Formation of spherical iron oxide minerals by oxidative hydrothermal alteration from metallic spherules

*Huimin Shao[1], Hiroshi Isobe[1]

1. Kumamoto University

Hematite spherule deposits in Meridiani Planum and Aram Chaos on Mars were discovered by Thermal Emission Spectrometer (TES) in Mars Global Surveyor spacecraft. The formation mechanism of these hematite spherules was widely discussed by researchers (Misra et al., 2014; Morris et al., 2005; Nie et al., 2020). Most of them suggest that the hematite spherules were formed as concretions by precipitation from aqueous fluids (Bowen et al., 2008; Kato et al., 2009) based on a similar formation process observed on the Earth. Thus, the occurrence of hematite deposits may suggest the past presence of water, which is quite significant for planetary science and possibly extraterrestrial life searching. However, Misra et al. (2014) proposed a possibility that the hematite spherules may be derived from cosmic spherules formed by ablation of iron meteorites according to the detailed comparison to cosmic spherules and terrestrial concretion analogs. Therefore, we carried out a series of experiments to synthesis hematite spherules by oxidative hydrothermal alteration.

The starting material used in this study was reproduced I-type cosmic spherules formed by high-temperature heating and quenching experiments (Shao et al., 2020) in a reduced atmosphere controlled by Ar (98%) and H_2 (2%) gas flow. Starting material was placed at the bottom of Ag-Pd tubes (inner dia. 2mm) with an open top. The Ag-Pd tube was sealed in a pure Ag tube (inner dia. 4.6mm) with pH4 sulfuric acid solution or pH7 deionized water, with or without $Ag_2C_2O_4$ for CO_2 source. The sealed Ag tubes were set in high-pressure vessels and oxygen fugacity was controlled by Mn_2O_3 outside the Ag tubes. The vessels were heated at 150°C and 200°C for 10 days or 40 days.

SEM and EDS were employed to observe the run products. Original spherical shape of the starting materials has remained in most of the run products. Magnetite, Wustite, and Fe-Ni metal were the main mineral of run products. Within the same duration, pH4 groups show more oxidized results than pH7 conditions. In the run products with CO_2, euhedral siderite ($FeCO_3$) crystals were also observed. Euhedral magnetite crystals grow with run durations, at the same time, higher temperature and lower pH conditions accelerate the growth of magnetite crystals.

The analysis of cross-sections of run products reveals that oxygen may migrate along the crystallographic boundaries of metallic iron to deep inside of metal-core with the presence of elongated magnetite aggregates. Kinetics of oxidation of metallic iron brought iron oxide growth to both inward and outward from the starting material's smooth surface. Iron also dissolved to fluid phases and formed euhedral magnetite crystals on the inside wall of sample tubes. Ni was concentrated in the metal vein or small nuggets up to 95 wt%, which was quite high compared with the original 6 wt% in starting material. Mn_2O_3- Mn_3O_4 buffer controls oxygen fugacity in hematite stability field. However, in the existing result of this study, hematite has not been observed yet. Therefore, we are expecting magnetite to hematite phase transition under a longer duration in future experiments.

Keywords: Martian surface, Hematite spherules, Hydrothermal alteration, Cosmic spherules