The discovery of Mn-precipitates in nakhlites Yamato 000802

Ayaka Nakamura[1], Masaaki Miyahara[1], Hiroki Suga[2,6], Akira Yamaguchi[3], Wakabayashi Daisuke[4], Shohei Yamashita[4], Yasuo Takeichi[4], Yoshio Takahashi[2], Eiji Ohtani[5]

[1]*Hiroshima University,* [2]*The University of Tokyo,* [3]*NIPR,* [4]*KEK,* [5]*Tohoku University,* [6]*JASRI*

Manganese (Mn) is sensitive to the redox states of fluids and can have six kinds of valence: +2 ~ +7. The valences of Mn depend on the pH-Eh conditions of the fluid that forms Mn-precipitate. Mn-oxides and -hydroxides are found not only on the earth but also in the sediments of Mars. Hence, Mn can become a clue for clarifying Martian surface conditions. One of the martian meteorites nakhlites records the aqueous alteration that probably occurred on Mars. Yamato (Y) 000593, Y 000749, and Y 000802 are the members of nakhlites. Previous works including ours (e.g. [1]) reported that many kinds of alteration minerals in Y 000593 and Y 000749. In contrast, the alteration minerals in Y 000802 were not investigated so far. Accordingly, we describe the alteration minerals in Y 000802 by FE-SEM, EMPA, and FIB-TEM. We found many Mn-precipitates in the mesostasis of Y 000802 and measured the redox states of Mn therein by STXM. Here, we report the alteration minerals found in Y 000802, especially focus on Mn-oxides and -hydroxides in the mesostasis.

Y 000802 consists mainly of olivine, clinopyroxene, and mesostasis. The mesostasis consists of plagioclase, K-feldspar, tridymite, pyrrhotite, phosphate mineral, and titanomagnetite. Many alteration textures in the shape of veinlets are found in the mesostasis. The alteration textures in the mesostasis can be divided into i) Fe-S-rich portion, ii) Si-Fe-rich portion, and iii) Mn-concentrated portions. Fe-S-rich portions are pervasively observed along with the fractures and grain-boundaries of the altered olivine grains besides in the mesostasis. Jarosite occurs in the Fe-S-rich portions. Laihunite, magnetite, and opal occur in the altered olivine grains next to the Fe-S-rich portions. Ferroan saponite (+ opal) replaces the plagioclase and K-feldspar grains with maintaining their original crystal habits in the Si-Fe-rich portions. Pyrrhotite and phosphate mineral grains show a dissolution texture. Jarosite, iron oxides, and iron hydroxides occur around the pyrrhotite and phosphate mineral grains.

Mn-concentrated portions are surrounded by Si-Fe-rich portions. Fe-S-rich portions in the shape of veinlets penetrate the Mn-concentrated portions. Two different types of Mn-concentrated portions occur i) an ultra-high-Mn-concentrated portion and ii) a high-Mn-concentrated portion. The Mn-concentrated portions accompany iron. The Mn/Fe atomic ratios of the ultra-high-Mn- and high-Mn-concentration portions are ~3 and ~1, respectively. Mn L-edge XANES spectra show the existence of Mn^{2+}, Mn^{3+}, and Mn^{4+} in the Mn-concentrated portions. Mn^{3+} along with Mn^{2+} is dominant in the ultra-high-Mn-concentrated portions, whereas Mn^{2+} (and trace Mn^{4+}) is dominant in the high-Mn concentrated portions. The weak peak of O K-edge XANES at 534 eV and C K-edge XANES at 290 eV appears in the Mn-concentrated portions, implying the existence of CO_3^{2-}. Based on the SAED patterns by TEM along with XANES by STXM analysis, the ultra-high-Mn-concentrated portions consist mainly of hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$), trace amounts of manganite (γ-MnOOH), and rhodochrosite ($MnCO_3$). Considering the abundance of iron in hausmannite, jacobsite ($Mn^{2+}[Mn^{3+}, Fe^{3+}]_2O_4$) coexists with hausmannite (solid-solution). The high-Mn-concentrated portions consist mainly of hausmannite and jacobsite. Pyrolusite (MnO_2) also may occur based on the trace adsorption peak corresponding to Mn^{4+}. The Mn-concentrated portions also include trace amounts of sulfur.

We suspect the alteration scenario recorded in Y 000802 as follows. High-temperature fluid intruded into the nakhlite body first, which induced the alteration from olivine to laihunite (+ opal and iron oxides/hydroxides). Mn ion dissolved from the olivine through the formation of laihunite. The dissolved Mn ions precipitated as hausmannite (-jacobsite) + rhodochrosite assemblage in the mesostasis. Simultaneously, plagioclase was replaced with ferroan saponite by the fluid. Subsequently, an acidic fluid, which is due to the dissolution of pyrrhotite, induced the alteration of the hausmannite + rhodochrosite assemblage. Parts of the hausmannite + rhodochrosite altered to manganite (and pyrolusite). SO_4^{2-} and Fe^{2+} released by the dissolution of pyrrhotite and potassium released from K-feldspar by the acidic fluid precipitated as jarosite. The last alteration by the acidic fluid occurs mainly on the earth because pyrrhotite can dissolve easily.

References

[1] Shiraishi et al. (2018) Aqueous alteration of Yamato 000749 based on multi-probe microscopic observation. The Ninth Symposium on Polar Science, abstract.