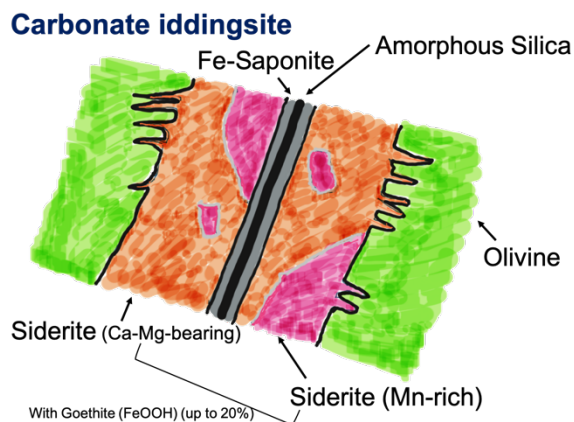


**A STUDY ABOUT MARTIAN WATER ENVIRONMENT BASED ON THE MICRO-XRF-XANES ANALYSIS FOR THE SECONDARY MINERALS FORMED IN A VEIN OF NAKHLITE YAMATO 000593.** H. Suga<sup>1</sup>, K. Suzuki<sup>1</sup>, A. Yamaguchi<sup>2</sup>, T. Usui<sup>3</sup>, O. Sekizawa<sup>4</sup>, K. Nitta<sup>4</sup>, and Y. Takahashi<sup>1</sup>, <sup>1</sup>Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, JAPAN ([hiroki-suga@eps.s.u-tokyo.ac.jp](mailto:hiroki-suga@eps.s.u-tokyo.ac.jp)), <sup>2</sup>National Institute of Polar Research, Tachikawa, Tokyo 190-8518, JAPAN, <sup>3</sup>Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), Sagami-hara, Kanagawa 252-5210, JAPAN, <sup>4</sup>Japan Synchrotron Radiation Research Institute, Kouto Sayo, Hyogo 679-5198, JAPAN.

**Introduction:** Martian meteorite nakhlite has attracted attention because it has various secondary mineral assemblages (such as iddingsite) formed by water-rock reaction on the Mars [e.g., 1]. The iddingsite holds physicochemical information of water when it formed on Mars. However, the formation processes of the minerals are not clear because both carbonates (precipitate under reductive alkaline conditions) and sulfates (precipitate under oxidative acidic conditions) that cannot coexist under an equilibrium condition were found [1-3]. Among these minerals, sulfate minerals are considered as a terrestrial contamination in several researches in contrast to carbonate minerals accompanied with various secondary minerals such as saponite and serpentine.

Here, we examined trace element distribution within the carbonate phases in Yamato 000593 (Y-000593) by synchrotron-based  $\mu$ -XRF-XANES and FE-SEM-EDS/FE-EPMA in order to determine the transition history of the Eh-pH conditions during the carbonate formation, which reconcile the coexistence of carbonate and sulfate phases in the iddingsite.

The detailed understanding of environment (e.g., fluid chemistry) allows us to give a new constraint on the physicochemical evolution of the water that altered the nakhlite body during the last ~6.5 million years.



**Figure 1.** Schematic paint of the carbonate vein in Y-000593.

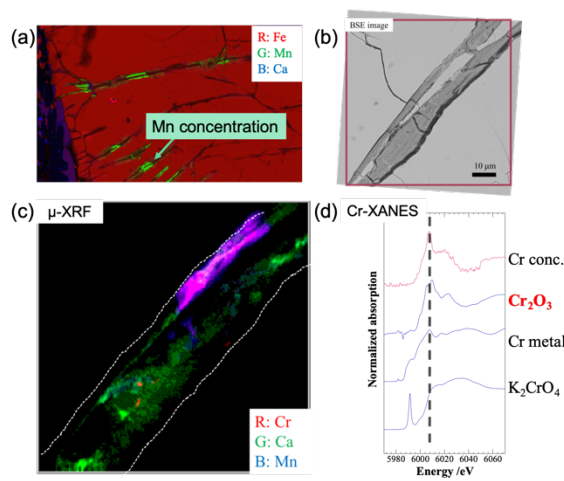
**Material and methods:** The polished thin section (PTS: #58-1 in NIPR) of Y-000593 was used for this study. First, the identification of secondary mineral phases in the iddingsite were conducted by FE-SEM-EDS and FE-EPMA at the University of Tokyo. After that, we investigated distribution of trace elements by  $\mu$ -XRF-XANES at BL37XU of SPring-8, and BL-4A/15A of KEK-PF. Subsequently, we tried to constrain the iddingsite formation environment (such as Eh-pH conditions) from the proportion of secondary minerals.

**Results and Discussions:** Carbonates ( $\text{FeCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{CaCO}_3$ ), iron oxides ( $\text{FeOOH}$ ), clay minerals (Fe-rich saponite), and Si-rich vein were identified in the iddingsite from the outside to the center of vein by FE-SEM-EDS and FE-EPMA analysis (Fig. 1). In particular, carbonate aggregates were mainly composed of  $(\text{Mn,Fe})\text{CO}_3$  and  $(\text{Ca,Fe})\text{CO}_3$ . The chemical composition of these carbonates is roughly similar to previous researches [e.g., 3,4]. This result suggested that the iddingsite was altered by  $\text{CO}_2$ -rich reductive alkaline fluid ( $\text{Eh} \leq 0.2$ ;  $\text{pH} = 9.0 \sim 11$ ) [5]. The difference between distributions of Mn and Ca suggests that fluid with different Eh-pH conditions flowed several times or water condition was changed during carbonate formation because  $(\text{Mn,Fe})\text{CO}_3$  and  $(\text{Ca,Fe})\text{CO}_3$  cannot overlap in the Eh-pH diagrams ( $(\text{Mn,Fe})\text{CO}_3$  precipitate at  $\text{Eh} = -0.4 \sim -0.0$ ;  $\text{pH} = 9.0 \sim 9.5$ ;  $(\text{Ca,Fe})\text{CO}_3$  precipitate at  $\text{Eh} = -0.3 \sim -0.1$ ;  $\text{pH} = 6.5 \sim 9.0$ ).

The  $\mu$ -XANES analysis revealed that  $\text{Cr}^{3+}$  coexisted in  $(\text{Mn,Fe})\text{CO}_3$ , since Cr cannot be enriched in  $\text{MnO}_2$  in general (Fig. 2). It is presumed that Mn precipitated originally as  $\text{MnOOH}$ , which was transformed into  $\text{MnCO}_3$  in the presence of alkaline fluid. In  $(\text{Ca,Fe})\text{CO}_3$ , 20% of Fe was present as  $\text{FeOOH}$ . It was implied that  $\text{FeOOH}$  is precursor of the  $\text{FeCO}_3$ . In addition, we detected  $\text{S}^{6+}$  in the iddingsite, of which chemical species are the clay mineral adsorbent (Fe-rich saponite),  $\text{Mn}^{2+}(\text{Mn}^{3+})\text{O}_4$ , and  $\text{MnCO}_3$  by XANES fitting (Fig. 3).

This results suggested that sulfate-bearing alkaline fluid flowed in the final stage of the iddingsite formation. Besides, its concentration decrease from the

mesostasis phase. Therefore,  $S^{6+}$  in the clay minerals portion related to the FeS in the mesostasis, and apart of FeS might flowed out as alkaline fluid.

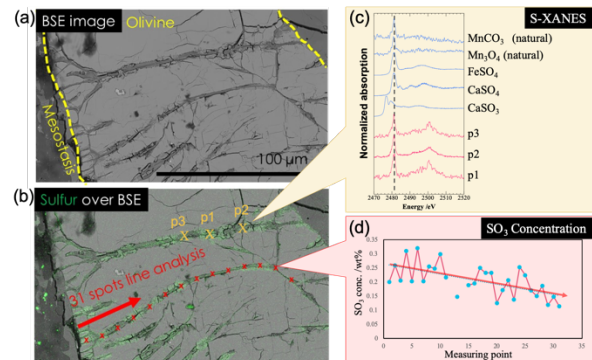


**Figure 2.** (a) RGB composited image of representative olivine which contain the carbonate iddingsite by EPMA. Red, green, and blue is indicates iron, manganese, and calcium, respectively. The heterogeneous greenish portions indicate Mn carbonate ( $MnFeCO_3$ ). (b) BSE image of the selected Mn carbonate iddingsite in the olivine. (c) RGB composited elemental image of the same area of (b) by  $\mu$ -XRF(-XAFS). Red, green, and blue is indicates Chromium, calcium, and Manganese, respectively. The purple portion is Mn-carbonate: clearly contain the Cr. (d): Representative Cr K-edge XANES spectra obtained from the Mn carbonate in the olivine (the pink portion of (C)). The spectrum of pink region has the similar peak energy at the  $Cr_2O_3$ . It is revealed that Cr in the Mn is  $Cr^{3+}$ .

**Summary:** From this study, we conclude that the carbonates in iddingsite formed by reductive alkaline fluid ( $Eh \leq 0.2$ ;  $pH=9.0-11$ ), opposite to sulfate formation. However, it is still not clear whether these carbonate minerals were locally formed or widespread in the nakhlite from the spatial distribution point of view. Therefore, we are trying to observe the 3D structure/elemental distribution of the iddingsite by XAFS-CT method in order to clarify the fluid path related to the formation process of the carbonate minerals.

**References:** [1] White L. M. et al. (2014), *Astrobiology*, 14, 170. [2] Noguchi T. et al. (2009), *JGR*, 114, E10004. [3] Tomkinson T. et al. (2013), *Nature Communications*, 4, 2662. [4] Piercy J. D. et al. (2018), *49th LPSC*, Abstract #2020. [5] Brookins D.

G. (1988), *Springer*, Eh-pH diagrams for geochemistry.



**Figure 3.** (a): BSE image of the representative Olivine grain in Y-000593. (b): Sulfur elemental image by EPMA (Green) over the BSE image. Sulfur distributed in the carbonate in the iddingsite universally. (c): S K-edge XANES spectra obtained from the spots showed in the orange cross marks in (a) p1-3. Spectra of standard materials also showed. (d): SO<sub>3</sub> concentration by EPMA obtained from red cross mark in the (a).