Formation processes of spherulitic magnetite in the Ryugu samples

E. Dobrică[1], H. A. Ishii[1], J. P. Bradley[1], K. Ohtaki[1], T. Noguchi[2,3], T. Matsumoto[4], A. J. Brearley[5], the Min-Pet Fine Sub-team and the Hayabusa2 initial analysis core
[1]*Hawai'i Institute of Geophysics & Planetology, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA (dobrica@hawaii.edu),* [2]*Division of Earth & Planetary Science, Kyoto University, Kyoto, Japan,* [3]*Department of Geology and Mineralogy, Kyushu University, Kyoto, Japan,* [4]*Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan,* [5]*Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM.*

Introduction: Samples returned from the carbonaceous asteroid 162173 Ryugu by the JAXA Hayabusa2 mission allow us to investigate primitive materials of our Solar System and their evolution [1-2]. Recent studies have shown that the Ryugu samples are composed of minerals similar to those of CI (Ivuna-like) carbonaceous chondrites indicating that the parent planetesimal from which Ryugu was derived experienced severe aqueous alteration [e.g., 1-2]. Our previous study described that magnetite in the Ryugu samples from chamber A occurs as framboids, plaquettes, spherulitic, and irregularly shaped grains [3-5]. They are products of alteration, and their formation is controlled by variation in the diffusion and growth rates during aqueous alteration on the parent body [4]. In this new study, we focus on spherulitic magnetite grains in the Ryugu from chamber C to understand the evolution of the aqueous alteration processes on the carbonaceous (C-type) asteroids [4].

Samples and Methods: Multiple spherulitic magnetite grains were identified embedded in the fine-grained materials returned by the Hayabusa2 spacecraft collected during both touchdowns (chambers A and C). Figure 1 shows the spherulitic magnetite (~13 μm in diameter) analyzed in this study and collected during the second landing operation (chamber C, C0105-039024). The grain is associated with fine-grained phyllosilicates, euhedral sulfides, and framboidal magnetites Fig. 1). We prepared one FIB section for electron microscopy studies using the Helios 660 dual-beam focused ion beam SEM (FIB-SEM) instrument at the University of Hawai'i at Mānoa and examined the section by transmission electron microscopy (TEM) using the JEOL NEOARM 200CF at the University of New Mexico.

Results: The spherulitic magnetite has an internal texture composed of individual radiating fibers varying in length from 5 μm to 8 μm. The fibers radiate from a spherical pore (Fig. 1, ~130 nm in diameter) located off-center. The widths of the fibers vary in size from 70 nm to 140 nm. The spherulitic magnetites are characterized by high porosity, with randomly distributed pores ranging from a few nanometers up to 2.2 μm in size; however, the magnetites with other morphologies (e.g., framboidal magnetite) are free of pores. Most pores are euhedral to subhedral in shape, located inside the fibers or at their boundaries. Additionally, we identified an amorphous rim (80- 350 nm in thickness) composed of 5 wt % Si, 4 wt% S, 2 wt% P, and 13 wt% C around the magnetite grain.

Discussion: Ryugu samples have been shown to a CI chondrite that exhibit some notable differences from CI meteorites [6-7]. One of the major similarities in Ryugu asteroid to CI chondrites is the presence of magnetites with different morphologies. Magnetite with a variety of morphologies has been studied for almost sixty years in one of the rarest groups of meteorites, the CI chondrites (only 9 meteorites belong to this group), and more recently in the unique, ungrouped Tagish Lake meteorite [8-9]. Our TEM observations further expand on the implications of magnetite formation in the Ryugu samples that show some difference to known CI chondrites [6-7]. The observations presented in this study show the presence of magnetite with different morphologies coexisting in close proximity.

Spherulites are common in terrestrial and extraterrestrial materials [8, 10-11]. They have been identified in a wide range of materials such as metals, alloys, polymers, oxides, liquid crystals, and various biological molecules. However, so far there is no generally accepted theory of spherulite crystallization mechanisms. The most important prerequisite for spherulitic growth is high crystallization driving forces, typical from a supersaturated or supercooled solution [11]. Furthermore, spherulites are ubiquitous in solids formed under highly nonequilibrium conditions [10, 12]. Systems that are in equilibrium tend to grow crystals with simple morphologies unless they are forced out of equilibrium by imposing a change in the environmental conditions [12]. Therefore, crystals can form complex spatial patterns in response to a disturbance from equilibrium that might induced kinetically driven growth to lower the free energy of the system. Though there are other factors that can influence the morphologies of crystals. For example, the presence of organic compounds can play a major role influencing growth of crystals by inhibiting growth on some crystal surfaces and favoring one morphology over another [6]. Similarly, it is also possible that certain anions or cations in solution can change the growth mechanism and change the morphology (Wark et al. 2008).

Previous studies of spherulites in meteorites suggested that this particular structure requires crystallization from a colloidal Fe hydroxide gel-like material [8]. Studies of terrestrial spherulite show that a viscous medium (i.e., gel) is not always necessary for spherulitic growth; however, impurities encourage spherulite formation [11]. The conditions necessary for the spherulite precipitation must maintain the growth rates (G) of the crystal itself higher than diffusion rates (D, G >> D) [8, 13]. Any changes related to variation in D/G ratio could generate crystals with different morphologies [13]. Therefore, the presence of magnetite with varying crystal morphologies in the returned samples suggests a variable range of crystal growth and diffusion rates in the Ryugu parent body. Petrographic observations suggested that magnetites with a spherulitic morphology are the one of the first minerals to crystallize from an aqueous fluid on the Ryugu parent body [14]. More precisely, the crystallization sequence of magnetite as a function of their morphologies is: spherulitic – plaquette/framboidal – equant/elongated [14]. This previous study indicated that the conditions during magnetite precipitation changed from high to low supersaturations [14], which supports our observations that the first magnetites that formed, the spherulitic crystals, precipitated from a highly supersaturated fluid that evolved in the degree of saturation. Our TEM study further expands on these results suggesting that at the beginning of the crystallization sequence, when the spherulitic magnetite formed, the fluid could have been under nonequilibrium conditions. These processes lead to polycrystalline growth structures imposed by the reach of the solution of a supersaturated state where nucleation is able to occur, resulting in the adjustment to a lower free energy condition. Furthermore, as the previous petrographic observations suggested [14], and the presence of numerous fragile, euhedral laths at the surfaces of these spherulitic magnetites, suggest that these crystals precipitated first in an unrestricted, high porous material.

Two important implications arise from the study of spherulitic magnetite. First, these crystals could potentially offer a unique opportunity to study the early aqueous fluids that circulated through the Ryugu parent body. No materials were identified in the unique pores identified in the spherulitic magnetite due to the sample preparation technique applied in this study; however, it is possible that these pores contain fluid inclusions prior to the FIB sample preparation. A second important implication that arises from the occurrence of spherulitic magnetite under nonequilibrium conditions is that a careful selection of the magnetite crystals is necessary for the use of the oxygen isotope fractionation between carbonates and magnetite to extract the temperature at which these minerals coprecipitated [15]. Since multiple generations of magnetite were identified in the Ryugu samples, the question is what type of magnetite forms in equilibrium with the carbonates, especially since dolomite and breunnerite formed after the formation of pentlandite, pyrrhotite, and apatite according to the crystallization sequence [14]. We suggest avoiding spherulitic magnetite for these measurement since the necessary assumption of equilibrium between minerals is not supported by our observations indicating rapid magnetite growth.

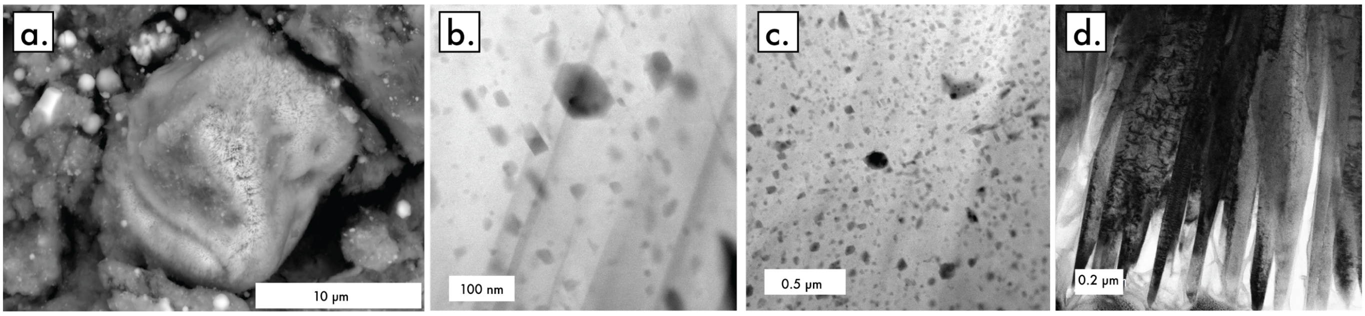

Figure 1. Backscattered electron (a), dark-field STEM (HAADF, b-c), and bright-field TEM images of the spherulitic magnetite analyzed in this study. The TEM data show the texture of the radiating fibers and the random distribution of euhedral to subhedral pores.

References

[1] Noguchi T. et al. (2022) 53rd LPSC, Abstract #1747. [2] Tachibana S. (2021) Sample Return Missions the Last Frontier of Solar System Exploration, Chapter 7, Elsevier, Editor Longobardo A., 147-162. [3] Alfing J. et al. (2019) Geochemistry, 79, 125532. [4] Dobrica E. et al. (2022) 53rd LPSC, Abstract #2188. [5] Lee M. R. et al. (2022) 53rd LPSC, Abstract #2203. [6] Nakamura T. et al. (2022), Science, doi 10.1126/science.abn8671. [7] Yokoyama T. et al. (2022) Science 10.1126/science.abn7850. [8] Kerridge J. F. (1979) Science 205, 395-397. [9] Kimura Y. et al. (2013) Nat. Comm. 4, 1-8. [10] Gránásy L. et al. (2005) Phys. Rev. E 72, 011605. [11] Shtukenberg A. G. et al. (2012) Chem. Rev., 112, 1805-1838. [12] Magill J. H. (2001) J. of Mater. Sci. 36, 3143-3164. [13] Lofgren G. (1974) Americ. J. Sci. 274, 243-273. [14] Tsuchiyama A. et al. (2022) 85th Annual Meeting of the Meteoritical Society, abstr. #6221. [15] Jilly-Rehak C. E. et al. (2018) Geochim. Cosmochim. Acta 222, 230-252.