A new X-ray fluorescence spectroscopy for extraterrestrial materials using a muon beam

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The recent development of the intense pulsed muon source at J-PARC MUSE, Japan Proton Accelerator Research Complex/MUon Science Establishment (10^9 s^-1 for a momentum of 60 MeV/c), enabled us to pioneer a new frontier in analytical sciences. Here, we report a non-destructive elemental analysis using muon capture. Controlling muon momentum from 32.5 to 57.5 MeV/c, we successfully demonstrate a depth-profile analysis of light elements (B, C, N, and O) from several mm-thick layered materials and non-destructive bulk analyses of meteorites containing organic materials. Muon beam analysis, enabling a bulk analysis of light to heavy elements without severe radioactivation, is a unique analytical method complementary to other non-destructive analyses. Furthermore, this technology can be used as a powerful tool to identify the content and distribution of organic components in future asteroidal return samples.

The muon is a lepton with a mass of 105.7 MeV/c², approximately 200 times heavier than the electron. The interaction between muons and materials has been used in various fields of research. Muon spin rotation, relaxation, and resonance (μSR) use polarised positive muons as sensitive magnetic microprobes with short-range interactions with materials. Muon tomography uses the highly transmissive nature of muons to image low-density regions of materials. Recent studies on tomographic imaging with cosmic ray muons have succeeded in imaging the density structure of volcanoes.

Muons entering materials lose their kinetic energy with less effective bremsstrahlung than electrons due to their heavier mass; they can also penetrate much deeper into materials than electrons. The penetration depth of muons depends on the density of the target material and the initial muon momentum. Negative muons are captured by atoms to form muonic atoms at the stopping depths. In a muonic atom, cascade transition of the trapped muon from higher to lower energy states occurs with the emission of characteristic muonic X-rays. As muons have an orbit closer to the atomic nucleus than electrons owing to its ~200 times heavier mass, the characteristic muonic X-ray has an energy ~200 times higher than that associated with electron transition (more than several ten keV even if the muon is captured in light elements). The muonic X-rays are thus intense enough to pass through the target material from the much deeper interior than the characteristic X-rays of electron transitions, thereby suggesting that muonic X-rays from muonic atoms can be applicable to non-destructive elemental analyses of the deep interior of materials, which cannot be performed with X-ray fluorescence spectroscopy or electron probe microanalysis.

In 1971, Rosen noted the great availability of muon beam analysis and proposed its application in the chemical analysis of tissues, as muon beam analysis would cause less damage to the host organism than neutron activation analyses. Muonic atom spectroscopy has been developed over the past four decades as a non-destructive analytical method; however, for a real application, one had to wait for an intense muon source. The intense pulsed muon source, J-PARC MUSE (Japan Proton Accelerator Research Complex, MUon Science Establishment), was constructed and succeeded in providing a decay muon rate of 10^9 s^-1 for a momentum of 60 MeV/c in November 2009, which is the most intense pulsed muon beam in the world. Although J-PARC was damaged by a magnitude 9 earthquake and a subsequent tsunami on 11 March 2011 ("Higashi-Nippon Dai-Shinsai"), it was successfully revived in February 2012.
We report a feasibility study of the non-destructive muon beam chemical analysis of light elements (C, N, O and B) from millimetre-to centimetre-sized samples, which are difficult to analyse via neutron activation analysis, using the D2 muon beam line at J-PARC MUSE. Moreover, the degree of radioactivation due to muon irradiation is much less than that of neutron activation analysis, thereby allowing various applications. A potential useful application of this technique is, for instance, non-destructive analyses of light elements in extraterrestrial samples, particularly those obtained in sample return missions. Two sample return missions, Hayabusa-2 and OSIRIS-REx, will aim for C-type asteroids, for which reflectance spectra resemble those of carbonaceous chondrites containing organic materials. Millimetre- to centimetre-sized asteroidal surface samples will be returned in the 2020s, and the non-destructive analyses of light elements will prove to be a powerful analytical tool to determine the contents and/or distribution of organic materials, which may have been prebiotic building blocks of life, in pebble-sized noble samples.

Results

The depth profiling of light elements from a layered sample. The muon beam analysis of a four-layered sample consisting of SiO₂ glass, graphite (C), boron nitride (BN), and SiO₂ glass was generated to obtain a depth profile of light elements. The sample is held by an aluminium holder in an aluminium vacuum chamber with a polyimide entrance window composed of polyimide foil.

The negative muon beam was collimated to approximately 2.7 cm in diameter and focused on the sample surface (50 mm × 75 mm), which was oriented at 45 degrees to the beam (Fig. 1). Adjusting the muon momentum from 32.5 MeV/c to 57.5 MeV/c, muonic X-rays from the sample were measured by a Ge detector. The accumulation time of X-ray signals was 3–4 hours for each muon momentum. Figure 2 shows the observed X-ray spectra for the different momentum of incident muon beams. The energies of muonic X-rays listed in Engfer et al. were used for peak identification. Note that the peaks at 66 and 89 keV represent Al signals from the sample holder and vacuum chamber. At the momentum of 32.5 MeV/c, the muSi-Lα (76 keV) and muO-Kα (133 keV) signals were detected with the background muAl-Lα (66 keV). The peaks of muSi-Lα and muO-Kα were also confirmed at the momentum of 37.5 and 40.0 MeV/c, although they disappeared at the momentum 42.5 MeV/c, where the muC-Kα (75 keV) signal was clearly observed. As the muC-Kα peak should come from the second graphite layer, these observations suggest that the muon beam penetrated through the first SiO₂ glass layer and into the depth of >2 mm of the sample at the momentum of 42.5 MeV/c. The findings also demonstrate that the characteristic muonic X-ray of carbon was emitted from a depth of >2 mm through the overlying SiO₂ glass layer without significant self-absorption and emission of muonic X-rays of Si and O. At the momentum of 50.0 MeV/c, the muC-Kα peak disappeared and only μB-Kα (52 keV) and μN-Kα (102 keV) signals from the third layer (boron nitride) were detected through the overlying SiO₂ and graphite layers. Finally, at the momentum of 57.5 MeV/c, the peaks of μB-Kα and μN-Kα disap-
The depths corresponding to the boundaries of sample layers (indicated by arrows) are consistent with the change in muonic X-ray intensities of each element from the layered sample. The muonic X-ray intensity of each element is normalised to that of Al at each momentum and to its maximum count along the depth profile. Analytical uncertainties (1σ) are estimated from the counting statistics of X-ray counts because the contributions of uncertainties in X-ray detection efficiency are much smaller than those of counting statistics (typically less than 5%). The stopping depth of muons at a given momentum is estimated from the Bethe-Bloch formula, and the expected layer boundaries are indicated by arrows.

Although there are further developments in experimental techniques, such as momentum filtering of the incident muon beam and a position-sensitive detector, we currently conclude that the non-destructive depth profile of light elements was successfully obtained up to ~7 mm in depth with a depth resolution of sub-mm. This result is hardly possible with other analytical techniques such as neutron activation analysis, X-ray fluorescence spectroscopy and electron probe microanalysis. Furthermore, muon beam analysis displays significant potential for the analysis of light element distributions within millimetre- to centimetre-sized samples.

**Elemental analysis of meteorite samples.** Muonic beam analysis was applied to primitive meteorites called chondrites. Chondrites have never been melted and remain physical aggregates of various components that formed in the early solar system prior to planet formation. Carbonaceous chondrites are one of the various chemical groups of chondrites, some of which contain abundant water as hydrated minerals and organic materials. They record the long evolutionary history of the solar system and prebiotic organic reservoirs. Thus, future asteroidal sample return missions (Hayabusa-2 and OSIRIS-REx) plan to sample such materials from asteroids without terrestrial contamination and with geologic contexts.

In this study, we carried out a non-destructive muon analysis of chips of carbonaceous chondrites, Murchison and Allende. The Murchison meteorite contains a copious amount of diverse extraterrestrial organic materials, while the Allende meteorite contains less carbon than the Murchison meteorite.

The negative muon beam, collimated to approximately 4 cm in diameter, irradiated to a ~5-mm-thick Murchison disk with the exposed surface area of ~5 cm × ~10 cm. The meteorite disk and the Ge detector were oriented at 45 and 90 degrees to the negative
Muon beam, respectively, in the same manner shown in Fig. 1. Aluminium foil was used to hang the sample inside the chamber. The exposure time was approximately 13 hours, and the momentum of the incident muon beam was set at 16 MeV/c, corresponding to the penetration depth of ~70 μm. For Allende meteorite analysis, the muon beam was collimated to approximately 2.7 cm in diameter at the sample surface of 50 mm × 75 mm. The sample was also hung with less amounts of Al foil than for the Murchison meteorite to reduce the background signal of Al. The exposure time was approximately 10 hours, and the incident muon momentum was set at 34 MeV/c (the penetration depth of ~1 mm).

Fluorescent X-rays of Mg, C, Si, Fe, Ca, and S were detected from the Murchison meteorite (blue), while those of Mg, Si, Fe, K, and Ca were detected from the Allende meteorite (red). The peaks of Al includes signals from the vacuum chamber and/or the sample holder. The peak of μC-Kα (75 keV) was detected from the Murchison meteorite,

| Table 1 | Characteristic muonic X-ray counts from carbonaceous chondrites, the Murchison and Allende meteorites |
|---------|--------------------------------------------------|
| Characteristic X-ray | Energy (keV) | Murchison | Allende |
| Ca-Mα   | 55         | n.d.      | 53 ± 23  |
| Mg-Lα   | 56         | 896 ± 66  | 183 ± 23 |
| Al-Lα   | 66         | 10796 ± 130 | 136 ± 30 |
| C-Kα    | 75         | 626 ± 52  | 6 ± 27   |
| Si-Lα   | 76         | 824 ± 58  | 175 ± 32 |
| Fe-Mα   | 94         | 1310 ± 63 | 265 ± 39 |
| O-Kα    | 133        | 4785 ± 111 | 800 ± 38 |
| K-Lα    | 140        | n.d.      | 94 ± 27  |
| Ca-Lα   | 156        | 213 ± 41  | 83 ± 28  |
| Al-Kα   | 346        | 9542 ± 100 | 359 ± 27 |
| S-Kα    | 516        | 121 ± 33  | 11 ± 9   |

n.d.: Not detected.

Figure 4 | Muonic X-ray energy spectra from carbonaceous chondrites: Murchison and Allende meteorites. Fluorescent X-rays of Mg, C, Si, Fe, Ca, and S were detected from the Murchison meteorite (blue), while those of Mg, Si, Fe, K, and Ca were detected from the Allende meteorite (red). The peaks of Al includes signals from the vacuum chamber and/or the sample holder. The peak of μC-Kα (75 keV) was detected from the Murchison meteorite,
emitted from the SiO$_2$ glass tube as well, which cannot be distinguished from the sample signals. Although further developments in analytical techniques are required, such as detector setting and collimation of the incident muon beam, our first attempt to non-destructively measure an extraterrestrial sample inside a glass tube succeeded with the detection of Mg and Fe.

**Discussion**

This study demonstrates that muon beam analysis is feasible for the non-destructive elemental analysis of light elements in extraterrestrial samples. This technique is complementary to other non-destructive analytical techniques, such as synchrotron X-ray microtomography and synchrotron X-ray diffraction, both of which have been used for preliminary examination of Itokawa particles$^{19-21}$, sealing in a glass tube is one of the effective ways to avoid terrestrial contamination of organic materials and volatiles and thus could be used in future sample return missions.

We also attempted to measure much smaller amounts of meteorite samples inside glass tubes to simulate non-destructive analyses of future return samples. Sealing extraterrestrial samples inside glass tubes was originally planned for samples from the asteroid Itokawa. Although Itokawa particles were not sealed in glass tubes due to their small sizes$^{19-21}$, sealing in a glass tube is one of the effective ways to avoid terrestrial contamination of organic materials and volatiles and thus could be used in future sample return missions.

Powdered Murchison meteorite (610 mg) was placed in a 5-cm-long SiO$_2$ glass tube, in which the inner and outer diameters were 4 mm and 6 mm, respectively. The muon beam collimated to approximately 2.5 cm in diameter, and the apparent cross section of the sample was 4 mm $\times$ 25 mm. After exposure of the muon beam with the momentum of 37 MeV/c for approximately 24 hours, clear signals of Mg and marginally resolved signals of Fe were detected through the 1-mm thick SiO$_2$ glass wall. The intense signal of Si originated from the SiO$_2$ glass tube. The muon beam momentum was set at 37 MeV/c, and the exposure time was 24 hours.

J-PARC MUSE plans to increase the power of the proton beam, of which irradiation of a graphite target produces the muon beam, up to 1 MW$^{13}$. The muon beam intensity will increase to $\sim$10$^7$ count/s (i.e., ten times larger than the current beam), which will yield a significant improvement in the counting statistics of muonic X-ray detection. The counting statistics will also be improved by development of the detection system (e.g., multiple Ge detectors covering a larger solid angle$^{25}$). With a more effective detector setting, the chemical structure states of Fe may be determined because the muonic X-ray structure of Fe can be used to identify the chemical bonding of elements. Synchrotron X-ray absorption near-edge structure (XANES) spectroscopy has been used to identify chemical bonding and functional groups in cometary organic matter sampled from the comet 81P/Wild 2 by the Stardust spacecraft$^{23}$. Nuclear reaction analysis (NRA) can be used to determine the contents and distribution of C, N, and O in minerals$^{26}$. The recent development of direct tomography with chemical bond contrast using synchrotron X-ray has made it possible to make a 3D map of the chemical bonding of light elements in a cm-sized sample with a spatial resolution of $\sim$100 $\mu$m$^{27}$. These techniques have not only benefits but also disadvantages, including severe radioactivation of samples, limitations in sample size and analytical area and/or depth, limited number of measurable elements, and difficulties in bulk analysis. Muon beam analysis is capable of performing a bulk analysis of light to heavy elements at one time without severe radioactivation and is thus a unique and complementary analytical method.

**Methods**

The muon science facility (MUSE) is located in the Materials and Life Science Facility (MLF), a facility that includes both neutron and muon science programs, at the Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan. MUSE currently

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**Figure 5** Correlation between the elemental concentration and the captured muon counts. The captured muon counts by each element, normalised to those of Mg, are plotted against the Mg-normalised weight concentrations of elements in meteorite samples$^{38}$ after correction of the energy-dependent detector efficiency and the emission probabilities of the Kx and Lx fluorescent lines. The captured muon counts correspond to the characteristic muonic X-ray counts. Error bars show analytical uncertainties (1$\sigma$) estimated from the counting statistics of X-ray counts.

**Figure 6** Muonic X-ray spectra from the powdered Murchison meteorite in an SiO$_2$ glass tube. A clear signal of Mg and a marginally resolved signal of Fe from the sample were detected through the 1-mm thick SiO$_2$ glass wall. The intense signal of Si originated from the SiO$_2$ glass tube. The muon beam momentum was set at 37 MeV/c, and the exposure time was 24 hours.

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has two beam lines to extract surface muons and decay muons from the muon source target into the experimental halls. Negative decay muons (5–120 MeV/c), which are obtained via the in-flight decay of μ⁻/μ⁺ confined by a strong longitudinal magnetic field of a superconducting solenoid magnet, were used in this study. Since November 26, 2010, the proton beam power from the Rapid Cycling Synchrotron has been steadily increased up to 220 kW, consequently delivering approximately 10⁷ count/s of decay muon beam (μ⁻ and μ⁺), until the earthquake on March 11, 2011. Although MUSE was seriously damaged from so-called ‘Higashi-Nippon Dai-Shinsai’, it recovered in six months and restarted operations for external users in February 2012. As a top priority analysis, this study was carried out in February 2012 and January 2013. The muon beam line at J-PARC/MUSE is now open for external users through a peer-reviewed proposal system (twice a year) as other analytical techniques in synchrotron facilities.

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Author contributions

K.T. and K.N. organised the entire research project and contributed to all aspects of this study. Y.M., M.K.K., N.K. and W.H. contributed to the development and set-up of the muon beam line at J-PARC MUSE, and T.O., S.T. and M.K.K. performed sample analyses with muon beam. A.T., M.E. and M.U. contributed to the discussion on the experimental set-up and comparison with other non-destructive techniques. K.T. and S.T. wrote the manuscript with T.O. and N.K. and all authors reviewed the manuscript.

Additional information

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