, C., Dai, Z., D'Hendecourt, L., Djouadi, Z.,
553 Dominguez, G., Duxbury, T., Dworkin, J. P., Ebel, D. S., Economou, T.
554 E., Fakra, S., Fairey, S. A. J., Fallon, S., Ferrini, G., Ferroir, T.,
555 Fleckenstein, H., Floss, C., Flynn, G., Franchi, I. A., Fries, M.,
556 Gainsforth, Z., Gallien, J.-P., Genge, M., Gilles, M. K., Gillet, P.,
557 Gilmour, J., Glavin, D. P., Gounelle, M., Grady, M. M., Graham, G. A.,
558 Grant, P. G., Green, S. F., Grossemy, F., Grossman, L., Grossman, J.
559 N., Guan, Y., Hagiya, K., Harvey, R., Heck, P., Herzog, G. F., Hoppe,
560 P., Hörz, F., Huth, J., Hutcheon, I. D., Ignatyev, K., Ishii, H., Ito, M.,
561 Jacob, D., Jacobsen, C., Jacobsen, S., Jones, S., Joswiak, D., Jurewicz,
562 A., Kearsley, A. T., Keller, L. P., Khodja, H., Kilcoyne, A. L. D., Kissel,
563 J., Krot, A., Langenhorst, F., Lanzirotti, A., Le, L., Leshin, L. A.,
564 Leitner, J., Lemelle, L., Leroux, H., Liu, M.-C., Luening, K., Lyon, I.,

565 MacPherson, G., Marcus, M. A., Marhas, K., Marty, B., Matrajt, G.,
566 McKeegan, K., Meibom, A., Mennella, V., Messenger, K., Messenger,
567 S., Mikouchi, T., Mostefaoui, S., Nakamura, T., Nakano, T., Newville,
568 M., Nittler, L. R., Ohnishi, I., Ohsumi, K., Okudaira, K.,
569 Papanastassiou, D. A., Palma, R., Palumbo, M. E., Pepin, R. O.,
570 Perkins, D., Perronnet, M., Pianetta, P., Rao, W., Rietmeijer, F. J. M.,
571 Robert, F., Rost, D., Rotundi, A., Ryan, R., Sandford, S. A., Schwandt,
572 C. S., See, T. H., Schlutter, D., Sheffield-Parker, J., Simionovici, A.,
573 Simon, S., Sitnitsky, I., Snead, C. J., Spencer, M. K., Stadermann, F.
574 J., Steele, A., Stephan, T., Stroud, R., Susini, J., Sutton, S. R., Suzuki,
575 Y., Taheri, M., Taylor, S., Teslich, N., Tomeoka, K., Tomioka, N.,
576 Toppani, A., Trigo-Rodríguez, J. M., Troadec, D., Tsuchiyama, A.,
577 Tuzzolino, A. J., Tyliczszak, T., Uesugi, K., Velbel, M., Vellenga, J.,
578 Vicenzi, E., Vincze, L., Warren, J., Weber, I., Weisberg, M., Westphal,
579 A. J., Wirick, S., Wooden, D., Wopenka, B., Wozniakiewicz, P., Wright,
580 I., Yabuta, H., Yano, H., Young, E. D., Zare, R. N., Zega, T., Ziegler,
581 K., Zimmerman, L., Zinner, E. and Zolensky, M. (2006) Comet
582 81P/Wild 2 Under a Microscope. *Science*. **314**, 1711-1716.

583 Burchell, M. J., Creighton, J. and Kearsley, A. T. (2004) Identification of
584 organic particles via Raman techniques after capture in
585 hypervelocity impacts on aerogel. *Journal of Raman Spectroscopy*.
586 **35**, 249-253.

587 Caillère, S. and Hénin, S. (1957) The chlorite and serpentine minerals. *The*
588 *differential thermal investigation of clays*. VIII (Mackenzie, R. C. ed.),
589 207-230, Mineralogical Society, London.

590 Cody, G. D., Ade, H., Alexander, C. M. O., Araki, T., Butterworth, A.,
 591 Fleckenstein, H., Flynn, G., Gilles, M. K., Jacobsen, C., Kilcoyne, A. L.
 592 D., Messenger, K., Sandford, S. A., Tyliczszak, T., Westphal, A. J.,
 593 Wirick, S. and Yabuta, H. (2008a) Quantitative organic and light-
 594 element analysis of comet 81P/Wild 2 particles using C-, N-, and O-
 595 μ -XANES. *Meteoritics & Planetary Science*. **43**, 353-365.

596 Cody, G. D., Alexander, C. M. O. D., Yabuta, H., Kilcoyne, A. L. D., Araki, T.,
 597 Ade, H., Dera, R., Fogel, M., Militzer, B. and Mysen, B. O. (2008b)
 598 Organic thermometry for chondritic parent bodies. *Earth and*
 599 *Planetary Science Letters*. **272**, 446-455.

600 Cottin, H., Kotler, J. M., Billi, D., Cockell, C., Demets, R., Ehrenfreund, P.,
 601 Elsaesser, A., d'Hendecourt, L., van Loon, J. J. W. A., Martins, Z.,
 602 Onofri, S., Quinn, R. C., Rabbow, E., Rettberg, P., Ricco, A. J.,
 603 Slenzka, K., de la Torre, R., de Vera, J.-P., Westall, F., Carrasco, N.,
 604 Fresneau, A., Kawaguchi, Y., Kebukawa, Y., Nguyen, D., Poch, O.,
 605 Saiagh, K., Stalport, F., Yamagishi, A., Yano, H. and Klammer, B. A.
 606 (2017) Space as a Tool for Astrobiology: Review and
 607 Recommendations for Experimentations in Earth Orbit and Beyond.
 608 *Space Science Reviews*. **209**, 83-181.

609 De Gregorio, B. T., Stroud, R. M., Nittler, L. R., Alexander, C. M. O. D.,
 610 Bassim, N. D., Cody, G. D., Kilcoyne, A. L. D., Sandford, S. A., Milam,
 611 S. N., Nuevo, M. and Zega, T. J. (2013) Isotopic and chemical
 612 variation of organic nanoglobules in primitive meteorites.
 613 *Meteoritics & Planetary Science*. **48**, 904-928.

614 De Gregorio, B. T., Stroud, R. M., Nittler, L. R., Alexander, C. M. O. D.,
615 Kilcoyne, A. L. D. and Zega, T. J. (2010) Isotopic anomalies in organic
616 nanoglobules from Comet 81P/Wild 2: Comparison to Murchison
617 nanoglobules and isotopic anomalies induced in terrestrial organics
618 by electron irradiation. *Geochimica et Cosmochimica Acta*. **74**,
619 4454-4470.

620 Derenne, S. and Robert, F. (2010) Model of molecular structure of the
621 insoluble organic matter isolated from Murchison meteorite.
622 *Meteoritics & Planetary Science*. **45**, 1461-1475.

623 Drolshagen, G. and ESA. (2009) Comparison of Meteoroid Models. *Final*
624 *Report, IADC AI 24.1*.

625 Fries, M., Burchell, M., Kearsley, A. and Steele, A. (2009) Capture effects in
626 carbonaceous material: A Stardust analogue study. *Meteoritics &*
627 *planetary science*. **31**, 1465.

628 Grover, R., Ree, F. and Holmes, N. (1992) Equation-of-state from SiO₂
629 aerogel Hugoniot data. *Shock Compression of Condensed Matter-*
630 *1991* (Dick, R. D., Forbes, J. W. and Tasker, D. G. eds.), 95-98,
631 Elsevier.

632 Hayatsu, R., Matsuoka, S., Scott, R. G., Studier, M. H. and Anders, E.
633 (1977) Origin of organic matter in the early solar system—VII. The
634 organic polymer in carbonaceous chondrites. *Geochimica et*
635 *Cosmochimica Acta*. **41**, 1325-1339.

636 Ito, M. and Messenger, S. (2008) Isotopic imaging of refractory inclusions
637 in meteorites with the NanoSIMS 50L. *Applied Surface Science*. **255**,
638 1446-1450.

639 Ito, M., Uesugi, M., Naraoka, H., Yabuta, H., Kitajima, F., Mita, H., Takano,
640 Y., Karouji, Y., Yada, T., Ishibashi, Y., Okada, T. and Abe, M. (2014)
641 H, C, and N isotopic compositions of Hayabusa category 3 organic
642 samples. *Earth, Planets and Space*. **66**, 91.

643 Jacobsen, C., Wirick, S., Flynn, G. and Zimba, C. (2000) Soft X-ray
644 spectroscopy from image sequences with sub-100 nm spatial
645 resolution. *Journal of Microscopy*. **197**, 173-184.

646 Kawaguchi, Y., Yokobori, S.-i., Hashimoto, H., Yano, H., Tabata, M., Kawai,
647 H. and Yamagishi, A. (2016) Investigation of the interplanetary
648 transfer of microbes in the Tanpopo mission at the Exposed Facility
649 of the International Space Station. *Astrobiology*. **16**, 363-376.

650 Kebukawa, Y., Nakashima, S. and Zolensky, M. E. (2010) Kinetics of
651 organic matter degradation in the Murchison meteorite for the
652 evaluation of parent-body temperature history. *Meteoritics &*
653 *Planetary Science*. **45**, 99-113.

654 Kebukawa, Y., Zolensky, M. E., Chan, Q. H. S., Nagao, K., Kilcoyne, A. L. D.,
655 Bodnar, R. J., Farley, C., Rahman, Z., Le, L. and Cody, G. D. (2017)
656 Characterization of carbonaceous matter in xenolithic clasts from
657 the Sharps (H3.4) meteorite: Constraints on the origin and thermal
658 processing. *Geochimica et Cosmochimica Acta*. **196**, 74-101.

659 Kilcoyne, A., Tyliczszak, T., Steele, W., Fakra, S., Hitchcock, P., Franck, K.,
660 Anderson, E., Harteneck, B., Rightor, E. and Mitchell, G. (2003)
661 Interferometer-controlled scanning transmission X-ray microscopes
662 at the Advanced Light Source. *Journal of Synchrotron Radiation*. **10**,
663 125-136.

664Kitazawa, Y., Fujiwara, A., Kadono, T., Imagawa, K., Okada, Y. and
665 Uematsu, K. (1999) Hypervelocity impact experiments on aerogel
666 dust collector. *Journal of Geophysical Research: Planets*. **104**,
667 22035-22052.

668Le Guillou, C., Bernard, S., Brearley, A. J. and Remusat, L. (2014) Evolution
669 of organic matter in Orgueil, Murchison and Renazzo during parent
670 body aqueous alteration: In situ investigations. *Geochimica et*
671 *Cosmochimica Acta*. **131**, 368-392.

672Llana-Fúnez, S., Brodie, K. H., Rutter, E. H. and Arkwright, J. C. (2007)
673 Experimental dehydration kinetics of serpentinite using pore
674 volumetry. *Journal of Metamorphic Geology*. **25**, 423-438.

675Macke, R. J., Consolmagno, G. J. and Britt, D. T. (2011) Density, porosity,
676 and magnetic susceptibility of carbonaceous chondrites. *Meteoritics*
677 *& Planetary Science*. **46**, 1842-1862.

678McCausland, P. J., Samson, C. and McLeod, T. (2011) Determination of
679 bulk density for small meteorite fragments via visible light 3-D laser
680 imaging. *Meteoritics & Planetary Science*. **46**, 1097-1109.

681Mimura, K., Okamoto, M., Sugitani, K. and Hashimoto, S. (2007) Selective
682 release of D and (13)C from insoluble organic matter of the
683 Murchison meteorite by impact shock. *Meteoritics & Planetary*
684 *Science*. **42**, 347-355.

685Mimura, K. and Toyama, S. (2005) Behavior of polycyclic aromatic
686 hydrocarbons at impact shock: Its implication for survival of organic
687 materials delivered to the early Earth. *Geochimica et Cosmochimica*
688 *Acta*. **69**, 201-209.

689 Nakamura-Messenger, K., Messenger, S., Keller, L. P., Clemett, S. J. and
690 Zolensky, M. E. (2006) Organic globules in the Tagish Lake
691 meteorite: Remnants of the protosolar disk. *Science*. **314**, 1439-
692 1442.

693 Noguchi, T., Nakamura, T., Okudaira, K., Yano, H., Sugita, S. and Burchell,
694 M. J. (2007) Thermal alteration of hydrated minerals during
695 hypervelocity capture to silica aerogel at the flyby speed of
696 Stardust. *Meteoritics & Planetary Science*. **42**, 357-372.

697 Ogata, Y., Yabuta, H., Nakashima, S., Okudaira, K., Moriwaki, T., Ikemoto,
698 Y., Hasegawa, S., Tabata, M., Yokobori, S.-i., Mita, H., Kobayashi, K.,
699 Imai, E., Hashimoto, H., Kawaguchi, Y., Sugino, T., Yano, H.,
700 Yamagishi, A. and Tanpopo Working Group (2013) Hypervelocity
701 capture of Murchison meteorite particles in aerogel: ground-based
702 experiment for the cosmic dusts capture at the International Space
703 Station. *29th International Symposium on Space Technology and
704 Science, Proceedings*. 2013-r-2051p.

705 Okudaira, K., Noguchi, T., Nakamura, T., Sugita, S., Sekine, Y. and Yano, H.
706 (2004) Evaluation of mineralogical alteration of micrometeoroid
707 analog materials captured in aerogel. *Advances in Space Research*.
708 **34**, 2299-2304.

709 Pearson, V., Sephton, M., Gilmour, I. and Franchi, I. (2001) Hydrogen
710 isotopic composition of the Tagish Lake meteorite: Comparison with
711 other carbonaceous chondrites. *Lunar and Planetary Science XXXII*.
712 1861.

713 Peterson, E., Horz, F. and Chang, S. (1997) Modification of amino acids at
 714 shock pressures of 3.5 to 32 GPa. *Geochimica et Cosmochimica*
 715 *Acta*. **61**, 3937-3950.

716 Piani, L., Robert, F. and Remusat, L. (2015) Micron-scale D/H
 717 heterogeneity in chondrite matrices: A signature of the pristine solar
 718 system water? *Earth and Planetary Science Letters*. **415**, 154-164.

719 Sandford, S. A., Aleon, J., Alexander, C. M. O. D., Araki, T., Bajt, S., Baratta,
 720 G. A., Borg, J., Bradley, J. P., Brownlee, D. E., Brucato, J. R., Burchell,
 721 M. J., Busemann, H., Butterworth, A., Clemett, S. J., Cody, G.,
 722 Colangeli, L., Cooper, G., D'Hendecourt, L., Djouadi, Z., Dworkin, J.
 723 P., Ferrini, G., Fleckenstein, H., Flynn, G. J., Franchi, I. A., Fries, M.,
 724 Gilles, M. K., Glavin, D. P., Gounelle, M., Grossemy, F., Jacobsen, C.,
 725 Keller, L. P., Kilcoyne, A. L. D., Leitner, J., Matrajt, G., Meibom, A.,
 726 Mennella, V., Mostefaoui, S., Nittler, L. R., Palumbo, M. E.,
 727 Papanastassiou, D. A., Robert, F., Rotundi, A., Snead, C. J., Spencer,
 728 M. K., Stadermann, F. J., Steele, A., Stephan, T., Tsou, P., Tyliczszak,
 729 T., Westphal, A. J., Wirick, S., Wopenka, B., Yabuta, H., Zare, R. N.
 730 and Zolensky, M. E. (2006) Organics captured from comet 81P/Wild
 731 2 by the Stardust spacecraft. *Science*. **314**, 1720-1724.

732 Sandford, S. A., Bajt, S., Clemett, S. J., Cody, G. D., Cooper, G., Degregorio,
 733 B. T., de Vera, V., Dworkin, J. P., Elsila, J. E. and Flynn, G. J. (2010)
 734 Assessment and control of organic and other contaminants
 735 associated with the Stardust sample return from comet 81P/Wild 2.
 736 *Meteoritics & Planetary Science*. **45**, 406-433.

737Smith, N., Stewart Jr, R., Osborn, A. and Scott, D. (1980) Pyrene: vapor
738 pressure, enthalpy of combustion, and chemical thermodynamic
739 properties. *The Journal of Chemical Thermodynamics*. **12**, 919-926.

740Stöhr, J. (1992) *NEXAFS spectroscopy*. Springer, 403pp.

741Tabata, M., Kawai, H., Yano, H., Imai, E., Hashimoto, H., Yokobori, S.-i. and
742 Yamagishi, A. (2016) Ultralow-density double-layer silica aerogel
743 fabrication for the intact capture of cosmic dust in low-Earth orbits.
744 *Journal of Sol-Gel Science and Technology*. **77**, 325-334.

745Tingle, T. N., Tyburczy, J. A., Ahrens, T. J. and Becker, C. H. (1992) The fate
746 of organic-matter during planetary accretion - Preliminary studies of
747 the organic-chemistry of experimentally shocked Murchison
748 meteorite. *Origins of Life and Evolution of the Biosphere*. **21**, 385-
749 397.

750Vinogradoff, V., Bernard, S., Le Guillou, C. and Remusat, L. (2018)
751 Evolution of interstellar organic compounds under asteroidal
752 hydrothermal conditions. *Icarus*. **305**, 358-370.

753Vinogradoff, V., Le Guillou, C., Bernard, S., Binet, L., Cartigny, P., Brearley,
754 A. J. and Remusat, L. (2017) Paris vs. Murchison: Impact of
755 hydrothermal alteration on organic matter in CM chondrites.
756 *Geochimica et Cosmochimica Acta*. **212**, 234-252.

757Yamagishi, A., Yano, H., Okudaira, K., Kobayashi, K., Yokobori, S.-I.,
758 Tabata, M., Kawai, H., Yamashita, M., Hashimoto, H. and Naraoka, H.
759 (2009) TANPOPO: astrobiology exposure and micrometeoroid
760 capture experiments. *Transactions of the Japan Society for*

761 *Aeronautical and Space Sciences, Space Technology Japan.* **7**,
762 Tk_49-Tk_55.
763
764
765

766**Tables**

767

768 Table 1. Conditions for two-stage light-gas gun experiments.

Shot number	Velocity	Aerogel density	Grain size	Vacuum
#399	4.4 km/s	0.01 g/cm ³	30 μm - 100 μm	7.5 Pa
#1473	5.9 km/s	0.01 g/cm ³	37 μm - 60 μm	9.5 Pa

769

770 Table 2. C-XANES characteristic energies. The Peak assignments
771 were based on [Cody et al. \(2008a\)](#) and [Vinogradoff et al. \(2018\)](#).

	Energy (eV)	Transition	Functional group
1	285.2	1s-π*	Aromatic/alkene
2	286.5	1s-π*	Ketone C=O
3	287.7	1s-3p/s	Aliphatic Carboxyl/ester
4	288.6	1s-π*	O-C=O Alcohol, ether C-
5	289.7	1s-3p/s	O
6	290.5	1s-π*	Carbonate CO ₃

772

773

774**Figure captions**

775Fig. 1. The scanning transmission X-ray microscopy (STXM) images (a) at
776390 eV for the Murchison shot sample #399 (4.4 km/s) grain 1 (A) and
777grain 2 (B), and #1473 (5.9 km/s) grain 1 (C) and grain 2 (D). The carbon
778X-ray absorption near-edge structure (C-XANES) spectra were obtained
779using the marked red rectangle areas are shown in Error: Reference
780source not found.

781

782Fig. 2. Carbon X-ray absorption near-edge structure (C-XANES) spectra of
783the Murchison shot sample #399 (4.4 km/s) (A, B) and #1473 (5.9 km/s)
784(C). Intact Murchison spectra (“Before”) are also shown for comparison.
785The peak assignments are shown in Table 2. Three-point smoothing was
786applied to each C-XANES spectrum.

787

788Fig. 3. STXM image contrast maps of the Murchison shot samples. (A)
789285.0 eV and (B) 287.5 eV image contrast maps from the area A3 in Fig.
7901a (#399, 4.4 km/s). (C) 285.0 eV and (D) 288.5 eV image contrast maps
791from the area B5 in Fig. 1b (#399, 4.4 km/s). (E) 288.5 eV image contrast
792maps from the area C1a in Fig. 1c (#1473, 5.9 km/s).

793

794Fig. 4. TEM images of amorphous membrane in the Murchison shot #399
795(4.4 km/s), sample obtained from the ultramicrotomed fragment “A2” (see
796also Fig. 1A), combined with EDS spectrum from each area.

797

798 Fig. 5. TEM images of minerals in the Murchison shot #1473 (5.9 km/s)
799 sample, carbonaceous materials from the inner part of the
800 ultramicrotomed fragment "C1" (A), serpentine or cronstedtite covered
801 with some carbon membranes obtained from the area "C1a" (outer region
802 of the "C1") (B), serpentine or cronstedtite obtained from "C1" (C, D) (see
803 also Fig. 1C).

804

805 Fig. 6. TEM images of carbonaceous matter and minerals in the Murchison
806 shot #1473 grain 1 (5.9 km/s), combined with EDS spectrum from each
807 area. (A) Carbon-rich area. (B) Serpentine with carbon obtained from the
808 area "C1a" (outer region of the "C1").

809

810 Fig. 7. NanoSIMS images of the Murchison shot #399 grain 1 (A-D, field of
811 view = $18 \mu\text{m}^2$) and grain 2 (E-H, field of view = $20 \mu\text{m}^2$). (A, E) secondary
812 electron (SE) images, (B, F) ^{12}C images, (C, G) ^1H images, and (D, H) δD
813 images. Average δD values of the grain 1 and 2 are $-22 \pm 20 \text{‰}$ and -39
814 $\pm 25 \text{‰}$, respectively.

815

816 Fig. 8. Impedance matching calculations. (a) Maximum shock pressure
817 was estimated as $\sim 0.5 \text{ GPa}$ for 4 km/s impact velocity in the case of 0.03
818 g/cm^3 aerogel. (b) Maximum shock pressure was estimated as $\sim 1 \text{ GPa}$ for
819 6 km/s impact velocity in the case of 0.03 g/cm^3 aerogel.

820

821 Fig. 9. Calculations of the decomposition rate of serpentine relative to the
822 rate at 630°C with temperature. Various reported activation energies

823(Llana-Fúnez et al. 2007; Alizadehhesari et al. 2012) were used for the
824calculations.