
Introduction: The Hayabusa2 spacecraft successfully brought back Earth materials from the Apollo, C-type asteroid Ryugu in December 2020. The returned samples include Ryugu's surface and subsurface particles collected by the first touchdown (TD) (Chamber A particles) and the second TD in the vicinity of the SCI artificial impact crater (Chamber C particles), respectively [1,2]. After cataloging and preliminary analysis at the JAXA curation facility [2], eight particles up to 4.1 mm in size were allocated to the Phase2 curation Kochi team for in-depth investigations [3]. The aim of the present study is to clarify the mineralogy of the Ryugu particles by transmission electron microscopy (TEM) for comparison to known carbonaceous chondrites which are thought to be derived from similar parent bodies. This investigation is part of the integrated Phase2 Kochi studies that also include bulk mineralogy and petrology, high precision O isotopic compositions, and SIMS analyses of anhydrous minerals and carbonates [3–7].

Experimental Methods: Approximately 150 to 200 nm-thick sections were extracted from 3 Ryugu particles (A0002, A0037, C0068) using a Hitachi SMI4050 FIB. After deposition of tungsten protection layers, regions-of-interest (up to 25 × 25 µm²) were cut out and thinned using a Ga⁺ ion beam at 30 kV and then finalized at 5 kV and probe current of 40 pA to minimize surface ion-damage layers. Subsequently, the ultrathin sections were mounted on scaled-up Cu grids (Kochi grid [8]) using a micromanipulator attached to the FIB. The sections were studied using a TEM (JEOL JEM-ARM200F) operated at 200 kV. Chemical analyses in TEM were performed using EDS with a 100 mm² SDD. For quantitative analyses, the intensities of the characteristic X-rays of each element were measured using a fixed acquisition time of 30 s, beam scan area of 0.01–0.02 µm², and beam current of ~50 pA in STEM mode. A natural pyrope-almandine garnet and pentlandite were used as standard materials for silicate and Fe-sulfide analyses, respectively.

Results: The Ryugu particles observed by TEM in the present study consist mainly of randomly oriented packets of phyllosilicate layers embedding Fe-sulfides and Fe-oxide grains. Coarse-grained (typically >30 nm in width of packet) phyllosilicate occurs as aggregates with feathery textures embedded in a fine-grained (<30 nm in width) phyllosilicate matrix. An HRTEM image and selected-area electron diffraction (SAED) patterns clarified that the phyllosilicates are intergrown serpentine and saponite with interlayer spacings of 0.7 nm and 1.1 nm, respectively (Fig. 1). Some fine-grained matrix phyllosilicates are poorly crystalline showing diffraction rings with d-spacing of 0.45, 0.25, and 0.15 nm. The coarse- and fine-grained phyllosilicates in the particles A0037 and C0068 have a similar chemical composition with the Mg/(Mg+Fe) ratio of 0.84±0.03 (Fig. 2). The composition is consistent with those of coarse-grained phyllosilicates in the Orgueil CI chondrite [9]. None of the observed Ryugu ultrathin-sections show any features attributable to moderate to strong shock metamorphism, such as breakdown/melting of phyllosilicates, previously reported in experimentally shocked hydrated carbonaceous chondrites [10,11].

Pyrrhotite is the second most abundant mineral after phyllosilicates. It generally occurs as euhedral grains up to 6 µm in size throughout the phyllosilicate matrix. SAED patterns of the pyrrhotite grains show the 4C structure. The 6C structure, which was previously reported in Orgueil [12], has yet to be found so far in our samples. Magnetite occurs as aggregates of spherical grains (<3 µm in size) corresponding to "framboids" in CI chondrites. Pentlandite occurs as smaller grains (<0.8 µm in size) than pyrrhotite and magnetite. It should be noted that Fe-sulfide grains occurring as plaque-like aggregates, the morphology that was previously reported in magnetite in the CI chondrites [13] and the Tagish Lake carbonaceous chondrite [14], were found in a section of A0002 (Fig. 3). Ferrihydrite, which was previously reported in Orgueil by TEM [9], is totally absent. Dolomite was found only in the particle A0002. Minor amounts of manganocromite and sphalerite were also found. Carbon nanoglobules (<0.7 µm in size) occur as hollow and solid-types in all the sections. A graphite grain (0.3 µm in size) with a 13C-rich isotopic composition [3] was discovered in a section of particle C0068.
Discussion: Compared to hydrated carbonaceous chondrites, the overall mineralogy of the Ryugu particles is the most of CI chondrites. Phyllosilicates, dolomite, and framboidal magnetite suggest that the Ryugu surface/subsurface materials have suffered extensive aqueous alteration. Given that magnetite plaquettes have only been found in hydrated chondrites [13,14], the presence of Fe-sulfide plaquettes in the Ryugu particles would also be evidence for prior hydrothermal processing. Recently, a pyrrhotite-group mineral smithite occurring as stacking-plate morphologies was reported in terrestrial sedimentary rocks [15]. This also supports the proposition that Fe-sulfide plaquettes in the Ryugu particles also formed at relatively low temperatures in the presence of water. The absence of ferrihydrite in the Ryugu particles, which were transported and analyzed with minimal air exposure, suggests that the presence of this mineral in Orgueil represents a terrestrial weathering product, formed after its fall to Earth.

Based on the fact that Ryugu is a rubble pile asteroid and the boulders on its surface are highly disrupted [1], one might expect that the returned Ryugu materials would display evidence of extensive impact processing. However, in all the particles examined, phyllosilicates show no evidence for dehydration and breakdown textures due to shock heating. This observation suggests that the heating temperature did not exceed ~500 °C, corresponding to the breakdown temperature of Mg-Fe-serpentine [16]. If the shock impedance of the Ryugu materials is assumed to be similar to those of CM chondrites, the upper bound of shock pressure for the Ryugu materials is ~2.5 GPa, based on numerical model calculations [17]. The present results suggest that a high-velocity impact capable of strongly modifying the mineralogy of the Ryugu particles did not take place. Further detailed characterizations of shock effects by multiscale, high-resolution TEM and SEM are currently ongoing.