RADIATION DOSE EFFECTS ON THE CARBON CHEMISTRY OF RYUGU ORGANIC MATTER: A CRITICAL STUDY USING SYNCHROTRON STXM. T. Ohigashi[1], M. Uesugi[2], H. Yuzawa[3], M. Ito[4], N. Tomioka[4], A. Yamaguchi[5], N. Imae[5], A. Nakato[5], N. Shirai[6], K. Uesugi[2], and M. Kimura[5]. [1]Institute for Material Structure Science, High Energy Accelerator Research Organization (KEK), Japan (ohigashi@post.kek.jp), [2]Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), Japan, [3]UVSOR Synchrotron Facility, Institute for Molecular Science, Japan, [4]Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan, [5]National Institute of Polar Research (NIPR), Japan, [6]Faculty of Science, Kanagawa University, Japan.

Introduction: Synchrotron-based Scanning Transmission X-ray Microscopy (STXM) is a powerful technique for characterizing organic matter in meteorites and extraterrestrial materials returned to Earth. It enables the visualization of localized organic materials and facilitates the identification of carbon, nitrogen, and oxygen functional groups through near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, also at sub-micrometer spatial resolution [e.g., 1, 2].

The analysis of organic matter in pristine Ryugu samples has been previously documented [e.g., 3–11]. This methodology integrates a suite of sub-micrometer-scale techniques, including NanoSIMS, TEM equipped with EELS, Raman spectrometry, FT-IR, and STXM-NEXAFS. These complementary methodologies allow for the determination of light-element isotopic compositions, mineralogical textures, crystallographic properties, and chemical functional groups, all with comparable spatial resolution. Studies employing STXM have revealed distinct organic signatures, such as aromatic-rich organic matter (e.g., IOM) [4–6] and diffuse carbon within phyllosilicates, which is predominantly aliphatic in nature [3, 6]. These observations suggest a complex diversity of carbon functional groups within the Ryugu samples, potentially reflecting their pristine and uncontaminated nature [e.g., 5].

In this study, we investigate the effects of X-ray radiation on the pristine Ryugu samples during STXM measurements, as well as the potential limitations associated with spectrum changes due to radiation dose and the spatial resolution. It should be noted that the STXM analyses for this study were conducted in October 2021 as part of Phase 2 curation activities in Kochi, and the preliminary result have been presented elsewhere [12].

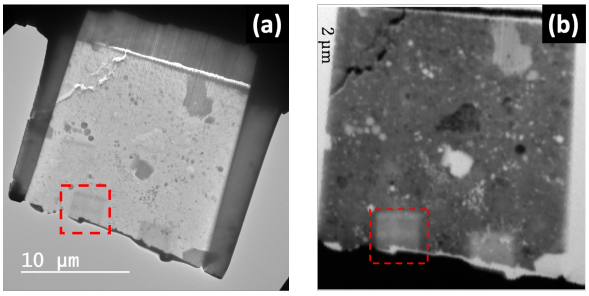

Figure 1. (a) TEM image, and (b) STXM carbon map of C0068-27 FIB section. Red dotted-line square is STXM analysis area.

Experimental: A 150- to 200-nm-thick section was extracted from a separate, unprocessed fragment (~100 µm in size) of the Ryugu particle C0068 using a Hitachi High Tech SMI4050 FIB instrument at the Kochi Institute for Core Sample Research, JAMSTEC (Figure 1). The fragment was not subjected to synchrotron radiation computed tomography at SPring-8 to avoid potential X-ray irradiation, and it was handled with minimal exposure to ambient air to prevent contamination and/or degradation.

Following deposition of tungsten protection layers, regions of interest (~20 × 20 µm²) were carefully cut out and thinned using a Ga^+ ion beam at an accelerating voltage of 30 kV. Final thinning was performed at 5 kV with a probe current of 40 pA to minimize surface damage. The resulting ultrathin section (hereafter referred to as C0068-27, Figure 1-a) was then mounted on a copper Kochi grid [13]. The FIB section was transferred to the STXM beamline at UVSOR using a facility-to-facility transfer container, which was filled with nitrogen (N_2) for transport [13].

Carbon K-edge spectra of the FIB section (C0068-27, Figure 1) were measured at the STXM beamline BL4U at the UVSOR-III Synchrotron Facility, Institute for Molecular Science. The beam was focused to a spot size of approximately 50 nm using Fresnel zone-plate optics (photon flux: 2.4×10^6 photons/s, $E/\Delta E \sim 3{,}000$). Energy step sizes were set at 0.1 eV for the fine structure region (283.6–292.0 eV) and 0.5 eV for the pre- and post-edge regions (280.0–283.5 eV and 292.5–300.0 eV). The acquisition time per pixel at each energy step was 2 ms.

Helium gas, at a pressure of ~20 mbar, was introduced into the analysis chamber to mitigate thermal drift in the X-ray optics and sample holder, as well as to reduce sample damage or oxidation. Carbon K-edge spectra were processed using a combination of aXis2000 and custom in-house software developed for STXM data reduction. The custom-built transfer vessel

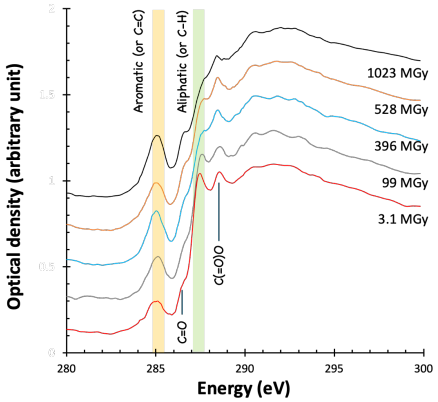

Figure 2. Changes with radiation damage in the Carbon K-edge spectra

and glove box were used to prevent oxidation and contamination during sample handling [14].

Results and Discussion: Figure 2 presents the selected carbon K-edge spectra obtained from repeated analyses of the same region of the Ryugu C0068-27 FIB section, measured across a radiation dose range from 3.1 to 1188 MGy (indicated by the red dotted square in Figure 1). Notably, the C-H bond peak (287.3 eV, associated with aliphatic hydrocarbons) exhibited significant sensitivity to X-ray irradiation, whereas the intensity of the C=C bond peak (285.3 eV, associated with aromatic structures) increased. These observations suggest that X-ray exposure during STXM measurements induces dose-dependent chemical modifications in the carbon K-edge spectra of the Ryugu sample.

Wang et al. [15] defined critical and acceptable radiation doses for organic samples analyzed using STXM. We adapted these definitions to better interpret the results from the Ryugu sample analysis, following the methodology outlined in [15]. Figure 3 shows the variation in the peak area of the C-H bond region (287–288 eV, with appropriate background subtraction) as a function of the radiation dose. The critical dose, defined as the dose at which the spectral peak area decreases by 63%, was determined to be 506 MGy. The acceptable

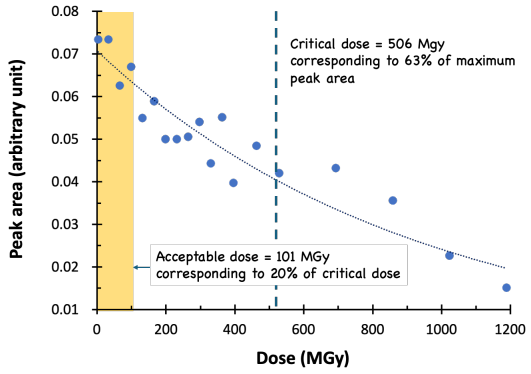

Figure 3. Normalized peak area at 287.3 eV as a function of dose (MGy)

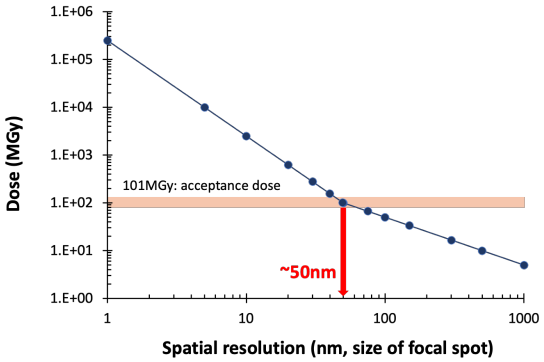

Figure 4. Spatial resolution (nm) as a function of radiation dose (MGy)

dose, defined as 20% of the critical dose, corresponds to 101 MGy for the analysis of pristine Ryugu samples.

Given the micro- to sub-micrometer scale of the samples, achieving higher spatial resolution is critical for accurate analysis. However, finer spatial resolution necessitates an increase in the radiation dose. Figure 4 illustrates the relationship between radiation dose and spatial resolution, revealing that the spatial resolution limit for this analytical configuration is approximately 50 nm, corresponding to an acceptable dose of 101 MGy.

As previously reported [e.g., 3–6, 16], the complex diversity of carbon and nitrogen functional groups observed in the Ryugu and Winchcombe samples may reflect their pristine, unaltered, and uncontaminated nature. Consequently, obtaining precise and reliable characterizations of the organic matter is essential. To minimize the risk of spectral artifacts—particularly when analyzing highly pristine extraterrestrial organic materials—it is crucial to optimize the STXM analytical parameters, including spatial resolution, pixel acquisition time, and photon flux.

References: [1] Cody G. D. et al. (2008) *Planet. Sci. Lett.,* 272, 446–455. [2] Sandford S. A. et al. (2006) *Science,* 314, 1720–1724. [3] Ito M. et al. (2022) *Nat Astron.*, 6, 1163–1171. [4] Yabuta H. et al. (2022) *Science,* 379, eabn9057. [5] De Gregorio B. et al. (2024) *Nat Commun.*, 15, 7488. [6] Changela H.G. et al. (2024) *Nat Commun.*, 15, 6165. [7] Nittler L. et al. (2024) EPSL 637, 118719. [8] Kebukawa Y. et al. (2023) *Meteor. Planet. Sci.*, 59, 1845–1858. [9] Quirico E. et al. (2023) *Meteor. Planet. Sci.*, 59, 1907–1924. [10] Komatsu M. et al. (2024) *Meteor. Planet. Sci.*, 59, 2166–2185. [11] Yesiltas M. et al. (2024) *JGR-Planet*, 129, 4. [12] Ohigashi T. et al. (2024) *XRM2024* abstract. [13] Ito M. et al. (2020) *Earth Planets Space*, 72, 133. [14] Ohigashi T. et al. (2023) *J. Electron Spectrosc. Relat. Phenom.,* 266 (147356). [15] Wang J. et al. (2009) *J. Electron Spectrosc. Relat. Phenom.*, 170 (25). [16] Vollmer C. et al. (2024) *Nat Commun.*, 15, 778.