LOW ENERGY H^+ AND He^+ ION IRRADIATION EXPERIMENTS OF IRON SULFIDE. T. Matsumoto[1], Y. Nakauchi[2], A. Takigawa[3], A. Tsuchiyama[4,5], Y. Asada[6], M. Abe[2], N. Watanabe[7], D. Harries[8], and F. Langenhorst[8], [1]Faculty of Arts and Science, Kyushu University (matsumoto.toru.502@m.kyushu-u.ac.jp). [2]Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, [3]The Hakubi Center for Advanced Research, Kyoto University, [4]Research Organization of Science and Technology, Ritsumeikan University, [5]Gunazhou Institute of Geochemistry, [6]Division of Earth and Planetary Sciences, Kyoto University,[7]Institute of Low Temperature Science, Hokkaido University, [8]Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena.

Introduction: Space weathering refers to alteration of materials exposed to the space environments [e.g., 1]. Solar wind ions, 1 keV H^+ ions (95.41 %) and 4 keV He^{++} ions (4.57 %) [2], are one of main causes of space weathering as with micrometeorite bombardment [1]. Iron sulfides are common minerals in early solar system materials and are important solid reservoir of cosmically major elements, iron and sulfur. Remote-sensing observation of the surface of S-type asteroid 433 Eros revealed significant sulfur depletion compared to the composition of ordinary chondrites [e.g., 3], which is considered to be caused by space weathering. Besides the remote-sensing data, intensive space weathering of iron sulfide has been reported in regolith grains from S-type asteroid Itokawa [4]. Understanding of space weathering of iron sulfide is essential for evaluation of chemical composition and surface evolution of S- and C- complex asteroids. Prior ion irradiation experiments of iron sulfide with 4 keV He^+ and 5 keV Ga^+ suggested selective sulfur loss by sputtering of sulfur atoms [5, 6, 7]. In addition, structural change by MeV Kr^{++} irradiation has been reported [8]. On the other hand, little is known about alteration of iron sulfides irradiated by hydrogen ions with low-energy, which are the most major components of solar wind [2]. Here, we report ion irradiation experiments of 1 keV H^+ and 4 keV He^+ to pyrrhotite (Fe_7S_8) that is one of common sulfide minerals in primitive chondritic materials.

Experiments: We prepared rectangular wafers (3 mm x 5 mm x 0.5 mm) from a single crystal of natural pyrrhotite (Chihuahua, Mexico). The (001) surfaces of the pyrrhotite were mechanically polished until 0.25 μm roughness. Then, we performed the chemical polishing with colloidal silica to remove the damage layer of the surface. The low-energy ion irradiation equipment developed in ISAS/JAXA was used in the experiments. A target holder with samples was transferred in an ultra-high vacuum chamber. The polished pyrrhotite surfaces were irradiated with 1 keV H^+ with doses of 10^{16}, 10^{17}, $3x10^{17}$,and 10^{18} ions/cm^2. We performed 4 keV He^+ irradiation experiments with doses of 10^{16}, 10^{17}, and 10^{18} ions/cm^2. During the ion irradiation, the flux of H^+ ions and He^+ ions were kept at ~$3x10^{12}$ and ~$5\text{-}7x10^{13}$ ions/cm^2/sec, respectively. All experiments were carried out in room temperature. The surface structures of irradiated samples were observed with an FE-SEM (Hitachi SU6600) with the accelerating voltage of l-2 kV. We lifted out ultra-thin sections from pyrrhotite samples irradiated by H^+ or He^+ with 10^{17} ions/cm^2 using focused ion beam systems (FEI Quanta 200 3DS; Quanta 3D FEG). To protect the irradiated surface during FIB sectioning, the irradiated surfaces were covered with carbon. We then, coated the surface with an electron-beam-deposited Pt layer followed by a Ga ion-beam-deposited Pt layer. We observed the sections using field-emission transmission electron microscopes (FE-TEM; JEOL JEM 3200FSK, FEI Tecnai G^2 FEG).

Results: *H^+ irradiation*: No morphological change was observed on the irradiated pyrrhotite surface with dose of 10^{16} ions/cm^2. Blisters of below 100 nm in diameters were distributed on the surface of the pyrrhotite samples irradiated with dose of higher than 10^{17} ions/cm^2. We observed numerous vesicles beneath the surface with blisters within 10-20 nm in depth (Fig. 1). The vesicles often possess euhedral shapes (Fig. 2) and are elongated parallel to the c-plane of the pyrrhotite. Electron diffraction revealed that the pyrrhotite crystal used in this study consists predominantly of 4C pyrrhotite (Fig. 2). Selected area diffractions from the damaged rim showed slight rotation of spots from the basic NiAs structure. Fast-Fourier-Transforms (FFT) of high resolution TEM images of the damaged rim showed absence of 4C superlattice reflection spots. This suggests disordering of cations and cation vacant sites in the pyrrhotite. Increase of the Fe/S ratio in the damaged rim was detected by energy dispersive X-ray spectroscopy (EDX).

He^+ irradiation: No morphological change was observed on the irradiated pyrrhotite surface with dose of 10^{16} ions/cm^2. Blisters of below 250 nm in diameters were distributed on the surface of the pyrrhotite samples irradiated with dose of higher than 10^{17} ions/cm^2. Elongated vesicles appeared beneath the surface with blisters (Fig. 1). Widely expanded vesicles are located just beneath blisters at 30-40 nm in depth . Electron diffraction showed slight rotation

of diffraction spots of the basic NiAs structure and absence of 4C superlattice reflection spots as with samples irradiated by H^+ ions. Increase of the Fe/S ratio in the damaged rim was also detected.

Discussion: The depth of the vesicles in the pyrrhotite broadly match the peak concentration depth of 1 keV H^+ of 10-20 nm and 4 keV He^+ of 20-40 nm, calculated by SRIM software [9]. These depths suggest that vesicles developed through accumulation of implanted gases. The euhedral vesicles formed by H^+ irradiation could explain euhedral voids found in pyrrhotite of interplanetary dust particles [10].

Our study showed that pyrrhotite retained short-range NiAs structures by low energy ion irradiation, although their longer-range vacancy-ordered superstructures is disordered. The similar tendency was observed in iron sulfides irradiated by 1 MeV Kr^{++} irradiation [8]. The behavior of iron sulfides contrasts with silicate minerals, which become fully amorphous by keV to MeV ion irradiation [e.g., 8, 11]. The susceptibility of ion-beam-induced amorphization has been explained based on the thermal spike model [12, 13]. The concept of the model was that an ion impact could create a small disordered region equivalent to a melt. This region cools rapidly to form an amorphous, or crystallization begins when the local temperature falls below the melting point. Iron sulfides have non-quenchable behavior from melts [14] and have simple atomic arrangement compared to silicate minerals. Hence, thermal spike mechanism was adopted for interpretation of amorphization resistance of iron sulfide to 1 MeV ion irradiation [8]. The thermal spike model may account for the crystalline features of the damaged layers in pyrrhotite with low energy H^+ and He^+ irradiation. The decrease of Fe/S ratio might be caused by preferential sputtering of sulfur [5,6,7], suggesting that solar wind can contribute to sulfur depletion on asteroids. Nucleation of iron metals observed in previous irradiation experiments [6,7] and natural samples [4] were not clear in this study. Further investigation focusing on the difference of chemical composition of iron sulfides, temperature, ion flux, and crystallographic orientation will shed light on the variety of modification of iron sulfide by space weathering.

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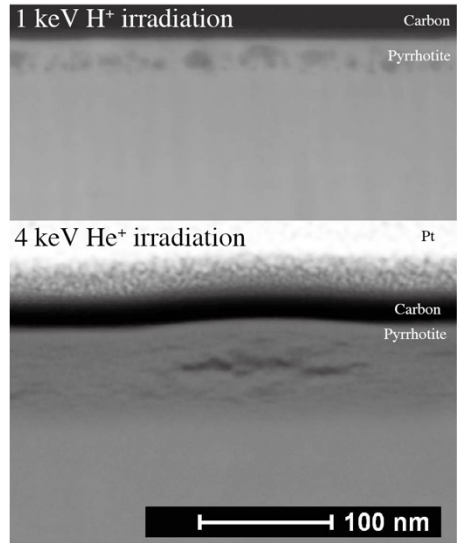

Fig. 1 Bright-field scanning transmission electron microscope images of pyrrhotite samples irradiated by H^+ (upper) and He^+ (lower) with $1x10^{17}$ ions/cm^2.

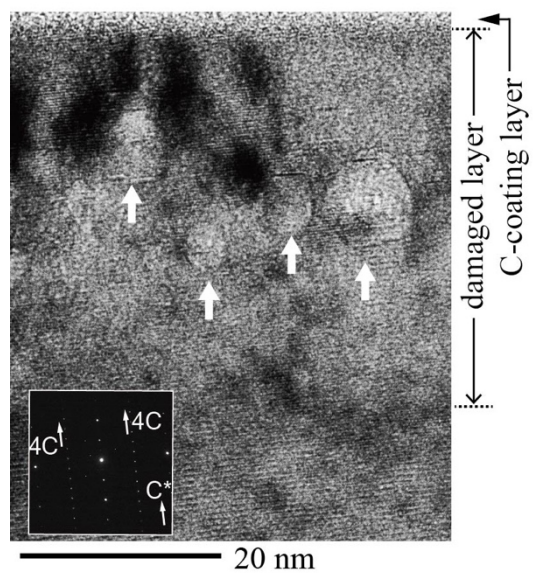

Fig.2. TEM bright field image of pyrrhotite surface irradiated by 1keV H^+ ions with $1x10^{17}$ ions/cm^2. Euhedral vesicles (arrowed) appear in the irradiation damaged layer. TEM selected area diffraction pattern from intact pyrrhotite in zone axis [100] is shown in the lower left. Pyrrhotite 4C superlattice reflections are marked.