LOCAL OLIVINE DARKENING BY THE FORMATION OF IRON NANOPARTICLES IN SHERGOTTITE OLIVINES. A. Takenouchi[1] and T. Mikouchi[1], [1]Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, E-mail: a.takenouchi@eps.s.u-tokyo.ac.jp

Introduction: Highly shocked Martian meteorites are known to contain brown colored olivine which is so-called "brown olivine" [1-4]. The brown coloration is induced by iron nanoparticles precipitated in olivine during shock events, and therefore brown olivine will provide us useful information of large-scale shock events. On the other hand, the presence of brown olivine possibly induces overlooking of olivine in remote sensing data because their reflectance spectra and magnetic susceptibilities significantly change from those of colorless olivine (e.g., no absorption at 1 μm) [5]. Therefore, revealing the formation mechanism of brown olivine is important not only for scaling shock events but also interpreting the remote sensing data.

The formation processes and conditions of iron nanoparticles in olivine have been suggested by [1-3] based on the Northwest Africa (NWA) 2737 chassignite whose shock history may have been complex due to multiple collisions [6]. On the other hand, our previous study [4] reported the formation processes and conditions of brown olivine based on the NWA 1950 shergottite whose shock history is simple compared with that of NWA 2737. Previous studies [2,3] and our study [4] suggested that iron nanoparticles are formed by a disproportionation reaction by shock due to the absence of SiO-rich phases around iron nanoparticles and the presence of Fe^{3+} in brown olivine. Brown olivine in NWA 1950 shows characteristic features such as lamellar textures and the extra Raman peaks around 660-690 cm^{-1} in addition to the original Raman peaks of olivine. Based on these observations and kinetic calculations, our study [4] indicated that brown olivine could have once transformed to olivine high-pressure phase(s). However, the lamellae are no longer high-pressure phases but olivine, and no high-pressure phases are retained due to back-transformation induced by high post shock temperature in the meteorite with brown olivine.

Our previous study [7] reported that olivine around shock melt pockets/veins is locally darkened and shows similar features of brown olivine in the meteorites without brown olivine. However, the presence of iron nanoparticles in such locally darkened olivine is not reported. Since high-pressure minerals are often found around such shock melt pockets/veins, we can investigate relationships between transformation to high-pressure phase(s) and olivine darkening by observing the locally darkened olivine around shock melt veins/pockets in detail.

Samples and Methods: In this study, we investigated the locally darkened olivine in two olivine-phyric shergottites Tissint and NWA 1068, which is also reported in [7]. Polished thin sections (PTSs) of each meteorite is investigated by scanning electron microscopy (SEM: JEOL JSM-7100F) with an electron back-scattered diffraction (EBSD) detector and Raman spectroscopy (JASCO NRS-1000), both at National Institute of Polar Research (NIPR). Then, the locally darkened olivine is cut by focused iron beam (FIB: Hitachi FB-2100) and the FIB section is observed by transmission electron microscopy (TEM: JEOL JEM-2010) with an energy dispersive spectroscopy (EDS), both at the University of Tokyo.

Results: Observation by optical microscopy reveals that our PTSs of Tissint and NWA 1068 contain locally darkened olivine around a shock melt vein and shock melt pockets, respectively (Fig. 1). In BSE images, the darkened areas show lamellar textures and such lamellae are ringwoodite judged from Raman spectra and EBSD analysis although the lamellar texture is ambiguous in NWA 1068. In the Raman analysis of the ringwoodite lamellae, an additional peak at 692 cm^{-1} is obtained. Raman analysis far from the shock melt vein (~50 μm) in the same grain shows the peak at 677 cm^{-1} in addition to olivine peaks. However, these additional peaks are single and different from doublet peaks observed in brown olivine. On the other hand, a part of the darkened area adjacent to the shock melt pocket in NWA 1068 contains no ringwoodite in spite of their similar appearance to those of ringwoodite such as lamellar textures. In contrast to ringwoodite in Tissint, the Raman spectra of such areas show doublet peaks at 640-676 cm^{-1} in addition to olivine peaks similar to those of brown olivine.

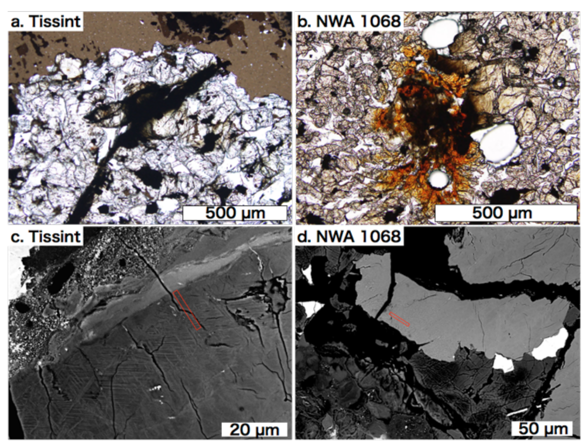

Fig. 1 Plane polarized light and BSE images of Tissint (a, c) and NWA 1068 (b, d). FIB sections are made from the areas indicated by red squares in Figs. 1c and 1d.

TEM observation of the lamellar areas in Tissint shows clear lamellar textures (Fig. 2a). There are several micro-faults cutting the lamellae and the micro-faults contain small amounts of nanoparticles. However, EDS analysis could not detect Fe enrichment in the nanoparticles and they are not found within the lamellar areas. Therefore, the darkened area observed around the shock melt vein in Tissint is not "brown olivine". On the other hand, olivine around shock melt pockets in NWA 1068 contains abundant nanoparticles (Fig. 2b). The nanoparticles are found within disturbed olivine crystal areas and not found within intact crystal areas, which is similar to the occurrence of iron nanoparticles in brown olivine. Although we have not identified the species of iron nanoparticles yet (iron metal, magnetite or others), our EDS analysis detects Fe enrichment in the nanoparticles compared with the host olivine. Due to the presence of iron nanoparticles and similar features to brown olivine, the darkened area around shock melt pockets in NWA 1068 is "brown olivine".

Discussion and Conclusion: In our observation, the darkened area next to the shock melt vein in Tissint shows a lamellar texture of ringwoodite while no iron nanoparticles were found. This observation indicates that iron nanoparticles are not formed only by transformation of olivine to its high-pressure mineral(s). Although the reason why the ringwoodite areas are darkened is still ambiguous, their small grain sizes possibly induce darkening of the areas. On the other hand, the darkened area next to shock melt pockets in NWA 1068 is "brown olivine" (containing iron nanoparticles) although ringwoodite is partly present around the shock melt pockets. This observation indicates that brown olivine is formed under conditions similar to those around shock melt pockets. The presence of ringwoodite around the darkened areas of olivine in NWA 1068 suggests that these areas could transform to high-pressure phase(s). However, smaller amounts of ringwoodite and more ambiguous lamellar textures in NWA 1068 compared with ringwoodite in Tissint implies that these areas may have experienced back-transformation from ringwoodite. Since only transformation to high-pressure phase(s) could not precipitate iron nanoparticles while they are found in back-transformed areas, the disproportionation reaction may have occurred during such back-transformation. This hypothesis may be reasonably explained by the observation of static high-pressure experiments. In the experiment performed by [8], olivine is transformed to several high-pressure phases, and then such high-pressure phases will contain non-negligible Fe^{3+} although the starting material (olivine) contains no Fe^{3+}. In this case, when the high-pressure phases are back-transformed, iron nanoparticles and vacancies are formed from parts of Fe^{3+} because olivine could not contain abundant Fe^{3+} (possibly described as $3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^- \rightarrow Fe^0 + 2Fe^{3+} + V$, where V represent a vacancy). Therefore, the formation of brown olivine could be an indicator of high pressure and high post shock temperature inducing transformation and back-transformation of olivine.

This study demonstrates that brown olivine (iron nanoparticles) is formed via high-pressure phases, and the back-transformation induces the precipitation of iron nanoparticles. Thus, brown olivine could be formed around craters on any large bodies and should be carefully considered in interpreting remote sensing data in order not to overlook the presence of olivine which is significantly important for considering the formation processes of large bodies such as asteroid 4 Vesta.

References: [1] Treiman A. H. et al. (2007) *JGR*, 112, E04002. [2] Van de Moortèle B. et al. (2007) *EPSL*, 262, 37-49. [3] Bläß U. W. et al. (2010) *EPSL*, 300, 255-263. [4] Takenouchi A. et al. (2017) *Meteorit. & Planet. Sci.*, 52, 2491-2504. [5] Pieters C. et al. (2008) *JGR*, 113, E06004. [6] Bogard D. D. and Garrison D. H. (2008) *EPSL*, 273, 386-392. [7] Takenouchi A. et al. (2015) *LPSC XLVI*, abst. #1650. [8] O'Neill H. St. C. et al. (1994) *Amer. Min.*, 78, 456-460.

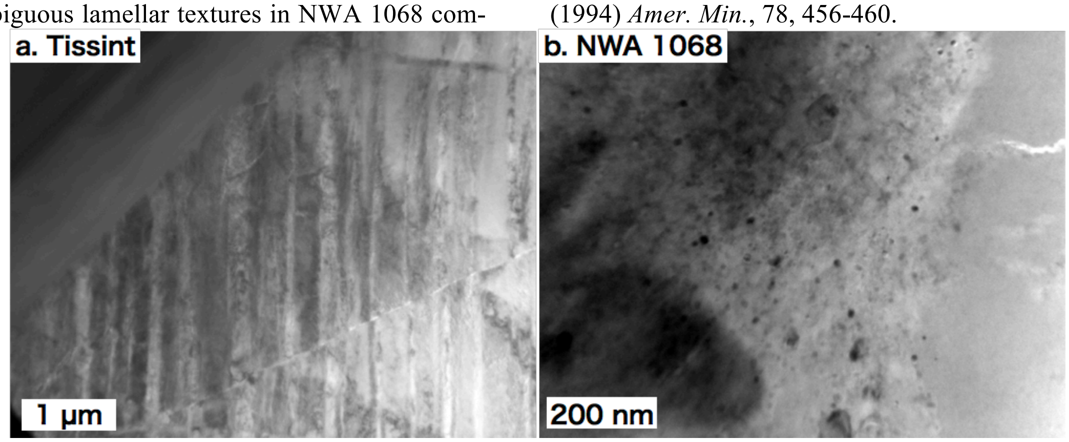

Fig. 2 TEM-bright field images of darkened areas of olivine around the shock melt vein/pocket in Tissint (a) and NWA 1068 (b).