Why is the asteroid Ryugu darker than CI chondrites?
- Consideration based on heating experiments of CI chondrites

Seima Ishida[1], Tomoki Nakamura[1], Megumi Matsumoto[1], Kana Amano[2], Takahiro Kawai[3], Shohei Yamashita[4] and Yoshio Takahashi[3]

[1]*Department of Earth Science, Tohoku University, Sendai 980-8578, Japan.* [2]*Institute of Mineralogy, Physics of Materials and Cosmochemistry, National Museum of Natural History, 75005 Paris, France.* [3]*Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan..* [4]*Photon Factory, Institute of Materials Structure Science, High-Energy Accelerator Research Organization, Tsukuba 305-0801, Japan.*

Introduction: Ryugu samples are chemically and mineralogically similar to CI chondrites[1][2]. On the other hand, there are significant differences between the reflectance spectra of Ryugu samples and CI chondrites, while those of Ryugu samples are similar to those of the CI chondrite samples heated at 300℃ under reducing conditions[3]. The previous study performed heating experiments of Orgueil CI chondrite and compared the spectrum of Orgueil heated at 150℃ for 3 hours in an N_2 atmosphere (preheated Orgueil), and those of Orgueil heated at 300℃ for 50 hours and 100 hours under reducing conditions, and those of the Ryugu samples (Fig. 1)[3]. Fig. 1 shows that the spectrum of Orgueil heated shortly at 150℃ differs significantly from those of the Ryugu samples, while those of Orgueil heated at 300℃ under reducing conditions are quite similar to those of the Ryugu samples, with becoming darker especially at the visible–near-infrared (Vis-NIR) wavelengths. The possible causes responsible for the spectral differences between the 150℃-heated Orgueil sample and the Ryugu samples are the formation of bright hydrous sulfates and/or the oxidation of Fe^{2+} to Fe^{3+} in phyllosilicate-rich matrix in Orgueil by terrestrial weathering[3]. However, it is not yet identified the cause of the spectral differences. Therefore, this study aims to understand what chemical and mineralogical changes occur in Orgueil samples during experimental heating at 300℃ under reducing conditions and to identify the actual causes of spectral differences between Orgueil and Ryugu samples. We conducted heating experiments of Orgueil samples at 100℃ and 300℃ under reducing conditions, at 100°C and 300°C in air (oxidizing conditions). All samples were examined using FE-SEM, FE-TEM, FT-IR, XRD, and STXM to characterize mineralogical and chemical changes by the experimental heating.

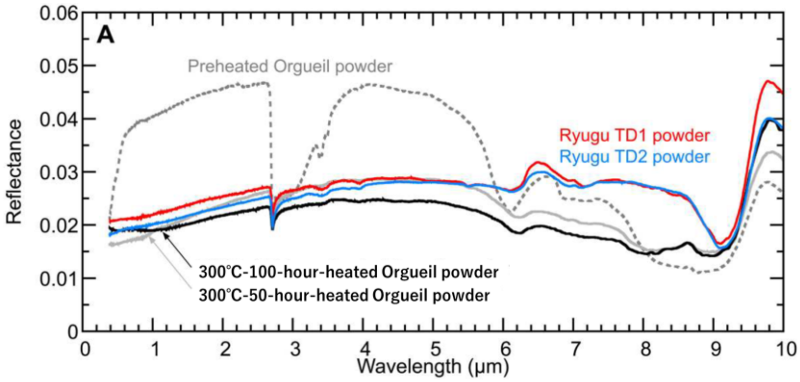

Fig. 1. Spectral comparison between Ryugu samples and Orgueil. There are reflectance spectra of powder samples of Ryugu, preheated Orgueil and 300°C-heated Orgueil under reducing conditions (Modified Fig. 5A in [3]).

Results and Discussion: Fig. 2 shows the spectra of unheated Orgueil and those of heated Orgueil. First, regarding the heating under reducing conditions (Fig. 2A), the spectra of Ryugu samples[1] were not reproduced by Orgueil heated at 100℃ under reducing conditions (Orgueil 100℃ re) but were reproduced by Orgueil heated at 300℃ under reducing conditions (Orgueil 300℃ re), and this result is consistent with the previous study[3]. Here we discuss possible causes of the spectral changes based on FE-SEM, FE-TEM, XRD, and STXM analyses. We found that the following changes occur in the Orgueil samples heated at 300℃ under reducing conditions: dehydration of sulfates, alteration of ferrihydrite, alteration of organic matter, and an increase in submicron-scale pores. Smectite, a major component of Orgueil, becomes brighter at the Vis-NIR wavelengths with an increase in submicron-scale pores[4][5]. Therefore, the increase in submicron-scale pores in Orgueil is not likely the reason why Orgueil becomes much darker by heating at 300℃ under reducing conditions. Synchrotron STXM (PF BL-19A) analysis showed that $Fe^{2+}/\Sigma Fe$ ratios of phyllosilicates in the unheated and 300℃-heated Orgueil samples are similar, suggesting that no reduction of Fe^{3+} took place during heating. This suggests that Fe valence in Orgueil phyllosilicates is not likely the cause responsible for the darkening of Orgueil spectra.

Second, regarding the heating under oxidizing conditions (Fig. 2B), the spectrum of Orgueil heated at 100°C under oxidizing conditions (Orgueil 100℃ ox) is a little brighter than that of unheated Orgueil (Orgueil unh ox) from 0.38 to 2.7 μm in wavelength. The spectrum of Orgueil heated at 300℃ under oxidizing conditions (Orgueil 300℃ ox) becomes much brighter from 0.38 to 6.0 μm in wavelength. Currently, we cannot identify the reason why the spectra of Orgueil heated under oxidizing conditions became brighter, but it is clear that the "masking effect" caused by dark organics and/or other dark material becomes weaker by heating under oxidizing conditions. It is known that adding a small amount of carbon black to white phyllosilicate montmorillonite results in a large darkening of the spectrum and reduction of the absorption strength at the Vis-NIR wavelengths (see also Fig. S9 in [3], originally from RELAB Spectral Database), which is called the "masking effect". The weakening of the masking effects is supported by the fact that the spectrum of Orgueil heated at 300°C under oxidizing conditions has a deeper peak at ~2.0 µm due to phyllosilicates than that of unheated Orgueil.

We performed reheating under reducing conditions of the Orgueil samples once heated under oxidizing conditions: the Orgueil samples that had been heated at 300°C under oxidizing conditions were heated again at 300°C under reducing conditions (Orgueil 300℃ oxre). Such heating under reducing conditions darkened Orgueil spectra once again and reproduced the spectra of the Ryugu samples (Fig. 2B). We found that the brightness change is reversible and the material responsible keeps staying in Orgueil during heating and just changes the brightness by some structural or chemical changes. The above results suggest that there are originally dark materials in CI chondrites that change their brightness significantly by heating at 300°C under oxidizing and reducing conditions.

Candidates responsible are sulfates, ferrihydrite, and organic matter, but we cannot identify which is a major component for the observed spectral change. We will continue detailed observation and analysis of the heated Orgueil samples to determine which process among dehydration of sulfates, alteration of ferrihydrite, and alteration of organic matter is mainly responsible for the spectral differences between the unheated and heated Orgueil and also between the unheated Orgueil and Ryugu samples.

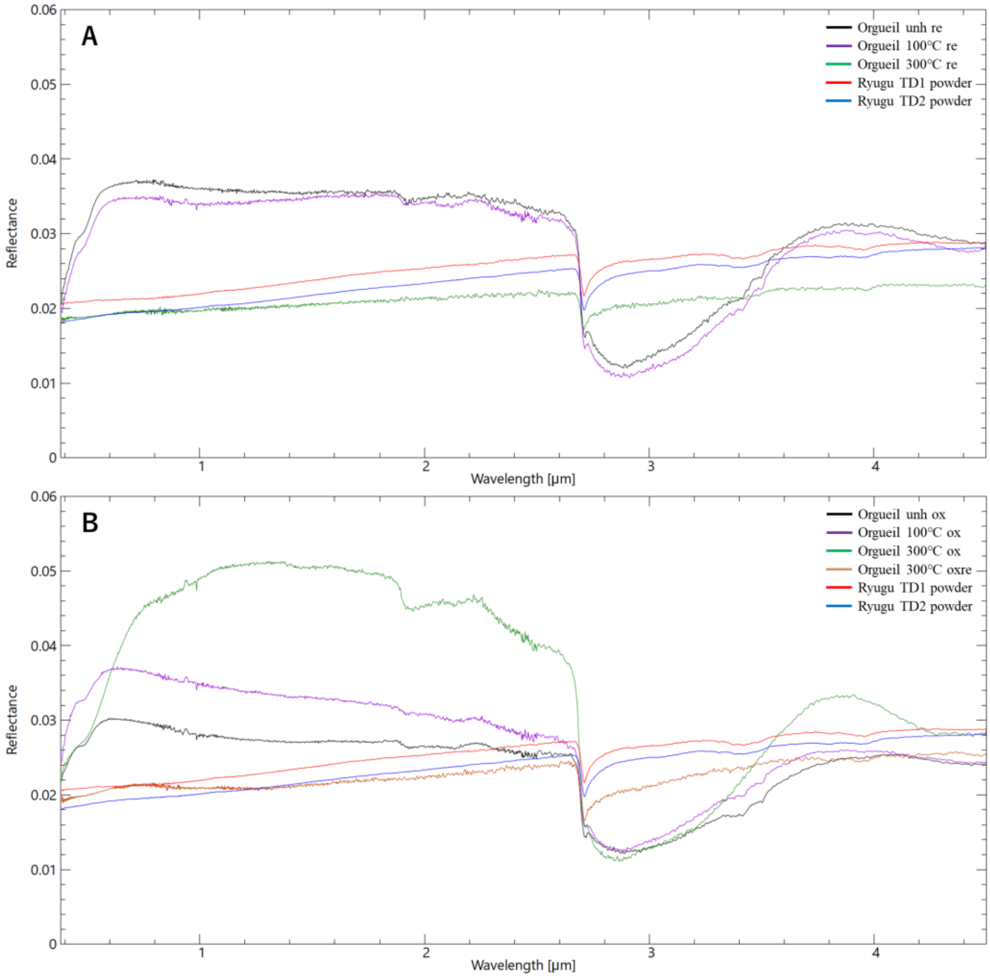

Fig. 2. (A) Reflectance spectra of the Ryugu samples, unheated Orgueil (Orgueil unh re) and Orgueil heated under reducing conditions (Orgueil 100℃ re and Orgueil 300℃ re). (B) Reflectance spectra of the Ryugu samples, unheated Orgueil (Orgueil unh ox), Orgueil heated under oxidizing conditions (Orgueil 100℃ ox and Orgueil 300℃ ox) and Orgueil reheated at 300℃ under reducing conditions after the heating at 300℃ under oxidizing conditions.

References

[1] Nakamura et al. (2023) Science, **379**, eabn8671. [2] Yokoyama et al. (2023) Science, **379**, eabn7850. [3] Amano et al. (2023) *Sci. Adv.* **9**, eadi3789. [4] Sultana et al. (2021) Icarus, **357**, 114141. [5] Poch et al. (2016) Icarus, **267**, 154–173.