New analytical tool for extraterrestrial material curation: A great advantage for an *in-situ* analysis and quick survey of organics

M. Ito[1], R. Kanemaru[2], J. Isa[3], A. Yamaguchi[4], M. Miyahara[5], T. Yada[2], Y. Niwa[6], A. Ishikawa[6], T. D. Yokoyama[7], H. Takahashi[7], M. Uesugi[8] and T. Usui[2].

[1]*JAMSTEC,* [2]*JAXA-ISAS,* [3]*Chiba Tech,* [4]*NIPR,* [5]*Hiroshima University,* [6]*TiTech,* [7]*JEOL Ltd.,* [8]*JASRI/SPring-8*

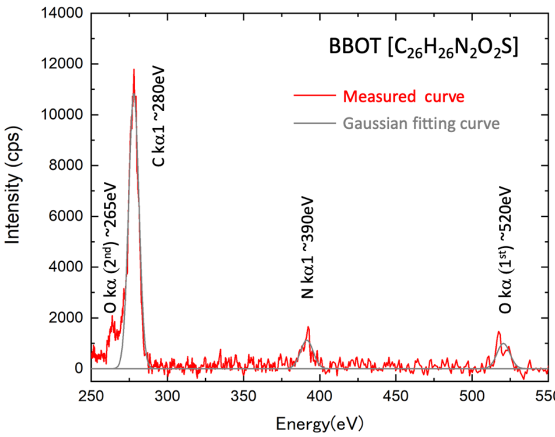
Introduction: Extraterrestrial organics in primitive meteorites, IDPs, returned samples from comets and asteroids (e.g., Brownlee et al., 2006; Yada et al., 2021) are one of the building blocks of the Solar System, and closely related with an origin of organics and life on Earth (e.g., Septon and Botta, 2005; Sandford et al., 2006). Now a day studies of organics in extraterrestrial materials are conducted by a combined and *in-situ* microanalysis such as NanoSIMS/SIMS for light element isotopes, STXM-XANES and AFM-IR for chemical functional groups, and TEM for textural observations (e.g., Garvie & Buseck, 2007; Floss et al., 2014; Kebukawa et al., 2019; Ito et al., 2022). Even a combined and *in-situ* microanalysis described above is a powerful tool to investigate nature of organics in extraterrestrial materials, analytical area is very limited of less than a few tens to few hundred µm in size. On the other hand, organics in primitive meteorites (i.e., carbonaceous chondrites) and returned samples from C-type asteroids contain a few weight percent of volume and are scattered all over a cm-mm sized sample with a µm scale.

A SXES (soft-X ray emission spectrometer) is a next generation analytical detector attached with SEM or EPMA system (Takahashi et al., 2016). Comparing with WDS (wavelength dispersive x-ray spectroscopy) detector, SXES can provides us (1) high spectral resolution (1.2 eV for FWHM of Zr Mζ) with energy ranges of 100 to 400 eV and 350 to 2300 eV, JS300N and JS2000 varied line spacing grating, respectively, allowing identify chemical shift (e.g., carbon functional group, Fe^{2+} and Fe^{3+}), (2) high detection sensitivity, (3) detection of multiple elements starting from lithium, and (4) low electron dose by both low accelerating voltage and beam current (Sakuda et al., 2010). The SXES-EPMA system could allow us to determine C and N abundances as well as phase identification and chemical bonding state (Takakura et al., 2022).

Here we present preliminary results of organics with different N/C and O/C ratios as standard materials, and C, N and O images of a C2-ung Tarda meteorite. We test the analytical capabilities of the SXES-EPMA system; (1) quick survey of organics in extraterrestrial materials, (2) an electron dose dependent, (3) analyzing a larger area (cm to mm in size), and (4) N/C and/or O/C ratios of organics for an initial characterization under a curation activity.

Experimental: We used the JEOL JXA-IHP200F FE-EPMA equipped with a SXES-ER detector (SS-94090EREP) at the JAXA curation with a defocused (50 µmϕ) and a focused beam of 10 nA and accelerating voltage of 5 keV for organic standards. BBOT [$C_{26}H_{26}N_2O_2S$], phenylalanine [$C_9H_{11}NO_2$], tryptophan [$C_{11}H_{12}N_2O_2$], Humic acid [C: 51, N:1.1, O:43], guanin [$C_5H_5N_5O$], thymine [$C_5H_6N_2O_2$] and cytosine [$C_4H_5N_3O$] were used for standard organic materials to optimize analytical conditions of spot and imaging analysis. Powdered organics are pressed into indium metal mount (1 cmϕ and 3 mm height), and then 20 nm of Au was coated on their surface.

Fig. 1 Typical SXES spectra of BBOT

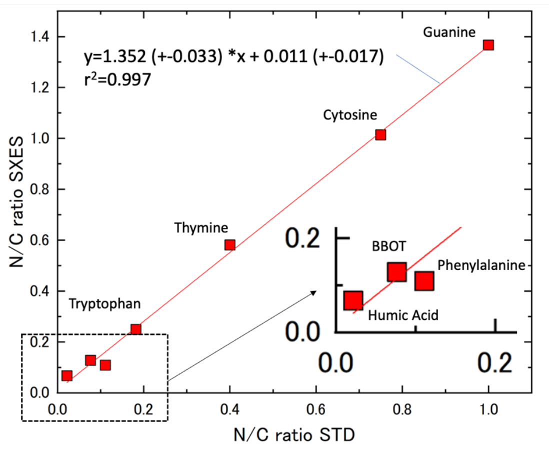


We prepared an epoxy-embedded polished thick section of Tarda (8 x 4 mm in size) with a 5 nm osmium coating on the surface. To acquire C, N and O elemental images of the Tarda, a 2 µm-focused electron beam of 30 nA with an accelerating voltage of 15 keV was used, irradiated over 64 × 48 μm^2 areas on the samples. Each analysis consisted of 3 scanned images of the same area, with individual images consisting of 80 × 60 pixels having a dwell time of 2 sec/pixel. The total acquisition time was approximately 12 hours (4 hours/1 scanned image) including dwell time and data fetching time from the detector to PC.

Results & Discussions: Figure 1 shows representative spectrum of BBOT ($C_{26}H_{26}N_2O_2S$) with N/C = 0.077 and O/C = 0.077. We observed clear peaks of $O_{k\alpha\,(2nd)}$ (~265 eV), $C_{k\alpha 1}$ (~280 eV), $N_{k\alpha 1}$ (~390 dpeV) and $O_{k\alpha\,(1st)}$ (~520 eV) with a spectral resolution of ~0.2 eV step. We, then, obtained the area of each peak by a Gaussian integral method. Figure 2 shows a calibration curve for N/C ratio (N/C ratio obtained by SXES analysis vs. N/C ratio of each standard). Note that we tried to obtain a calibration curve for O/C ratio in organic standards with the same manner but no luck. Further investigation is neccesary to have a better calibration curves for O/C ratio in organics. We also plan to conduct phase identifications or chemical bond state of organics based on shapes of $C_{k\alpha 1}$ though analyses of known organics as a standard material with the SXES- EPMA system suggested by Takakura et al. (2022).

Tarda is classified as C2 ungroup meteorite that potentially derived from D-type asteroid (Marrocchi et al., 2021). Figure 3 shows images of epoxy-mounted Tarda; (a) $C_{k\alpha 1}$, (b) $N_{k\alpha 1}$, (c) $O_{k\alpha\,(1st)}$, (d) BSE, and (e) SXES spectra of N-rich organics, typical matrix and epoxy for comparison. We found micro-meter sized N-rich organics showing different characteristics in SXES spectra of the surrounding matrix and epoxy (Fig. 3e-1 to 3e-3; cf. spectra of epoxy was obtained by a broad beam-spot analysis mode). The SXES spectra of N-rich organics show different from that of epoxy and matrix (Fig. 3 e1-3). We observed that SXES spectrum shape changes and intensities are smaller with frames due to the electron irradiation damages during acquisition. We, therefore, used 1st frame dataset of C, N and O SXES images and spectrum extracted from these images. Although one can find a *region-of-interest* corresponding to organics by a combination of C, N and O images together with SXES spectra of the ROI, it is necessary to optimize analytical conditions of beam current, acquisition time, accelerating voltage to introduce less or not artificial chemical changes for organics.

Fig. 2 Calibration curve for N/C ratio in organics



Conclusions: This is “a first-attempt” for an *in-situ* investigations of organics in standards and Tarda carbonaceous chondrite utilizing the SXES-EPMA. It is, however, potentially useful for visualizing a spatially distributions of C and N, and N/C ratios of organics in extraterrestrial materials including returned samples from C-type asteroid Ryugu and Bennu. Newly installed EPMA/SEM with the JEOL SXES-EPMA system at JAXA curation will open a new window for better characterizations of extraterrestrial organics under a curation activity.

Acknowledgment: A technical support of SXES-EPMA operation by JEOL Ltd. (Mr. Domon) is highly appreciated.

References: Brownlee D. et al. (2006) *Science* 314, 1711–1716; Floss *et al.* (2014) *Geochim Cosmochim Acta* 139:1–25; Garvie & Buseck (2007) *Meteorit. Planet. Sci.* 42:2111–2117; Ito *et al.* (2022) *Nat. Astron.* 10.1038/s41550-022-01745-5; Kebukawa *et al.* (2019) *Scientific Reports* 9:3169; Marrocchi *et al.* (2021) *ApJL* 913:L9; Sakuda *et al.* (2016) *European Microscopy Congress 2016: Proc.*, 847–848; Sandford *et al.* (2006) *Science* 314:1720–1724; Sephton &Botta (2005) *Inter J Astrobiol* 4:269–276; Takahashi *et al.* (2016) *IOP Conf. Ser.: Mater. Sci. Eng.* 109:012017; Takakura *et al.* (2022) *Microsc. Microanal*. 28:1014; Yada, T. et al. (2021) *Nat. Astron.* 6, 214–220.

Fig. 3 SXES elemental and BSE images and spectra of Tarda