The terrestrial weathering processes of Ryugu grains

M. Miyahara[1], T. Noguchi[2], T. Matsumoto[2], N. Tomioka[3], A. Miyake[2], Y. Igami[2], Y. Seto[4],
[1]*Hiroshima Univ., Japan*; [2]*Kyoto Univ., Japan;* [3]*JAMSTEC, Japan;* [4]*Osaka Metropolitan Univ., Japan*

Introduction: The Hayabusa2 analysis teams show that the Ryugu grains consist mainly of a matrix: saponite and serpentine along with small amounts of magnetite, iron sulfides, carbonates, and phosphates (Nakamura et al., 2023; Noguchi et al., 2024). The mineralogical and geochemical characteristics of the Ryugu grains are most similar to the CI chondrites (Ito et al., 2022; Nakamura et al., 2023; Yokoyama et al., 2023). CI chondrites are the most difficult to recover on earth as meteorites due to their friability. After falling to earth, the fragments are affected by terrestial weathering (reactions between a rock and air/water) and gradually lose the original characteristics of CI chondrites. An Antarctic meteorite may be less affected by terrestrial weathering because the meteorites were stored in an ice field after the fall. However, based on terrestrial ages by cosmogenic radionuclides, the average residence time of Antarctic meteorites is about 10^5 years (Nishiizumi et al., 1989). A reaction between terrestrial water/ice and meteorites would continue even in an Antarctic ice field (Bland et al., 2006), so it is difficult to clarify intrinsic aqueous alteration that occurred on a parent body using only meteorites.

How the terrestrial weathering of CI chondrites proceeds should be clarified to understand the intrinsic aqueous alteration that occurred in C-type asteroids. However, we cannot clarify the terrestrial weathering process only by artificial alteration experiments on CI chondrites, because as mentioned above, most meteorites have spent a long time in terrestrial conditions after the fall. We propose to clarify the early stage terrestrial weathering process of CI chondrites by using the Ryugu grains. In this research project, Ryugu grains will be exposed to the atmosphere for a long time, and changes in the surface of the grains will be repeatedly observed by FEG-SEM. In the final stage, cross-sectional observations near their surfaces will be made with a TEM to clarify how the initial stages of terrestrial weathering of CI chondrites proceed.

Sample histories and experimental methods: The sample plate C0105-042_000_00 (hereinafter referred to as C0105-042), which was once analyzed by the Hayabusa2 Initial Analysis "Sand" team and reassigned by the approval of the 2nd AO, was used for this research. Ryugu small grains on C0105-042 were observed by secondary electron (SE) imaging (at a low accelerating voltage of 3.0–5.0 kV) to investigate the surface morphology using a FEG-SEM. The first and second FEG-SEM observations were performed without any coating. After the second observation (26 days after the arrival of the sample to the "Sand" team), Ryugu small grains on C0105-042 were coated with carbon after osmium. After the third observation (149 days after the arrival of the sample to "Sand" team), the C0105-042 plate was returned once to JAXA following the completion of the initial analysis group's activities. C0105-042 had been stored in a vacuum desiccator except for the FEG-SEM observations.

The fourth observation (497 days after the first arrival of the sample to the "Sand" team) was performed immediately after the realocation of C0105-042. After the fourth observation, C0105-042 was exposed to the atmosphere in a special desiccator installed in a clean room. The temperature and humidity in the desiccator were maintained at approximately 20–23°C and 30–40%. After the beginning of the atmospheric exposure, the fifth and sixth FEG-SEM observations were performed 104 and 245 days later, respectively. After the sixth observation, C0105-042 was placed in a vacuum desiccator to complete the atmospheric exposure experiment. After being coated with osmium and carbon to prevent Ga-ion damage to the grain surface, several portions of the Ryugu small grains were excavated by an FIB device and processed into TEM ultrathin films to study their terrestrial weathering processes.

Results and discussion: FEG-SEM observations of C0105-042 immediately after the reallocation by JAXA show that the morphology of the grain surface had changed significantly, even though the sample had been stored in a nitrogen-filled desiccator. In some of the grains where cracks had observed at the initial analysis period, the width of the cracks was even larger, and some of the grains were broken into smaller pieces. Numerous fine-grained precipitates about 100 nm or less in size were formed on the surface of Mg-Fe phyllosilicates, magnetite, dolomite, and pyrrhotite. Mycelial-like precipitates less than about 500 nm in length were formed in the spaces between the magnetite particles. Amoeboid precipitates covered the surface of iron sulfide particles. As the exposure time of the Ryugu grains to the atmosphere increased, some of the Ryugu small grains that had developed wide cracks fell out completely. The Ryugu small grains have been completely covered with fine-grained precipitates layers and the size has become coarser (>200–300 nm). All pyrrhotite particles were completely covered with amoeboid precipitates. Therefore, it is difficult to observe their original outlines.

TEM images show that fine-grained precipitate layers covering the entire Ryugu grains consist of amorphous or poorly crystallized materials. Based on the EDS spectra, the precipitates are mainly composed of carbon and oxygen with a small amount of silicon and magnesium. The average thickness of the precipitate layers is approximately 100 nm. Evidence of alteration was observed in the pyrrhotite particles near the Ryugu grain surface, although not exposed on the surface: i.e., the edges of the pyrrhotite particles are depleted in sulfur. Sulfur released from pyrrhotite has not been confirmed around the particles. The volume fraction of the altered portion increases as the pyrrhotite particle size decreases. For a pyrrhotite particle with a diameter of about 30 nm, the volume fraction of the altered portion is 70% or more. Around the altered pyrrhotite particles, froth-like textures are observed in carbonaceous materials. The amoeboid precipitates on a pyrrhotite single crystal are amorphous or poorly crystallized materials depleted in iron along with sulfur compared to the original pyrrhotite. EDS analyses clarified that the amoeboid precipitates are oxidized or hydrated. The average thickness of the amoeboid precipitate layer is about 450 nm.

Under oxic acidic conditions, pyrrhotite can dissolve rapidly and generate Fe^{2+} and H_2S, although the dissolution rate decreases under neutral and alkaline conditions (Belzile et al., 2004). The absence of sulfur (S_0) and sulfate (SO_4^{2-}) around the altered pyrrhotite particles may support the generation of H_2S by the dissolution reaction under oxic conditions. Froth-like texture,

which are present in the carbonaceous materials around the altered pyrrhotite particles, may indicate degassing of CO_2 due to the reaction between H_2S and the carbonaceous materials. The alteration rate was calculated using a pyrrhotite single crystal completely exposed to air, given the time of exposure to air and the thickness of the alteration layer. The estimated alteration rate is about 2 nm/day. This alteration rate is upper limit because a small amount of amoeboid precipitate was present on the surface prior to the exposure experiment.

The estimated formation rate of fine-grained precipitate layers covering the entire Ryugu grains is about 0.5 nm/day. The origin of the fine-grained precipitate layers is not clear at this time. There are two possible scenarios to explain the origin. In scenario 1, the dissolved intrinsic carbonaceous material are reprecipitated on the grain surface. Carbonaceous materials around pyrrhotite particles are dissolved by H_2S. The dissolved carbonaceous materials may migrate and precipitate on the surface of the Ryugu grains. In scenario 2, extrinsic carbonaceous materials are precipitated on the surface of the Ryugu grains. Epoxy resin used to adhere the Ryugu grains to an Au plate or unknown materials including carbon, probably from a decicator, may cause contamination.

Current exposure experiments show that the terrestrial weathering of the Ryugu grains has proceeded from the surface to the interior, but their detailed chemical reactions are not clear. Imae et al. (2024) also conducted the terrestrial weathering experiments on Ryugu grains and reported that small-sized euhedral Ca-sulphate particles on the surface. Such alteration products has not been found in our exposure experiments. Further investigations, such as the speciation of sulfur and iron, are needed to clarify the terrestrial weathering processes of Ryugu grains.

References

Belzile et al. (2004) A review on pyrrhotite oxidation. *Journal of Geochemical Exploration* **84**, 65–76.

Bland et al. (2006) Weathering of chondritic meteorites. University of Arizona Press, Arizona. pp. 942.

Imae et al. (2024) Mineralogical approach on laboratory weathering of uncontaminated Ryugu particles: Comparison with Orgueil and perspective for storage and analysis. *Meteoritics & Planetary Science* **59**, 1705–1722.

Ito et al. (2022) A pristine record of outer solar system materials from asteroid Ryugu's returned sample. *Nature Astronomy* **6**, 1163–1171.

Nakamura et al (2023) Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples. *Science* **379**, eabn8671.

Nishiizumi et al. (1989) Update on terrestrial ages of Antarctic meteorites. *Earth and Planetary Science Letters* **93**, 299–313.

Noguchi et al. (2024) Mineralogy and petrology of fine-grained samples recovered from the asteroid (162173) Ryugu. *Meteoritics & Planetary Science* **59**, 1877–1906.

Yokoyama et al. (2023) Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites. *Science* **379**, eabn7850.