CHEMICAL SPECIATION ANALYSES OF ALTERATION PRODUCTS IN NAKHLITES Y 000593

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Introduction: Nakhlites are considered to record water-rock reactions occurred on the Mars. Iddingsite is one of alteration textures occurring in the nakhlites. The constituents, chemical species, and their coordinations in the iddingsite textures depend on pH, temperature, rock/water ratio and pressure conditions during the water-rock alteration reactions. Accordingly, the scrutiny of the iddingsite textures in the nakhlites becomes a clue for elucidating environment on the Mars during a wet-period. Jarosite ($[KFe_3(SO_4)_2(OH)_6]$) is one of major alteration products occurring in the iddingsites. A member of nakhlites, Yamato (Y) 000593 and Millar Range (MIL) 03346 include considerable amounts of jarosite [1–3]. Jarosite and alunite ($[KAl_3(SO_4)_2(OH)_6]$) were detected by Mars rovers on several provinces such as Meridiani plume and Cross crater, suggesting the existence of surface (or subsurface) liquid water (high acidic brine) at least one period in the Martian history [4, 5]. It is expected that jarosite-bearing nakhlites become a keystone for direct linkage between Martian meteorites and Martian surface materials. Iddingsite textures are observed preferentially in and around olivine grains of the nakhlites. The Iddingsite is only about several 10 μm across. In this present study, we adopted FIB-assisted site-specific STXM/NEXAFS technique [e.g., 6] besides conventional FE-SEM, TEM/STEM and Raman analyses to clarify the chemical species, redox-states, mineral species and occurrences of the alteration products occurring in the iddingsite textures of naklites, Y 000593. We also discuss the alteration conditions recorded in the Y 000593.

Materials and experimental methods: Y 000593 chunk sample was allocated from NIPR. We polished the chunk sample using a lapping film (3M^{TM}). We observed the iddingsite textures of the polished Y 000593 sample using FE-SEM. A laser micro-Raman spectroscope was employed for mineral identification. Several portions were selected for STXM analysis, and thin slices were extracted from the portions by FIB. STXM analysis was conducted at BL4U, UVSOR. Finally, the thin slices were observed with TEM/STEM-EDS.

Results and discussion: The Y 000593 studied here consists mainly of augite and minor amounts of olivine. Iddingsite textures were observed along the fractures in the olivine grains and boundaries between the olivine grains and surrounding augite grains. Laifunite $[(Fe^{2+}Fe^{3+})_2(SiO_4)_2]$, which is the alteration product of olivine, occurs in the vicinities of fractures in the iddingsite textures. Fe- and O-XANES obtained by STXM indicate that most iron in original olivine is ferrous (Fe^{2+}/Fe^{3+} = 0.72), whereas most iron in laifunite is ferric (Fe^{2+}/Fe^{3+} = 0.52). Fe^{2+}/Fe^{3+} ratio decreases discontinuously from olivine to laifunite. The constituents filling the fractures in the iddingsite textures are complex mixtures of silica-rich, sulfur-rich and/or chlorine-rich materials. Based on TEM/STEM-EDS analysis, the silica-rich materials are opal. Cl-XANES could not be obtained from the chlorine-rich portion, because we do not have an adequate reference material. Alternatively, C- and O-XANES indicated that the chlorine-rich portion includes carbon, oxygen and aromatic hydrocarbons (C=C). S-XANES revealed that sulfur in the sulfur-rich portion exists as hexavalent rather than zero-valent. Considering TEM/STEM-EDS analysis besides S-XANES, some sulfur-rich portions include natrojarosite $[NaFe_3(SO_4)_2(OH)_6]$ that is one of the quad phases of jarosite. Natrojarosite forms in low pH (= 1–4), low temperature (80–240 °C) and SO_4-rich liquid [7]. The other nakhlites (Nakhla, Governador Valadares and Lafayette) include siderite ($[FeCO_3]$), suggestive of mid pH (= 6–8) and low temperature (150–200 °C) conditions [8]. Y 000593 may record the late-stage acid-sulfate alteration event occurred on the Mars [2]. On the other hand, laihunite form from olivine in high-pH (alkaline) environment under 300–800 °C [9, 10]. There are clear differences in the formation conditions between the natrojarosite + opal assemblage and laifunite in Y 00593. Considering the arrangements of alteration products in the iddingsite textures of Y 000593, the natrojarosite + opal assemblage formed subsequent to laifunite. It is likely that the natrojarosite + opal assemblage and laifunite formed separately during different alteration events. Alternatively, it is possible that high-temperature liquid with high-pH altered olivine, and formed laifunite first. Subsequently, with decreasing temperature and pH, natrojarosite and opal were precipitated from the liquid. Chemical species analysis of iddingsite in nakhlites by STXM is now bringing new clue for chasing the sequence of alteration conditions.

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