

A study on Martian water environment based on the μ -XRF-XANES analysis for the secondary minerals formed in a nakhlite meteorite (Y 000593) vein

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Martian meteorite nakhlite has attracted attention because it has various secondary mineral assemblages (such as iddingsite) formed by water-rock reaction on the Mars. 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. 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 Y 000593 by FE-SEM-EDS/FE-EPMA and synchrotron-based μ -XRF-XANES 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.

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 μ -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.

Carbonates (FeCO_3 , MnCO_3 , CaCO_3), iron oxides (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. In particular, carbonate aggregates were mainly composed of $(\text{Mn,Fe})\text{CO}_3$ and $(\text{Ca,Fe})\text{CO}_3$. This result suggested that the iddingsite was altered by CO_2 -rich reductive alkaline fluid ($\text{Eh} \leq 0.2$: $\text{pH} = 9.0 \sim 11$) [Brookins, 1998]. 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 μ -XANES analysis revealed that Cr(III) coexisted in $(\text{Mn,Fe})\text{CO}_3$, since Cr cannot be enriched in MnO_2 in general. It is presumed that Mn precipitated originally as MnOOH , which was transformed into MnCO_3 in the presence of alkaline fluid. In $(\text{Ca,Fe})\text{CO}_3$, 20% of Fe was present as FeOOH . It was implied that FeOOH is precursor of the FeCO_3 . In addition, we detected S(VI) 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 MnCO_3 by XANES fitting. 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(VI) in the clay minerals portion related to the FeS in the mesostasis, and apart of FeS might flowed out as alkaline fluid.

From this study, we conclude that the carbonates in iddingsite formed by reductive alkaline fluid ($E_h \leq 0.2$: 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.

Keywords: Mars, Martian meteorite, Synchrotron radiation X-ray analysis