Application of X-Ray Microscopy

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A synchrotron-based scanning transmission X-ray microscope (STXM) is a technique to perform 2-dimensional (2-D) X-ray absorption spectroscopy with high spatial resolution up to 30 nm. By noticing the X-ray absorption edge of the specific element, 2-D chemical state of a sample can be obtained. Since characteristics of UVSOR is suitable for using extreme ultra-violet and soft X-ray region, the STXM in UVSOR is suitable to analyze soft materials and organic materials. The unique features of STXM, such as high transmittance of X-ray and relatively wide working distance, gain flexibility of the sample and its environment. Therefore, we have been developing special observation/analytical techniques mainly by designing sample cells for STXM. Especially, nowadays, an in-situ/operando analysis is attracting more attentions of researchers because that is an important technique to understand intrinsic state of the samples. For example, heating and cooling of the sample, humidity control system and electrochemistry, 2-D orientation of molecules, 3-D chemical state mapping, a sample transfer system without exposing to air and microscopic analysis of chemical state of lithium have been developed to explore a new filed of science. These techniques are difficult to perform by using the other microscopic techniques.

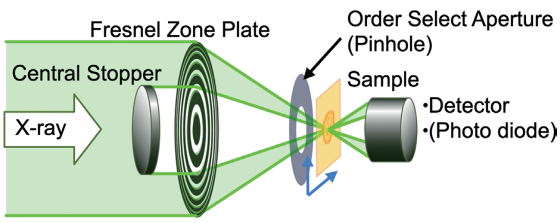

Figure 1. Schematic optical system of STXM.

Selected Publications

- T. Ohigashi, M. Nagasaka, T. Horigome, N. Kosugi, S. M. Rosendahl and A. P. Hitchcock, "Development of In-Situ Sample Cells for Scanning Tranmission X-Ray Microscopy," *AIP Conf. Proc*. **1741**, 050002 (2016).
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- T. Ohigashi, H. Yuzawa and N. Kosugi, "A Low-Pass Filtering Fresnel Zone Plate for Soft X-Ray Microscopic Analysis down to the Lithium K-Edge Region," *Rev. Sci. Instrum.* **91**, 103110 (2020).
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- J.-J. V. Véles, Y.-Y. Chin, M.-H. Tsai, O. J. Burton, R. Wang, S. Hofmann, W.-H. Hsu, T. Ohigashi, W.-F. Pong and C.-H. Chuang, "Evidence of Synergistic Elecrocatalysis at a Cobalt Oxide-Graphene Interface through Nanochemical Mapping of Scanning Transmission X-Ray Microscopy," *Chin. J. Phys.* **76**, 135–144 (2022).

1. Analysis of Organic Materials in Returned Samples from the Asteroid *Ryugu* by STXM

In 2014, a small spacecraft Hayabusa2 was launched to an asteroid 1999 JU3, named Ryugu, 280,000,000 km away from the earth. Hayabusa2 accumulates 5.4 g of pebbles and sands from surface (stored in a chamber A) and subsurface (in a chamber C) of Ryugu and the sample chambers came back to the earth in the end of 2020.[1)] Compared to ordinally meteorites, those samples from Ryugu are expected to retain pristine information of the asteroid since they did not suffer from heating by the atmosphere and contamination by terrestrial materials. Moreover, the samples in the chamber C are likely to have less space weathering than those of the chamber A. Therefore, the samples in the chamber C could be one of the standards of nature of extraterrestrial material. Our team, Phase2 curation Kochi team (collaborative team among JAXA, JAMSTEC, NIPR, SPring-8 and IMS), has developed “a linkage analytical system” to analyze the sample by using various apparatus, such as synchrotron-based X-ray diffraction (XRD), computed tomography (CT), focused-ion-beam (FIB) process, transmission electron microscopy (TEM), NanoSIMS and STXM, without exposing to the air through whole process and a protocol for analysis with minimum destructive process and damages.[2)] Ryugu is primarily considered as a carbonaceous asteroid so that abundant of organic material is expected. Main concerns of Phase2 Kochi team are water and organic materials. Therefore, the STXM at BL4U in UVSOR is a promising tool to analyze localized organic materials with high spatial resolution around 30 nm. In BL4U, a sample transfer system, a special sample cell, an FIB grid (namely Kochi grid), and a container to transfer between facilities, which enable to transfer the sample from a glovebox to a main chamber of the STXM without exposing to air, have been developed for the analysis of the Ryugu samples.

First of all, 3-dimensional structure and crystallography of a grain C0068 in the chamber C were confirmed by CT and XRD in SPring-8 to determine a region of interest (ROI) without any destructive process. The ROI was roughly cut out by using a diamond saw and was finished as an ultra-thin section sample by using FIB process in JAMSTEC as dimension of 25×25×0.1 (thick) μm^3 on the Kochi-grid.[2)] That ultra-thin section sample is used for high spatial resolution analyses by TEM, NanoSIMS and STXM. The procedures including the sample preparation, measurement and transportation between research institutes were performed under grade 1 nitrogen gas condition.

Figure 2(a) shows representative NEXAFS spectra of aromatic (C=C)-rich (plotted in red), C–H bonding-rich regions (green), matrix (blue) of the sample C0068,25 and Murchison meteorite (gray) around C K-edge. From this comparison, the peak at 287.5 eV, assigned as C–H bonding including aliphatic, is remarkable feature of the Ryugu samples. Their distributions are depicted in Figure 2(c) as RGB-color composite mapping. In regard to the distributions, the aromatic-rich region (shown in red) is less than the other components. Figure 2(b) shows spatial distribution of carbon-related materials. Then, the dark area has no (or much less) carbon-related component. Detailed analyses of dashed line squares in Figures 2(b) and 2(c) were performed by using TEM (shown in Figures 2(d) and 2(e)). The corresponding dark spot areas are confirmed as pyrrhotite and pentlandite. A large nanoglobule is consisted of amorphous silicate as a core and aromatic-rich organic materials around that.

Further analysis of the Ryugu samples is in progress. As one of the topics, we notice a potential relationship between space weathering and evolution of organic materials.

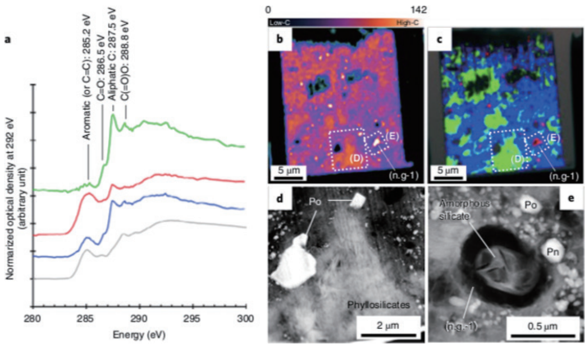

Figure 2.[3)] (a) NEXAFS spectra around C K-edge normalized to 292 eV of aromatic (C=C)-rich regions (red), C–H bonding-rich regions (green) and matrix (blue). The grey line is a spectrum of Murchison insoluble organic matter. (b) An STXM image dominated by carbon. (c) An RGB mapping with aromatic-rich (C=C) areas (red), C–H bonding-rich areas (green) and matrix (blue). (d) C–H bonding-rich organics concentrated in coarse-grained phyllosilicates in an area enlarged from the white dashed boxes in (b) and (c). (e) A large nanoglobule extracted from the dashed white boxes in (b) and (c) where Po and Pn are pyrrhotite and pentlandite, respectively.

References

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