Long-term Proposal Report 1
Energy scanning X-ray diffraction study of extraterrestrial materials using synchrotron radiation

Project Leader: Michael Zolensky[1]
Other Team members: Kazumasa Ohsumi[2], Takashi Mikouchi[3], Kenji Hagiya[4], Naoto Yagi[2], Yasuko Terada[2], Mutsumi Komatsu[5]

[1]NASA Johnson Space Center, Houston, USA
[2]Japan Synchrotron Radiation Research Institute (JASRI)/SPring-8, Hyogo, Japan
[3]School of Science, The University of Tokyo, Tokyo, Japan
[4]Graduate School of Life Science, University of Hyogo, Hyogo, Japan
[5]Waseda Institute for Advanced Study, Tokyo, Japan

Introduction

In order to understand the birth and evolution of the solar system, it is essential to analyze extraterrestrial materials such as meteorites, lunar samples, Stardust mission comet Wild-2 dust and Hayabusa mission asteroid Itokawa samples. Because many of these samples were formed under extreme conditions quite different from the present earth, they often contain minerals rarely found on the earth. However, these extraterrestrial samples are usually available only in small quantities, which makes it difficult to fully characterize these rare minerals. Recently, analysis of extraterrestrial materials is mainly focused on chemical characteristics such as chemical and isotope compositions, and unfortunately, crystallographic data of these extraterrestrial materials are missing in most cases. This is mainly because these rare minerals are small and it is difficult to obtain diffraction data. However, the crystal structures of such rare and small minerals record critical information about their formation conditions in the early solar system because they are often present as several polymorphs formed at certain pressure vs. temperature conditions, and they require characterization at the highest possible resolution. We achieved many of the originally proposed goals, and were able to add new subtasks when important new meteorites became available. We were able to measure the crystal lattice parameters of several Hayabusa mission grains.

X-ray Diffraction at SPring-8

We have been working for the past three years on synchrotron radiation X-ray diffraction (SXRD) studies at SPring-8 beamline 37XU (Proposal No. 2011A0035-2013B0035), employing a micro-beam diameter as small as 1 μm at SPring-8. SXRD is useful when combined with other analytical techniques such as synchrotron X-ray fluorescence (SXRF) and synchrotron based X-ray computed microtomography (SXRCT) determining chemical compositions and physical properties at the nano scale. We use a stationary sample method and polychromatic X-rays because the irradiated area of the sample is always the same and fixed, meaning that all diffraction spots occur from the same area of the sample. In beam line 37XU an undulator is installed and its radiation is further monochromatized using a Si(111) double-crystal monochromator. The X-ray energy is automatically adjusted by changing the undulator gap and the angle of a monochromator. A Kirkpatrick and Baez mirror is situated upstream of the sample giving a beam size of 0.7(V) x 2(H) mm^2 at the sample position. Diffraction patterns are collected on the two-dimensional detector (CMOS Flat panel detector, Hamamatsu Photonics K.K.). The samples are attached to an XYZ-stage, and the target micro area in the sample was adjusted on the micro-beam position under an optical microscope. We applied energies from 30.00 to 20.00 keV (l = 0.4133 - 0.6199 Å) at increments of 40 eV with each exposure time being 0.5 seconds. The instrument parameters were calculated from the coordinates on the Debye-Scherrer rings in the diffraction pattern of Si powder (NIST 640c) taken at 30 keV and the values were used for further analysis[1, 2]. We used 72 eight hour shifts over the three year period 2009 - 2013.

Sutter's Mill Meteorite

We made critical measurements of the crystal structures and cell parameters of secondary alteration minerals in the Sutter's Mill meteorite, a unique meteorite which contains xenolithic materials as will be materials collected by the OSIRIS-REx and Hayabusa 2 sample return missions. We showed that the Sutter's Mill meteorite is a regolith breccia of very reduced and very oxidized materials, a very surprising result[3, 4]. The most interesting result has been the identification of the mineral oldhamite (CaS) (Figure 1), which is found exclusively in the most reduced meteorites, whereas the bulk of the Sutter's Mill meteorite is very oxidized. This result indicates a mechanical mixing (though impacts) of oxidized and reduced asteroids early in solar system history.

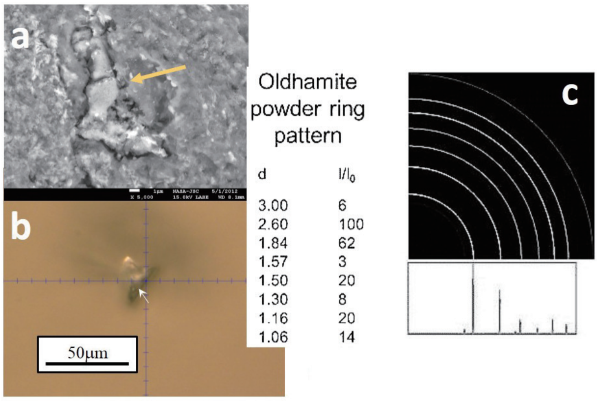

Figure 1. Oldhamite (CaS) in the Sutter's Mill meteorite. (a) Secondary electron image of oldahamite grain in situ. Scale bar measures 1 μm. (b) Optical image of separated oldhamite grain before XRD analysis. (c) Resultant powder XRD pattern, compared to calculated pattern for oldhamite.

Itokawa Samples

We made critical structural analyses of dust samples of asteroid Itokawa returned to Earth by the Hayabusa mission. We made SXRD crystal structure and unit cell measurements of analogous meteorites as standards. The degree of crystallite crystallinity significantly varies within individual grains, a hallmark of shock metamorphism (Figure 2), with diffraction spots which would normally be circular spots becoming smeared out and diffuse due to atomic disorder. These have been the first crystallographic analysis of loose asteroid regolith grains, and permit us for the first time to definitely link one class of meteorites (ordinary chondrites) to one class of asteroids (S class) and understand for the first time how regolith processes have modified the mineralogies of asteroid materials[5 - 9].

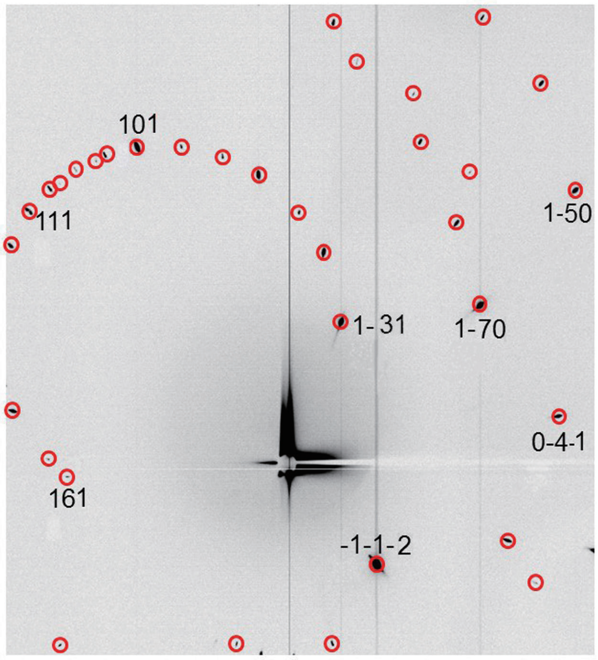

Figure 2. Laue pattern of Itokawa olivine obtained by superimposing 251 patterns taken with monochromatic X-rays between 20.00 - 30.00 keV. The resultant 34 diffraction spots of the olivine crystal are indicated by open circles. Some spots are also indicated with their indices. Non-circular diffraction spots reveal the degree of shock experienced by the olivine grain.

Early Lunar Impactors

We made critical mineralogical identifications of surviving pieces of late impactors hitting the Moon, as a text of models of the origin and early history of the terrestrial planets. These impactor fragments indicate primitive asteroids were common Earth-Moon crossing impactors during the latter stages of the basin-forming epoch, opening a new window into the collisional processes that shaped the Earth at the dawn of life[10].

Chelyabinsk Meteorite

We made analysis of the shock state of olivine in the Chelyabinsk meteorite, which fell in 2012, injuring more than 1,000 persons. Chelyabinsk turns out to be a moderately-shocked meteorite, but clearly records at least 3 separate shock events spanning 4.5 billion years[11]. Our work thus supports parallel investigations of the impact record of the asteroid belt.

Amoeboid Olivine Aggregates

We made preliminary crystallographic and structural analyses of amoeboid olivine aggregates (AOAs) in carbonaceous chondrites that are sensitive indicators of condensation conditions in the solar nebula and parent body alteration/metamorphic processes[12, 13].

Comet Wild-2 Grains

We made crystallographic measurements of olivine and pyroxene crystals which dominate the Comet Wild-2 samples returned to Earth by the Stardust mission[14]. We measured cell dimensions olivine in the coarse-grained terminal particles of Stardust aerogel tracks and a comprehensive dataset of analogous olivine grains (5 - 30 μm) isolated in chondrite matrix. The results have completely changed our understanding of the origin and evolution of the outer solar nebula.

Conclusions

The results of our varied analyses do not permit many final conclusions to be drawn, since most of these are for research that is still in progress. However we can conclude that SXRD is a very powerful, still underutilized tool in planetary science. For certain investigations, such as those we have presented here, SXRD is the only way to make progress, particularly since the technique is essentially nondestructive, preserving these tiny precious, and frequently unique samples for future investigations. We can also conclude that the Wild-2 and Itokawa samples were much more diverse than was expected, and that we should be prepared for similar surprises with every future sample return mission. Our investigation of the lunar samples demonstrated that even after more than 40 years of study those samples are not well understood, and also that with each new return of astromaterials we can expect to look again at previously collected samples and see new dimensions in the rocks. The work on Chelyabinsk points out a powerful reason to have active, long-term SPring-8 proposals, because this permitted us to quickly make the necessary measurements on this unexpected sample in the brief time before the sample interacted with the terrestrial atmosphere.

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