An artificial laboratory alteration of the Ryugu samples: Comparison with the Orgueil CI chondrite and implication to the long durational sample storage

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Introduction: It has been revealed that the returned sample from the C-type asteroid Ryugu by Hayabusa2 corresponds to the CI chondrites (e.g., Ito et al., 2022; Nakamura T. et al., 2022). These grains have escaped from the Earth's atmospheric reaction at most, and the handling of the Ryugu particles in Phase 1 (Ph1) at JAXA and Phase 2 Kochi (Ph2K) curation was carried out in the glove boxes for Ryugu particles in purified nitrogen gas or vacuum under the condition of nearly entirely unexposed for terrestrial air. Initial investigation by the Ph2K team has focused on the unexposed air for the handling, sample transportation and analyses (Ito et al., 2022; Liu et al., 2022; Greenwood et al., 2022) avoiding potential affect to analytical results.

CIs have been known only in five worldwide *falls* and have not been recovered as *finds* at all. It has been recently reported that it occurs only from one micrometeorite (Dobrica et al., 2022). The limited numbers of CI meteorites and CI-like micrometeorites may be responsible to their susceptible nature on the Earth. The Orgueil CI chondrite can be more susceptible to terrestrial weathering than those of the other meteorites, and a significant amount of gypsum has rapidly formed after the fall (Gounelle and Zolensky, 2001).

In the present study, we examined the effects of the interaction of small Ryugu particles less than 0.5 mm with terrestrial air, that is, an artificial laboratory alteration under a controlled environment of humidity and temperature. We compared the results with that of the Orgueil CI chondrite as well as the Ryugu particles before laboratory alteration. The terrestrial alteration behavior of Ryugu particles is important for a clarification toward a direct linkage with Orgueil. It is also important for considering the long durational storage of the extraterrestrial materials, primarily reactive extraterrestrial materials on the Earth, such as the CI chondrites.

Experimental conditions: C0087 (~1 mg powder) and A0029 plus A0037 (~1 mg powder) were stored in a valve-opened desiccator in an air-conditioned laboratory room at NIPR and in a vacuumed desiccator by a diaphragm rotary pump at the Antarctic meteorite storage room, respectively, for more than five months after the initial X-ray diffraction measurements using Cu Kα (XRD; Rigaku SmartLab) (Ito et al. 2022). C0087 in a valve-opened desiccator was kept under the conditions of typical temperatures of 21–24 ºC and humidity of ~30% in January to February and 26–29ºC and 55–40% in March to June. A0029 plus A0037 in a vacuum desiccator was kept under the conditions of 22 ºC and ~50% (or less). XRD was used to find any detectable weathering products for these samples. XRD analytical conditions were described in Ito et al. (2022). We used a field emission scanning electron microscope (FE-SEM; JEOL JSM-7100F) with an energy dispersive X-ray spectrometer (EDS; Oxford AZtecEnergy X-Max^{N} 50) to search for micrometer-scale weathering products on their surface with the analytical conditions of 15 kV and ~1 nA with carbon coating. Grain surfaces of C0087 and A0029 plus A0037 for several grains (~0.1–0.3 mm in size) were placed on a carbon nanotube or a carbon adhesive tape. A polished section of C0087 grains was then observed.

Results: XRD: Main constituent mineral phases of the Ryugu grains are saponite, serpentine, magnetite, dolomite, and pyrrhotite (Ito et al., 2022). No significant changes were observed from initial XRD patterns, however, a very subtle peak appears at 2θ = ~12º (*d*-spacing of ~0.7 nm) (Fig. 1).

FE-SEM-EDS: Many tiny Ca-S oxides, 500 nm to 1 µm, have been identified on the peripheries of polished section of C0087 (Fig. 2) but not from A0029 plus A0037, since the EDS spectra of the grains commonly showed the peaks of calcium, sulfur, and oxygen. The observed Ca-S oxide occurs as isolate grains only on the grain surface (Fig. 2).

Discussion: A slightly increased peak at 2θ = ~12º from XRD may reflect the increased crystallinity of serpentine and/or saponite for C0087 and A0029 plus A0037 (Fig. 1). The presence of abundantly observed Ca-S oxide grains on the surface for C0087 under the FE-SEM may suggest that it is an alteration product in the laboratory. The most plausible candidate for the Ca-S oxide phase could be gypsum. Further investigations (ultra-high magnification observations and their crystallography) of these phases by a transmission electron microscopy will be carried out. Nakamura T. et al. (2022) reported the small gypsum on calcite surface implying the alteration product on either Ryugu or the Earth. However, the occurrence quite differs from the present observation in C0087, which also suggest that the gypsum plausibly originated from the laboratory alteration. Sulfur-bearing species are mainly pyrrhotite in the Ryugu particles. Ca-bearing species are mainly dolomite, and a minor occurrence of apatite. Pyrrhotite and dolomite might have joined the terrestrial alteration as be observed from Orgueil. However, the alteration features from pyrrhotite and dolomite have not been clearly identified yet from Ryugu's artificial alteration products. The reaction mechanism to form gypsum on the grain surface is also not still clarified but could be due to fluid mobilizations of Ca and S ionswith H_2O derived from the air to form gypsum on the grain surface from the occurrence. On the other hand, Orgueil shows that finer grains and rims of euhedral coarser grains of pyrrhotites as well as dolomites have been altered, and significant gypsum has been observed on the surface of Orgueil (Fig. 2).

Summary: The degree of alterations of the Ryugu particles in the laboratory conditions was not severer than those of Orgueil (Fig. 2). This may be partly because of the limited periods and laboratory conditions for alteration.

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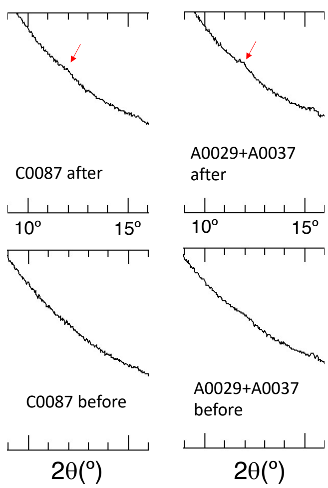

Figure 1. XRD pattern of 2θ = ~12º.

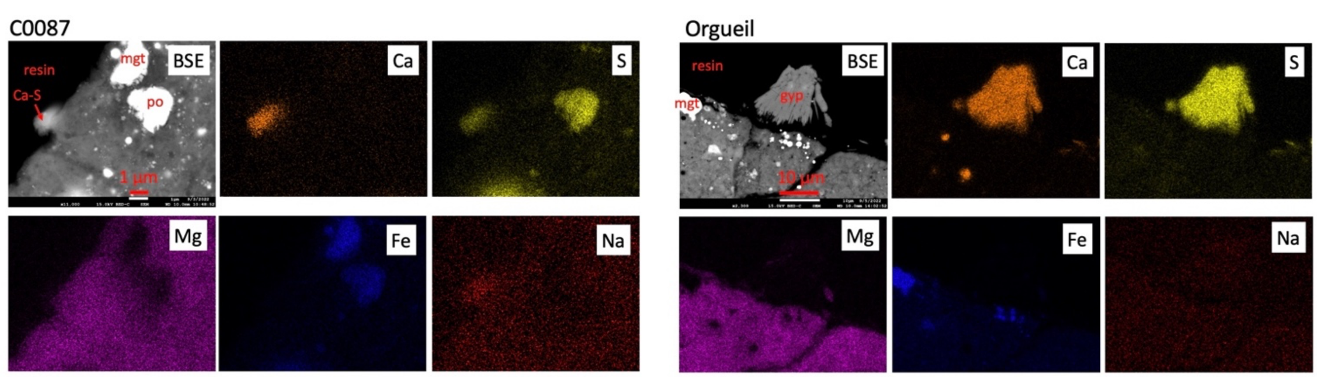

Figure 2. Back scattered electron (BSE) images and the elemental maps of Ca, S, Mg, Fe, and Na of a texture bearing the Ca-S oxide phase in C0087 and a texture bearing the gypsum in the Orgueil chondrite, which is shown as a red circle, respectively. Also note that minor Na is included for Ca-S oxide in C0087, but not for gypsum in Orgueil. mgt = magnetite. Ca-S = Ca-S oxide. po = pyrrhotite. gyp = gypsum. Gypsum in Orgueil was identified from µRaman and XRD.