The Difference Acidic Condition of Aqueous Alteration Event of Nakhla and Yamato 000593 Based on Chemical Speciation

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Nakhlites (*e.g.,* Nakhla, Lafayette, Governador Valadares, Millar Range (MIL) 03346, and Yamato (Y) 000593) originating from the near-surface of the Mars are expected to record a water-rock reaction (alteration) occurred on the Mars. One of the representative alteration textures is “iddingsite texture”, which is observed in and around the olivine grain of nakhlites [*e.g.,* 1]. A nonstoichiometric distorted olivine-type mineral laifunite [$(Fe^{2+}Fe^{3+})_2(SiO_4)_2$], which is one of the alteration products of original olivine, was formed in the iddingsite texture [2]. The iddingsite was crosscut by fusion crust, indicating that the iddingsite including laifunite was formed on the Mars before it was delivered to the Earth [3]. A member of Nakhlites, Y 000593 and MIL 03346, which are expected to originate from the subsurface (~10 m in depth) of the Mars, has a remarkable amount of jarosite [KFe3(SO4)2(OH)6]-bearing iddingsite [2, 4]. Iron sulfates including jarosite were detected on several provinces of Mars’ s surface such as Meridiani plume, strongly suggesting the existence of surface (or sub-surface) liquid water (probably high acidic brine) at least one period in the Martian history [5, 6]. These jarosite-bearing nakhlites would become a keystone for a direct linkage between Martian meteorites and Martian surface materials. Therefore, we have tried to describe secondary minerals in the Yamoato 000593 for elucidating environment on the Mars during a wet-period by using a microscopic speciation technique; a FIB-assisted STXM combined with a TEM/STEM observation.

A polished chip sample of Y 000593 (subsample, 120) was prepared for this study. Iddingsite textures were observed using a FE-SEM/EDS first. A laser micro-Raman spectroscope was employed for phase identification. Ultra-thin sections of iddingsite textures were prepared by a FIB system for STXM and FE-TEM/STEM analyses.

Laihunite, Opal-A [$SiO_2 \cdot nH_2O$], jarosite, natrojarosite [$NaFe_3(SO_4)_2(OH)_6$], goethite [FeO(OH)], and ferrihydrite [$5Fe_2O_3\ 9H_2O$] were identified from the iddingsite of Y 000593 based FIB-assited STXM-TEM/STEM analyses subsequent to FE-SEM/EDS and Raman analyses. The presence of natrojarosite, one of the quad phase of jarosite [7], suggests that Y 000593 experienced low pH (= 1-4), low temperature (80-240 ˚C), and SO_4-rich aqueous alteration process. Iddingsite can form below 500 , and most of them were formed between 100 and 50 [8], which is consistent with the alteration temperature of Y 000593 deduced from the existence of natrojarosite. The alteration condition of Nakhala with siderite ($FeCO_3$)-bearing iddingsite texture was estimated to be about mid pH (= 6-8), low temperature (150-200), and CO_2-rich fluid [9]. Because Mars rover Opportunity detected sulfate minerals such as jarosite and natrojarosite, Y 000593 is a better sample than the other near-surface nakhlaites to understand the late-stage acid-sulfate alteration event. Laihunite (was formed at temperatures between 400-800 in [10]) was only reported from Y 000593 and MIL 03346 in the near-surface nakhlaites, implying that these two nakhalite might have experience different alteration process compared to other near-surface nakhlaites [4]. Our STXM-TEM/STEM analyses reveal the alteration process from original olivine to laihunite; Fe^{2+}/Fe^{3+} ratio gradually decreases from olivine to laihunite, which probably corresponds to the difference of superlattices of laihunite (2M and 3M phase) [11]. Short time oxidation related to formation of the 2M phase [11], suggests that Y 000593 experienced a temporary heating event. We found mismatch on the formation temperatures between natrojarosite and laihunite. The

discrepancy may indicate that these minerals were formed different alteration events; i.e., laihunite was formed before the late-stage acid-sulfate alteration event.

[1] Treiman, 2005. [2] Noguchi et al., 2009. [3] Treiman and Goodrich, 2002. [4] Hallis and Taylor, 2011. [5] Klingelhöfer et al., 2004. [6] Ehlmann et al., 2016. [7] Papike et al., 2006. [8] Treiman et al., 1993. [9] Bridges and Schwenzer, 2012. [10] Banfield et al., 1990. [11] Tomioka et al., 2012.

Keywords: Nakhlite, Yamato 000593, Iron sulfate mineral, Laihunite, Acidic aqueous alteration on the Mars, FIB-assisted STXM/TEM

