### **Materials Science**

#### **High-energy X-ray Scattering and** X-ray Absorption Fine Structure (XAFS)

## Visualization of large cage-like network structure of glass and solvated electrons

Generally, glass is formed by melting a raw material to a melt (liquid) state at high temperature followed by cooling. Not all materials can be made into glass: many materials form crystals instead of glass when a melt is cooled. To understand the glass formation of materials, the research group focused on CaO-Al<sub>2</sub>O<sub>3</sub> systems that form or do not form glass depending on slight differences in the composition (material with a high glass-forming ability: 64 mol%CaO-36 mol%Al<sub>2</sub>O<sub>3</sub>; material with a low glass-forming ability: 50 mol%CaO-50 mol%Al<sub>2</sub>O<sub>3</sub>). To form glass using a material with a low glass-forming ability, the material was maintained as a melt without a container (containerless processing) and then rapidly cooled to form glass (Fig. 1). The atomic structures of the glasses were examined by high-energy X-ray scattering and X-ray absorption fine structure (XAFS) at SPring-8 (Fig. 2). The data were analyzed by large-scale theoretical calculations using a supercomputer to determine the atomic and electronic structures of the glasses. The results indicate that a large"cage-like network structure" (Fig. 3) forms in the materials with a high glass-forming ability. In contrast, such a structure does not exist in the materials with a low glass-forming ability. Researchers have recently reported that electride glass can be formed by solvated electrons through the removal of oxygen in a reducing atmosphere. The solvated electrons are located in the cage-like network structure and were found to lead to an energetically stable a stable glass structure by the large-scale theoretical calculation.

Fig. 1 Oxide melt levitated at high temperature (by courtesy of Atsunobu Masuno, The University

of Tokyo



Fig. 2 Results of (a) high-energy X-ray scattering and (b) XAFS at Ca K absorption edge (blue and red dots) shown with the results of large-scale theoretical calculation (black lines)



mol%Al<sub>2</sub>O<sub>3</sub> material with a high glass-forming ability

BL01B1, BL04B2

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**Materials Science** 

X-ray Diffraction of Ultrathin-Film Structure

### Successful fabrication and structural determination of crystal-oriented nanofilm of porous coordination polymer

Porous coordination polymers (PCPs) are material groups that exhibit high gas adsorption/separation properties and high regularity (crystallinity) and have various functions, such as high-efficiency separation and concentration of gas molecules and specific reactions inside the pores. Therefore, integrating PCPs with different functionalities enables the fabrication of various energy-related devices, such as highly efficient fuel cells. To develop such devices, multiple PCP nanofilm should be grown in the same direction (i.e., oriented growth) so that the different PCPs can be closely integrated. Thus far, however, the fabrication of crystal-oriented nanofilm has been successful only for two-dimensional PCPs. A technology for realizing the oriented growth of three-dimensionally rigid PCP crystals has long been demanded for increasing the functional diversity, the device durability, and the adhesion between different PCPs during integration.

In this study, a crystal-oriented nanofilm of three-dimensionally rigid PCP has been successfully fabricated by appropriately selecting a metal substrate suitable for oriented growth, a surface processing method of the substrate, and building blocks that can be controlled in terms of the growth direction while maintaining their rigidity in three dimensions (Fig. 1). In addition, the reversible gas adsorption/desorption behavior was observed in this nanofilm, and this behavior does not involve any change of the skeletal structure, reflecting the rigidity of this nanofilm. The observation of the oriented growth of the nanofilm and its structural change during the gas adsorption/desorption process was achieved using high-brilliance X-rays and the measurement system installed on the BL13XU beamline of SPring-8, which enables precise diffraction experiments of surfaces and interfaces (Fig. 2).

The results of this study are the basis of fundamental technologies for fabricating new functional devices that integrate PCPs with different functionalities. The research and development of functional devices using nanocrystalline thin films will be greatly accelerated and various applications such as highly efficient fuel cells are expected.





Fig. 2 Synchrotron radiation X-ray diffraction profile of grown three-dimensionally oriented PCP nanocrystalline thin film

### Earth Science

**High Pressure** 

# Large Amount of Hydrogen Existing in Earth's Core Primitive Earth Contained About 50 Times as Much Water as Current Amount of Seawater —

It has been known for 70 years that large amounts of light elements (elements with a low atomic number) other than iron and nickel are contained in the metallic core at the center of the Earth. The density of the liquid core (outer core) is 8% smaller than that of liquid iron; this difference is called the density deficit. However, the core light element composition has been a great mystery of Earth science. We have been performing X-ray diffraction measurements under high pressure and high temperature, which simulate the conditions deep inside the Earth's interior using a device called a diamond-anvil cell (Fig. 1) at the high-pressure research beamline (BL10XU). Recently, we have found that most of water on the growing Earth was incorporated into the core as hydrogen when metallic iron moved toward the center of the Earth to form the core (Fig. 2). This observation suggests that hydrogen is the main light element Fig. 1 High-pressure generating device in the core. An amount of water at least equal to the amount of seawater on using diamond anvils. A high pressure is the Earth's surface exists in the rock of the mantle of the present Earth. applied to a sample using two diamond tips. Considering that the amount of water not incorporated into metals is A high temperature is achieved by irradiating approximately twice the amount of seawater, the core should contain the sample with a laser. The state of the 0.3-0.6 wt% of hydrogen. Such amount of hydrogen would account for minute sample under high pressure and high temperature can be analyzed by X-ray 30-60% of the density deficit of the outer core. It is also likely that a large diffraction measurements amount of water has been incorporated as hydrogen in the core of not only the Earth but any terrestrial (rocky) planet having a mass exceeding 10% of the Earth, such as Mars. The large amount of hydrogen in the Earth's core Impactor 🔘 must originally have existed as water, the amount of which is equivalent to Fig. 2 Process of metallic core formation 40-70 times the current amount of seawater. It is considered that such a during Earth accretion. The Earth at that time was covered with a magma ocean. large amount of water was brought from outside of the solar system (from Magma The metals contained in the substances the current asteroid belt or further outside) during the growth of the primitive (impactors) newly accumulated on the Earth. Organic substances must also have been brought to the Earth with Solid Earth fell like raindrops through the magma water. Studies are being carried out to find the location on the Earth of the mantle ocean while moving toward the center of carbon in these organic substances. the Earth. The water contained in the Metallic magma was incorporated into the metals core BL10XU Kei Hirose (The University of Tokyo) as hydrogen.

**Planetary Science** 

Micro-CT

## Formation and Evolution of Carbonaceous Asteroid Ryugu: **Evidence Obtained by CT Imaging of Returned Samples**

Samples of the carbonaceous asteroid Ryugu were brought to Earth by the asteroid exploration spacecraft Hayabusa2 in December 2020. As part of the initial analysis of the returned samples, we investigated the formation and evolution process of the asteroid Ryugu by performing a multiscale, non-destructive, three-dimensional analysis that combined different X-ray computed tomography (CT) techniques available at SPring-8. The returned samples were black particles ranging 10 µm-8 mm in size (Fig. 1). The three dimensional images of the larger particles with a diameter of 100 µm or more and those of the particles smaller than 100 µm were obtained using the X-ray CT system at BL20XU and BL47XU, respectively. At BL20XU, the volume of the samples was accurately determined by CT imaging with a spatial resolution of 1 µm or less. The density of the samples was determined from the mass measured using an electronic balance (Fig. 1). These analyses were performed without exposure to air to avoid the contamination of the samples. The mean density of the samples was 1.79 ± 0.08 g/cm<sup>3</sup>, which is considerably higher than the density of the entire asteroid Ryugu (1.19 g/cm<sup>3</sup>). This result indicates that the asteroid Ryugu contains pores accounting for at least 30% of its total volume. Consistent with this finding, Ryugu is an asteroid having a rubble-pile structure, namely, one formed by the accumulation of masses of rock generated by the collisional destruction of the parent body.

At BL47XU, CT imaging with a spatial resolution of ~100 nm was performed using two modes, imaging absorption-contrast CT and phase-contrast scanning-imaging CT, to investigate the three-dimensional spatial distribution of the substances composing the samples. We discovered fluid inclusion confined in a hexagonal iron sulfide crystal (Fig. 2). This fluid once existed on the parent body of Ryugu. When subjected to cryo time-of-flight scanning ion mass spectrometry (cryo-TOF-SIMS) analysis, the fluid was found to be carbonated and to contain salt and organic substances. This result suggests that the parent body of Ryugu formed in the low-temperature region of the solar system beyond Jupiter's orbit. The outcomes of this study provide important clues about how and where in the solar system carbonaceous asteroids formed, evolved, and were destroyed to achieve their present form.

BL20XU, BL47XU Megumi Matsumoto (Tohoku University), Akira Tsuchiyama (Ritsumeikan University), Masayuki Uesugi (JASRI) Article: T. Nakamura et al., Science 379, eabn8671 (2023). DOI: 10.1126 / science.abn8671

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BL13XU

#### X-ray Diffraction (XRD) under High Temperature and





Fig. 1 Optical microscopic image and CT slice image of C0002 particle (third-largest particle collected by Havabusa2)



Fig. 2 CT image of carbonated liquid water that fills hole in hexagonal tabular crystal (iron sulfide)