

In-situ detection of nitrogen-bearing organics in Noachian Martian carbonates: Implication for nitrogen-cycle on early Mars.

M. KOIKE^{1*}, R. NAKADA², I. KAJITANI^{3,4}, T. USUI^{3,5},
Y. TAMENORI⁶, H. SUGAHARA³, AND A. KOBAYASHI^{5,7}

¹Hiroshima Univ. (*email: mizuhokoike@hiroshima-u.ac.jp)

²Kochi, JAMSTEC, ³ISAS, JAXA, ⁴EPS, Univ. Tokyo,

⁵ELSI, Tokyo Tech, ⁶Res. Util., JASRI, ⁷GPS, Caltech

Investigation of Martian organics is a hot topic in the planetary science. Martian meteorite, ALH 84001 is known to contain carbonates that precipitated from near-surface fluids on Mars 4 billion years ago. These carbonates can provide important clues on the condition of Noachian Mars. As nitrogen (N) is an essential element for terrestrial life, *in-situ* study of N in Martian samples would help our understanding for geo/bio-chemical activities. Here, we report the first micrometer-scale, *in-situ* chemical speciation of nitrogen conducted on ALH carbonates.

Orange-colored carbonates were observed in a rock fragment of ALH 84001, 248. We peeled them off carefully using a EM grade silver tape in a class 100 clean room at Tokyo Tech. Then, their surfaces were etched slightly by a Ga ion beam using FIB-SEM at JAXA to reduce possible contaminants. A silicate grain from the same rock was prepared in the same manner to monitor possible contamination. Their nitrogen K-edge micro X-ray absorption near-edge structure (XANES) was measured on BL27SU of the SPring-8 synchrotron facility. N-bearing inorganic and organic compounds were analyzed as references. The X-ray beam was focused on the samples with a spot size of < 30 μm. The energy range of 385–425 eV was scanned with a step of 0.2 eV.

XANES spectra of the carbonates showed two prominent absorptions at 398.9 eV and 399.9 eV, with smaller peaks at 400.7–402 eV and a broader peak at 408 eV, consistent with those of N-bearing organic groups, but not for NaNO₃, NH₄Cl, or N₂. On other hand, the silicate grain and the silver tape did not show any of those features. Consequently, ALH carbonates may contain inherent N-bearing organics.

Our findings indicate that N-bearing organics have been preserved for 4 billion years in ALH carbonates, avoiding severe degradation by strong oxidants, UV, cosmic rays, or thermal processes on Martian near-surface system. The importance of ‘nitrogen-cycle’ on Noachian Mars will be revealed by future studies.

Ref: Koike et al. (2020) *Nature Comm.* 11, 1988. and references therein.