RIM FORMATION OF BARRED OLIVINE CHONDRULES: CONDITION FOR RAPID CRYSTAL GROWTH ALONG DROPLET SURFACE. H. Miura, *Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Japan (miurah@m.tohoku.ac.jp)*, E. Yokoyama, *Gakushuin University, Japan*, K. Nagashima, *Osaka University, Japan*, K. Tsukamoto, *Tohoku University, Japan*.

INTRODUCTION: Chondrules are millimeter-sized, once-molten, spherical-shaped grains mainly composed of silicate materials. They have various types of internal textures; porphyritic, barred-olivine, radial pyroxene, and cryptocrystalline. Many authors have been carried out dynamic crystallization experiments to constrain the formation mechanism of each texture ([1] and references therein). Barred-olivine (BO) chondrules are characterized by parallel set(s) of olivine bars in a thin section. It has been considered that olivine bar crystals are actually platy in three-dimension [2]. A BO chondrule usually has an olivine crystal that covers the chondrule surface. This olivine rim has the same crystallographic orientation as inner olivine platelets, which connect to the rim. The textures similar to that of BO chondrule have been reproduced successfully in some experiments [3–5], however, the formation mechanism of the rim has not been understood yet.

Tsukamoto et al. carried out crystallization experiment of a forsterite melt droplet which cools very rapidly ($R_{\rm cool} \approx 100 - 1000\,{\rm K/s}$) by using aeroacoustic levitation system and *in situ* observation of the crystallization process [3,4]. They found that the droplet crystallized in a very short period of time (less than 1 sec) at temperature much lower than melting point by a few hundred kelvins or more. The internal texture showed rim and parallel bar structure in thin section. On the other hand, Tsuchiyama et al. also succeeded in reproducing textures similar to classic BO together with olivine rim by evaporation in vacuum [5]. The cooling rate was $R_{\rm cool} = 1000\,{\rm K/hr}$, which is much smaller than [3,4]. The supercooling at the time when the crystallization started was unknown because they did not conduct *in situ* observation. They considered that the rim was formed by the rapid crystal growth along the droplet surface, which should become cooler than the interior by the latent heat of the evaporation. However, their idea has not been tested enough.

To clarify the formation mechanism of the rim, we analytically derive the condition of the rapid crystal growth along the droplet surface as a function of the cooling rate $R_{\rm cool}$. The cooling rate determines the temperature difference between the center and surface of the droplet $\delta T_{\rm c-s}$. Here, we consider the energy exchange only at the droplet surface, and it does not matter what the cooling process is, *e.g.,* latent heat of evaporation, radiative cooling, and so forth. If $\delta T_{\rm c-s}$ is large enough, the crystal growth across the droplet center will be delayed, so the rapid crystal growth along the surface should occur. We compare the condition for rim formation derived in this paper with droplet crystallization experiments [3–5] and numerical simulations of crystallization of a supercooled melt droplet based on a phase-field method [6,7].

CONDITION OF RIM FORMATION: Let us consider a supercooled melt droplet, which solidifies from a nucleus at the surface (see Fig. 1). The condition for rim pattern formation

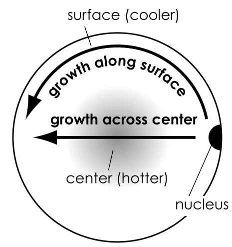

Figure 1: Possible crystal growth passes inside a supercooled melt droplet. Rapid growth along the surface is required for the rim pattern formation.

can be derived a competition of crystal growth between along the surface and across the center [6]. In the case across the center, the distance of the crystal growth pass becomes the shortest, however, the growth velocity at the center is smaller than at surface because the center is hotter than the surface due to some cooling process at the droplet surface. Therefore, the crystal growth along the surface takes a shorter time than across the center $\delta T_{\rm c-s}$ is large enough. The temperature difference is given by [6]

$$\delta T_{\rm c-s} = \frac{c_0 r_{\rm d}^2 R_{\rm cool}}{6\kappa_{\rm L}}, \quad (1)$$

where c_0 is the heat capacity per unit volume, $r_{\rm d}$ is the droplet radius, $R_{\rm cool}$ is the cooling rate of the droplet, and $\kappa_{\rm L}$ is the thermal conductivity of the melt droplet. The temperature distribution inside the droplet $T(r)$, where r is the distance from the droplet center, is given by

$$T(x) = T(0) - \delta T_{\rm c-s} x^2, \quad (2)$$

where $x \equiv r/r_{\rm d}$. The distribution of supercooling inside the droplet at the time when the solidification started, $\Delta T(r)$, is written as

$$\Delta T(r) = \Delta T_{\rm s} - \delta T_{\rm c-s}\left(1 - x^2\right), \quad (3)$$

where $\Delta T_{\rm s}$ is the supercooling at the droplet surface. Here, let us assume the growth velocity of the crystal being $V(\Delta T) \propto \Delta T^\beta$, where the index is $\beta \approx 2.5 - 3.5$ according to the dendrite growth theory [8,9]. The growth timescale[1] along the droplet surface $t_{\rm s}$ is calculated as

$$t_{\rm s} = \frac{\pi r_{\rm d}}{V(\Delta T_{\rm s})}, \quad (4)$$

where it should be noted that the growth velocity V is constant. On the other hand, the growth velocity across the droplet center

[1] The growth timescale is defined as the time for which the crystal grows from the nucleus to the opposite side (see Fig. 1).

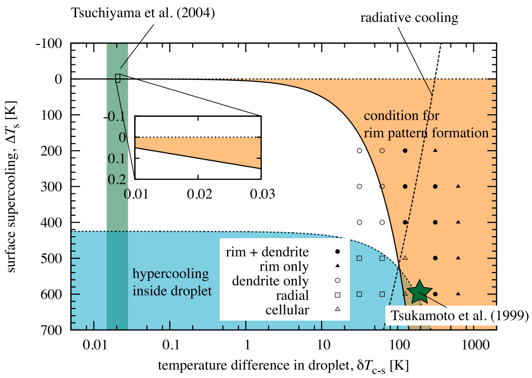

Figure 2: Condition for rim pattern formation (orange region). The horizontal axis $\delta T_{\mathrm{c-s}}$ is the temperature difference between the center and surface of the droplet, and the vertical axis ΔT_{s} is the supercooling at the droplet surface when the crystal growth started. A curve labeled by "radiative cooling" shows the estimated $\delta T_{\mathrm{c-s}}$ when the droplet cools by the radiative cooling. The blue region indicates the condition for the droplet being hypercooled everywhere the interior. The green star and belt are experimental conditions conducted by [3–5] (see text). Symbols show results of numerical simulations of crystal growth inside a supercooled melt droplet based on a phase-field method [6,7] (see text).

is not constant because of the temperature gradient inside the droplet (see Eqs. (2) and (3)). The growth timescale across the center t_{c} is given by the following integral form;

$$t_{\mathrm{c}} = 2 \int_0^{r_{\mathrm{d}}} \frac{dr}{V(\Delta T(r))}. \qquad (5)$$

The condition for the rapid crystal growth along the droplet surface is given by $t_{\mathrm{s}} < t_{\mathrm{c}}$, which is rewritten as

$$\alpha \equiv \frac{\delta T_{\mathrm{c-s}}}{\Delta T_{\mathrm{s}}} \gtrsim 0.2 \qquad (6)$$

after numerical integration of Eq. (5).

DISCUSSION: An orange region in Fig. 2 shows the condition for rim pattern formation (Eq. (6)). The horizontal axis $\delta T_{\mathrm{c-s}}$ is the temperature difference between the center and surface of the droplet, and the vertical axis ΔT_{s} is the supercooling at the droplet surface when the crystal growth started. When the temperature difference is as small as $\delta T_{\mathrm{c-s}} \approx 0.01$ K, the crystallization should start at low supercooling as $\Delta T_{\mathrm{s}} \lesssim 0.1$ K for the rim pattern formation. In contrast, when the crystallization takes place at larger supercooling as $\Delta T_{\mathrm{s}} \gtrsim 100$ K, the large temperature difference is required for the rim pattern formation, namely, the droplet should cool very rapidly.

We conducted numerical simulations of crystal growth inside a supercooled melt droplet based on a phase-field method [7] and compared with Eq. (6) on Fig. 2. Filled symbols corresponds to the calculation conditions at which the rim pattern was reproduced, and open symbols to not reproduced. It is found that almost all cases in which the rim pattern was reproduced are consistent with the condition for rim pattern formation given by Eq. (6).

Result of the droplet crystallization experiment using levitation method [3,4] is consistent with Eq. (6). They observed the droplet surface temperature *in situ* during the experiment, and obtained $\Delta T_{\mathrm{s}} \approx 600$ K and $R_{\mathrm{cool}} \approx 350$ K/s at the time when the crystallization took place. From Eq. (1), we obtain $\delta T_{\mathrm{c-s}} \approx 170$ K with $r_{\mathrm{d}} = 1$ mm. We display the experimental result in Fig. 2 by a green star, which satisfies the condition for rim pattern formation. The BO texture with rim was reproduced in their experiments, so Eq. (6) is consistent with their experiment. It should be noted that $\delta T_{\mathrm{c-s}}$ is slightly larger than that expected from the radiative cooling, which is considered to be the fastest cooling process in the early solar nebula environment. The super radiative cooling was realized in their experiments because of the heat conduction by gas-jet [10], so it is not expected to occur at chondrule formation. The condition for rim pattern formation is satisfied at smaller cooling rate when ΔT_{s} is smaller. In addition, one must keep in mind that the chemical composition of the melt droplet that they used in their experiments (pure forsteritic composition) was far from that of real chondrules. The applicability of Eq. (6) to a multi-component melt droplet like as chondrule melts should be investigated carefully.

Tsuchiyama et al. inferred that the rim was formed in their experiment because the droplet surface became cooler than the interior by the latent heat of the evaporation [5]. In their experiments, ΔT_{s} was unknown because they did not observe the droplet temperature *in situ*. The cooling rate was $R_{\mathrm{cool}} \approx 1000$ K/hr from their experimental condition. We evaluate $\delta T_{\mathrm{c-s}} \approx 0.02$ K from Eq. (1) with $r_{\mathrm{d}} = 1$ mm. From Eq. (6), it is found that $\Delta T_{\mathrm{s}} \lesssim 0.1$ K is required for the rim pattern formation. The suitable range of supercooling is so narrow that the timing of nucleation is very severe; considering the cooling rate of $R_{\mathrm{cool}} = 1000$ K/hr, the admitted period for the nucleation is only 0.36 s. If the nucleation misses the timing, the rapid crystal growth along the surface would not occur. The homogeneous nucleation inside the droplet at such low supercooling was found to be difficult in the levitating situation for the single-component melt droplet [3,4,11]. The homogeneous nucleation for a multi-component melt droplet, such as a chondrule melt droplet, has not been investigated in details, so it should be clarified in the future.

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