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

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Abstract

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

INTRODUCTION

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

Japanese Experiment Module (JEM) ‘Kibo’ on the International Space Station (ISS) (Cottin *et al.*, 2017; Kawaguchi *et al.*, 2016; Yamagishi *et al.*, 2009). One of the sub-divided themes of the Tanpopo mission is the capture of intact organic bearing micrometeoroids in low Earth orbit. The micrometeoroids impact the ISS at several kilometers per second, and therefore a low-density silica aerogel would be suitable for capturing relatively intact micrometeoroids. However, the highly insulative nature of aerogel may cause heating of captured materials by the friction generated as a result of the high velocity impact (e.g., Noguchi *et al.*, 2007).

Some earlier studies showed that phyllosilicates, within the few micrometer alteration rims of serpentine, cronstedtite, and the Murchison meteorite particles, were intact after 2-6 km/s impact into 0.03 g/cm^3 density aerogel, despite the significant volume loss from the particle’s outside surface during the penetration processes (Noguchi *et al.*, 2007; Okudaira *et al.*, 2004). For example, detailed examination of the “keystone” samples from the Stardust mission, showed that the upper parts of the entrant hollow tracks are lined with relatively large amounts of melted aerogel and dissolved projectile, but the track ends contain largely un-melted cometary fragments (Brownlee *et al.*, 2006). Although, some organic matter in the cometary dust particles survived approximately 6.1 km/s impact into the aerogel tiles (e.g., Cody *et al.*, 2008a; Sandford *et al.*, 2006), one cannot exclude the possibility that they could be chemically altered by the impact (Sandford *et al.*, 2010).

Modification of the organic matter (OM) have been examined using several analogue materials fired into Stardust-like aerogels at velocities around 6 km/s. This suggested that the degree of alteration of organic compounds significantly depends on the nature of the organic compounds and the matrix materials (Sandford *et al.*, 2006). Cocoa powder mixed with small soda-lime glass spheres underwent extensive alteration including both bond-breaking and bond-creation, with the OM found distributed along the bulb-shaped track, while Allende meteorites that evidence polycyclic aromatic hydrocarbons (PAHs), were not greatly altered (Sandford *et al.*, 2006). Particles of poly(methyl methacrylate) and poly(ethyl methacrylate) that were fired into aerogel (density 0.06 g/cm^3) at ~5 km/s showed no distinct chemical modification based on Raman spectroscopy (Burchell *et al.*, 2004). However, coal samples fired into aerogel targets (0.03 g/cm^3) at velocities of around 6 km/s showed that particle surfaces are largely homogenized during capture, apparently indicating a devolatilization step during capture processing, with both graphitization and amorphization found in the coal samples (Fries *et al.*, 2009).

To evaluate the effect of hyper-velocity capture of micrometeoroids, laboratory experiments with flight-grade ultralow-density aerogel (0.01 g/cm^3) have been conducted for the Murchison meteorite powder as an analogue of micrometeoroids that contain OM, using a two-stage light gas gun (Ogata *et al.*, 2013). Ogata et al. (2013) reported that infrared and Raman spectroscopic measurements of Murchison recovered from 4 km/s impact, showed that a major part of the OM survived. Accordingly, we evaluate the modification of Murchison recovered from 4.4 km/s and 5.9 km/s impacts using scanning transmission X-ray microscopy (STXM), transmission electron microscopy (TEM), and high-resolution secondary ion mass spectrometry (NanoSIMS). In the following, we present a summary of the experimental techniques used to investigate the possible changes to the OM in the meteorites, followed by a discussion and conclusion.

EXPERIMENTAL

Two-Stage Light-Gas Gun Experiments

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

Sample Preparation

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

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

STXM-XANES

X-ray absorption near edge structure (XANES) analyses for the carbon and nitrogen *K*-edges were performed using the STXM at beam line 5.3.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory (Kilcoyne *et al.*, 2003). Details of the experimental methods have been described in Kebukawa *et al.* (2017). Beam focusing utilized Fresnel zone plate optics for a theoretical spot size of ~31 nm. The C, N-XANES spectra were acquired using a multi-spectral imaging method (“Stacks” method; Jacobsen *et al.*, 2000). The energy step size (ΔE) employed was 0.1 to 0.2 eV in the fine structure portions of the near-edge region (283–296 eV), and 0.5 to 1 eV in the pre-edge and post-edge regions (278–283 and 296–301 eV for C). The acquisition time per energy step (dwell time) varied from 2 to 4 ms (up to 9 ms). An X-ray absorption spectrum was acquired by using the Beer-Lambert law, $-\ln(I/I_0)$, where I is the intensity of the photons from the sample region and I_0 is the intensity of the photons from a blank area next to the sample region.

TEM

In order to examine heating effects due to the capture of the particles by the aerogel, we conducted transmission electron microscopy (TEM) analysis on the recovered grains after 4.4 km/s impact (#399) and 5.9 km/s impact (#1473). TEM analysis was performed using a JEOL JEM-2100F microscope equipped with an energy dispersive X-ray spectrometer (EDX) at Tohoku University. The acceleration voltage was 200 kV.

NanoSIMS

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

RESULTS

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.*

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

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

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

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

TEM ANALYSIS

The same sample sections were analyzed with TEM after STXM measurements to search for minerals that can be used as indicators of heating/shock processes. Fig. 4 shows TEM images of the shot #399 (4.4 km/s) samples with corresponding energy dispersive X-ray (EDS) spectra. The outer surfaces of minerals are mostly covered with amorphous carbonaceous matter (Fig. 4A and 4B). Part of the carbonaceous matter form bridging structure between mineral particles (Fig. 4A and 4B). These observations were consistent with C-XANES spectra of the organic matter in the Murchison that did not show significant changes after the impact, although TEM cannot analyze changes in molecular structures.

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

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

NanoSIMS ANALYSIS

In order to examine isotope fractionation in the captured particles by aerogel, hydrogen isotopic composition of the ultramicrotomed fragments of the Murchison shot #399 sample recovered after 4.4 km/s impact was obtained using NanoSIMS (Fig. 7). The hydrogen isotopic composition were analyzed on fragments that were not subjected to TEM analysis, to avoid any isotope fractionation due to electron beam damage (De Gregorio *et al.*, 2010). The average δD values of the #399 grain 1 and 2 are –22 ± 20 ‰ and –39 ± 25 ‰, respectively. These values are consistent 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/cm^3) whose coefficients (C and S) are available in order to estimate the C and S values of 0.03 g/cm^3 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/cm^3), serpentine (2.62 g/cm^3) and iron (7.85 g/cm^3). 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

0.03 g/cm^3 aerogel targets. The result is consistent with Fig. 21 in Kitazawa *et al.* (1999). Since the density of the Murchison meteorite is 2.15-2.40 g/cm^3 (Macke *et al.*, 2011; McCausland *et al.*, 2011), the shock pressures of Murchison meteorite projectiles into 0.01 g/cm^3 aerogel projectiles collectors should not exceed 1 GPa as in our experiments.

DISCUSSION

TEM observation showed no clear evidence for alteration of the grains recovered after both 4.4 km/s impact (shot #399) and 5.9 km/s impact (shot #1473) into the 0.01 g/cm^3 aerogel. In addition, the TEM measurements showed that cronstedtite and serpentine did not decompose after impact into the aerogel. Since the reported decomposition temperature of cronstedtite is 470 °C (Caillère and Hénin, 1957), and that of serpentine is 600-660 °C (Akai, 1992), the temperature of the remaining part of the grains could not have exceeded 470 °C. However, one cannot exclude the possibility that the Murchison grains experienced a higher temperature for a short duration that did not allow dehydration of cronstedtite. The decomposition of phyllosilicates is a time-temperature sensitive process, i.e., the decomposition occurs more rapidly at a higher temperature, generally following the Arrhenius law. The phyllosilicates can survive for short periods of time at temperatures well above the published laboratory decomposition temperature that is expected in our experiments. Thus, we calculated how decomposition rate could change depends on the temperatures using reported activation energies 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: $k = A\exp(-Ea/RT)$ 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 (~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 ºC) 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/cm^3 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 ~20-25 μm (grain 1) and 10-15 μm (grain 2) in size for 4.4 km/s impact, and 30-40 μm (grain 1) and 10-15μm (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.

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

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

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

In the case of the higher velocity (5.9 km/s) impact, large amounts of organic matter in the Murchison meteorite are ablated/vaporized upon entry into the aerogel. A C-XANES spectrum of one of the Murchison grains recovered after 5.9 km/s impact (#1473 grain 1) probably indicates dearomatization of the organic matter (Fig. 2c). This conclusion is partially consistent with earlier experiments using terrestrial coal samples fired into aerogel targets (0.03 g/cm^3) at velocities of ~6 km/s and showed that both graphitization and amorphization occur, possibly due to devolatilization and re-condensation within the particles (Fries *et al.*, 2009). We did not see any evidence of graphitization in the Murchison particles recovered from the impacts. However, because the chemical structure of organic matter in the Murchison is more susceptible to heating, and/or the OM in Murchison is diffused in the matrix minerals it is more susceptible to ablation and volatilization compared to compacted organic matter such as coal grains. The majority (~70%) of the OM exists in the form of insoluble organic matter (IOM) that consist of aromatic units with up to four rings bridged by aliphatic carbon chain, ether, and ester moieties (e.g., Derenne and Robert, 2010; Hayatsu *et al.*, 1977). Previous kinetically controlled flash heating experiments indicated that the likelihood of vaporized organic matter by cracking these bonds between aromatic units, is faster than aromatization (Cody *et al.*, 2008b; Kebukawa *et al.*, 2010). Thus, the IOM fragments could be easily vaporized even by residual heat. For example, the vapor pressures of a simple form of a four ring aromatic hydrocarbon, pyrene, are 17.1 Pa at 398 K and 345.3 Pa at 458 K (Smith *et al.*, 1980), and thus would easily vaporize under our experimental conditions (<10 Pa).

In the case of the cometary dust particles captured by Stardust mission, some particles (e.g., #2 and #3 in Fig. 1 of Cody et al., 2008a) show a large peak at 288.7 eV with a small peak at 285 eV and these characteristics are similar to our C-XANES spectra of the Murchison recovered after 5.9 km/s impact (#1473). It might imply that some of the Stardust recovered particles would have been affected by the capture process.

No shock features were recognized in the recovered Murchison grains by TEM. However, the possibility of shock process cannot be excluded since the analyzed area by TEM were limited. Previous higher velocity (>6 km/s) experiments using higher density aerogel (0.03 g/cm^3) showed no remarkable shock features (Noguchi *et al.*, 2007). In addition, little or no loss of organic matter was observed in a Murchison meteorite shocked to ~20 GPa, by thermal-desorption photoionization mass spectrometry which is sensitive to labile fragments from IOM (Tingle *et al.*, 1992). Mimura and Toyama (2005) showed that decompositions of PAHs started at ~10 GPa and over 95% of PAHs were decomposed at 30 GPa (shock temperature was 1480 K at 30 GPa). These experiments showed that shock pressures less than a few tens of GPa did not affect organic matter significantly, which is much higher compared to our experiments. Thus, the alteration of the organic matter is mostly due to friction heating rather than shock heating. Moreover, labile fractions such as amino acids could have been more easily modified, e.g., a 3.5 GPa shock reduced ~50 % amino acids that were embedded in a mineral matrix (Peterson *et al.*, 1997). Thus, modification of labile functional groups evident in C-XANES (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 ± 20 ‰ and –39 ± 25 ‰, respectively while pristine Murchison is –42 ± 15 ‰). 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 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

We evaluated the degradation of the Murchison meteorite with impact velocities of 4.4 km/s and 5.9 km/s captured by 0.01 g/cm^3 aerogel which was developed for the Tanpopo mission. No significant degradation of the recovered Murchison grains was observed by TEM. However, significant spectral changes were observed in C-XANES spectra of the Murchison grains recovered from the 5.9 km/s impact. While no significant changes in the recovered samples in C-XANES spectra and hydrogen isotopic ratio and mineralogical composition were observed for the 4.4 km/s impact.

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

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Tables

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

Table 2. C-XANES characteristic energies. The Peak assignments 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
4	288.6	1s–π*	Carboxyl/ester O–C=O
5	289.7	1s–3p/s	Alcohol, ether C–O
6	290.5	1s–π*	Carbonate CO_3

Figure captions

Fig. 1. The scanning transmission X-ray microscopy (STXM) images (a) at 390 eV for the Murchison shot sample #399 (4.4 km/s) grain 1 (A) and grain 2 (B), and #1473 (5.9 km/s) grain 1 (C) and grain 2 (D). The carbon X-ray absorption near-edge structure (C-XANES) spectra were obtained using the marked red rectangle areas are shown in Error: Reference source not found.

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

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

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

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

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

Fig. 7. NanoSIMS images of the Murchison shot #399 grain 1 (A-D, field of view = 18 μm^2) and grain 2 (E-H, field of view = 20 μm^2). (A, E) secondary electron (SE) images, (B, F) ^{12}C images, (C, G) ^{1}H images, and (D, H) δD images. Average δD values of the grain 1 and 2 are –22 ± 20 ‰ and –39 ± 25 ‰, respectively.

Fig. 8. Impedance matching calculations. (a) Maximum shock pressure was estimated as ~0.5 GPa for 4 km/s impact velocity in the case of 0.03 g/cm3 aerogel. (b) Maximum shock pressure was estimated as ~1 GPa for 6 km/s impact velocity in the case of 0.03 g/cm3 aerogel.

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

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