In-situ detection of early Noachian nitrogen-bearing organics from Martian carbonates

*小池 みずほ[1]、中田 亮一[2]、梶谷 伊織[1,3]、臼井 寛裕[1,4]、為則 雄祐[5]、菅原 春菜[1]、小林 厚子[4,6]
*Mizuho Koike[1], Ryoichi Nakada[2], Kajitani Iori[1,3], Tomohiro Usui[1,4], Yusuke Tamenori[5], Haruna Sugahara[1], Atsuko Kobayashi[4,6]

1. 宇宙航空研究開発機構　宇宙科学研究所、2. 海洋研究開発機構　高知コア研究所、3. 東京大学大学院理学系研究科　地球惑星科学専攻、4. 東京工業大学　地球生命研究所、5. 高輝度光科学研究センター　放射光利用研究基盤センター、6. Division of Geological and Planetary Sciences, California Institute of Technology
1. Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency , 2. Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology, 3. Department of Earth and Planetary Science, The University of Tokyo, 4. Earth-Life Science Institute, Tokyo Institute of Technology, 5. Research and Utilization Division, Japan Synchrotron Radiation Research Institute, 6. Division of Geological and Planetary Sciences, California Institute of Technology

Origin and preservation of organic material on Mars is a hot topic among planetary science. Martian organic records were identified from both Martian regolith and several meteorites. Allan Hills (ALH) 84001, a unique early Noachian igneous rock, is known to contain trace amounts of carbonates that precipitated through low-temperature hydrous alteration at ~4.0 –3.9 Ga on Mars. Nitrogen, an essential element for all terrestrial life, is an infromative geochemical tracer for co-evolutions of planetary systems. Here we report micrometer-scale in-situ analyses of nitrogen K-edge X-ray absorption near-edge structure (N μ-XANES) on the ALH carbonates for the first time.

Brown-orange colored carbonates on a rock fragment of ALH 84001, 248, were observed under an optical microscope in a class 100 clean room at the Earth-Life Science Institute, Tokyo Tech. The carbonates were fragile and easily peeled off by our new handpicking method. To reduce experimental contaminations, in addition, the surface of the carbonates was sputtered for ~1 μm depth using Ga ion beam of FIB-SEM at Extraterrestrial Sample Curation Center, JAXA. A silicate grain from the same rock was prepared in the same manner for contamination check. The N μ-XANES analysis was conducted at BL27SU of SPring-8 synchrotron facility. Several N-bearing inorganic and organic compounds were analyzed as references. The X-ray beam was cut by closing slit to 10 μm (V) ×30 μm (H). The energy range for the μ-XANES analysis was 385 –425 eV with a step of 0.2 eV.

XANES spectra of ALH cargbonates present two prominent absorptions at 398.9 eV and 399.9 eV with additional smaller peaks at 400.7–402 eV. The features do not match to $NaNO_3$, NH_4Cl, or N_2, but are consistent with those of organic nitrogens. ALH carbonates seems to contain a variety of N-bearing organics, whereas contribution of inorganic N is insignificant. In contrast, the ALH silicate and other possible contaminants do not present any N-related features, suggesting the experimental contamination is negligible. Previous bulk destructive analyses of ALH 84001 reported the severe contamination of carbon (mainly, organic carbon) from Antarctic ice/meltwater. It is difficult to exclude all possible contaminants, though, our *in-situ* analytical technique reduces the risk of Antractic contamination by focusing on the fresh interiors of the samples.

If the N-bearing organics are from Mars, they hould have survived for 4 Ga. Strong oxidants, such as percheorate and nitrate, exist on present Martian regolith and in younger meteorites. However, our ALH carbonates do not present NO_x features, suggesting that the 4-Ga fluid was less oxidic.

©2020. Japan Geoscience Union. All Right Reserved.

Thermodynamically estimated forms of N in that fluid are N_2(aq) and NH_4^+, suitable for the co-existing N-bearing organic matter. The organics were subsequently trapped into ALH carbonates and preserved at Martian subsurface.

Possible origins for Martian organics are A) *in-situ* synthesis and/or B) meteoritical supply. In case A, fixation of N from N_2 is required at first. Although oxidized N is found on Mars, reduced N species have not been found due to their instability. However, some abiotic paths for NH_3 and CN, proposed for Hadean Earth, could be applied on early Mars. Once NH_3 is formed, it behaves as key starting chemical for more complex N-bearing molecules. Meteoritic supply (B) is also plausible. Carbonaceous chondrites, as well as comet and IDPs contain a variety of N-bearing molecules. Large amounts of tham may have been supplied onto early Mars, although their flux are not determined. Whatever the origin, the presence of organic and reduced N indicates the importance of ‘Martian nitrogen-cycle’. We expect that further hidden records of Martian nitrogen-cycle will be acquired by future exploration and sample return missions, as well as advanced analyses of meteorites.

Ref: Koike et al. (in prep.) and references therein.

キーワード：Carbonates、Nitrogen speciation、Martian organic records、in-situ analysis、Allan Hills 84001
Keywords: Carbonates, Nitrogen speciation, Martian organic records, in-situ analysis, Allan Hills 84001

©2020. Japan Geoscience Union. All Right Reserved.