Nitrization of magnetite on the surface of C-type asteroid Ryugu.

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Introductions: JAXA's Hayabusa2 spacecraft recovered samples from the C-type carbonaceous asteroid Ryugu [1]. The initial analysis of the Ryugu samples showed that they correspond to CI carbonaceous chondrite meteorites [2, 3]. Because the Ryugu samples were collected from the surface of Ryugu, they provide us with the first opportunity to understand phenomena occurring at the surface of the carbonaceous asteroid. Materials on airless bodies are gradually modified by exposure to solar wind and micrometeorite impacts. This process is called space weathering [4]. The evidence of space weathering has been found in Ryugu samples through the initial analysis. Dehydration of the phyllosilicate surface is the major modification by space weathering on Ryugu [5]. In addition, loss of volatile elements including hydrogen, carbon, oxygen, and sulfur have been identified in space-weathered anhydrous minerals [6]. In this study, we focused on the surface modifications of Ryugu samples related to nitrogen. It has been suggested that the nitrogen isotopes in Ryugu samples are affected by surface processes [7]. Thus far, there is no mineralogical observation related to the behavior of nitrogen on Ryugu's surface. The goal of this study is to understand how nitrogen is involved in the chemical evolution of regolith on Ryugu. Here, we describe nitrogen concentration on the surfaces of space-weathered magnetites in Ryugu samples.

Methods: We investigated three fine Ryugu grains, A104-021012, A104-028098, and A104-026006. These three grains were preserved in a glove-box filled with purified nitrogen gas. The grains are attached on gold plates using epoxy resin, and were observed by scanning electron microscopy (SEM) to analyze their surface morphologies. After the surface observation, electron-transparent sections were extracted from the grain surface using a focused ion beam system. The extracted sections were observed by scanning transmission electron microscopy (TEM/STEM). We applied 4D-STEM imaging (electron diffraction mapping using nano-beam) to identify nanometer-sized inclusions.

Results: FIB sections from A104-021012 and A104-028098 include assemblages of framboidal magnetites with 0.5 to 1 μm in diameter. An FIB section from A104-026006 contains a spherulitic magnetite with 10 μm in diameter. These magnetite grains are embedded in the fine-grained matrix composed mainly of phyllosilicates. Their exposed surfaces show porous textures that suggest surface modifications. STEM-EDS analysis showed that magnetites in A104-0210012 have the uppermost layers showing high Fe/O ratio. Electron diffraction patterns corresponding to body-centered cubic (bcc) iron were obtained from the iron-rich layer. Magnetite grains in A104-026006 and A104-028098 also have iron-rich layers at the surface. In addition, the iron-rich layers are also rich in sulfur and nitrogen (Fig.1). Electron diffraction patterns from the iron-rich layer in A104-026006 indicate the appearance of bcc-iron metal and troilite. Additionally, we obtained electron diffraction patterns showing a cubic crystal that has the lattice parameter corresponding to roaldite (Fe_4N). Thin coatings of silicon and magnesium were identified on the modified magnetites in A104-021012, A104-028098, and A104-026006.

Discussion: The increase of Fe/O ratio and the formation of iron metals at the magnetite surface is likely due to selective loss of oxygen from magnetite caused by solar wind implantation and micrometeorite bombardments [6]. Because sulfur and nitrogen are not included in bulk magnetite, these elements would have been supplied to the exposed surfaces of magnetite. Impact vapors produced from carbonaceous chondrite likely have high sulfur fugacity enough to form iron sulfides [8]. Therefore, the sulfur enrichment and troilite formation at the magnetite surface in Ryugu samples may have been caused by sulfization of iron metals, when the space-weathered magnetite is exposed to vapors formed by micro-impacts. Iron nitrides have been identified in carbonaceous chondrites as the products formed by gas-metal interaction in the NH_3-rich nebular gas [9], and in iron meteorites as metamorphic products under high pressure [10]. In contrast, iron nitrides we observed are likely associated with space weathering of magnetite and may have been formed thorough surface processes on Ryugu. One possible mechanism for the concentration of nitrogen is implantation of solar wind nitrogen as suggested in lunar regolith samples from the Moon [11]. Another possible mechanism is the chemical reaction between space-weathered magnetites and nitrogen compounds included in impact vapors on Ryugu. Because iron metal is highly reactive with ammonia gas that leads to the formation of iron nitrides [12], nitrization of iron metals on space weathered magnetites may have occurred when the surfaces are exposed to ammonia-beaning gases. Ammonia may be included in impact vapors from CI chondrite materials [13]. In addition. ammonia-rich vapors can be produced from nitrogen-rich organic materials, and/or ammonium compounds, such as NH_4^+ salts and NH_4^+ phyllosilicates, that could be supplied to the Ryugu's surface as interplanetary dust. Our observation will shed light on the migration of nitrogen and/or influx of nitrogen on the carbonaceous asteroid.

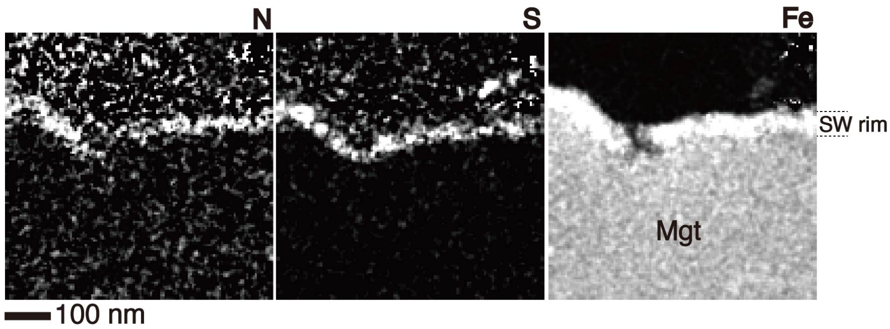

Figure 1. Elemental maps of magnetite surface (A104-026006) obtained by STEM-EDS analysis. Left, center, and right figures show the distributions of nitrogen, sulfur, and iron, respectively. SW-rim indicates the space-weathered rim enriched in iron, sulfur, and nitrogen. Mgt indicates magnetite.

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