

**IN-SITU DETECTION OF 4.0Ga NITROGEN-BEARING ORGANICS IN MARTIAN CARBONATES: IMPLICATIONS FOR NOACHIAN NITROGEN-CYCLE.** M. Koike<sup>1\*</sup>, R. Nakada<sup>2</sup>, I. Kajitani<sup>1,3</sup>, T. Usui<sup>1,4</sup>, Y. Tamenori<sup>5</sup>, H. Sugahara<sup>1</sup>, and A. Kobayashi<sup>4,6</sup>, <sup>1</sup>ISAS, JAXA (\*email: [mizuhokoike.0@gmail.com](mailto:mizuhokoike.0@gmail.com)), <sup>2</sup>Kochi, JAMSTEC, <sup>3</sup>Earth & Planet. Sci., Univ. of Tokyo, <sup>4</sup>ELSI, Tokyo Tech, <sup>5</sup>Research & Utilization, JASRI, <sup>6</sup>Geol. & Planet. Sci., Caltech

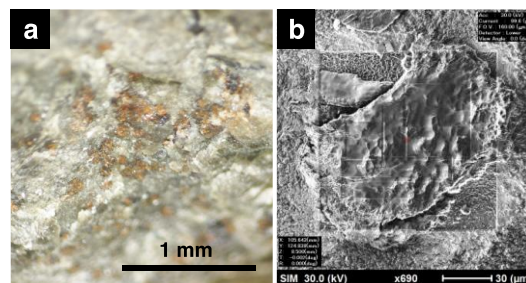
**Introduction:** Revealing the origin of organic material on Mars is a hot topic in the current planetary science. NASA's Curiosity recently reported various organics from 3.5 Ga mudstones in Gale crater [1]. Organics were also detected from several Martian meteorites [2]. Allan Hills (ALH) 84001, a unique early Noachian igneous rock, is known to contain trace amounts of carbonates that precipitated through low-temperature aqueous alteration at 4.0 Ga on Mars [3]. Previous studies reported the presence of organic components in these carbonates [2], although their origins are not clear mainly due to terrestrial contamination.

Nitrogen (N), an essential element for terrestrial biochemistry, is a useful geochemical tracer for co-evolutions of planetary atmospheres, hydrospheres, lithospheres, and biospheres. *In-situ* chemical speciation of N from Martian samples will provide valuable insights. In this study, we first accomplished the micrometer-scale *in-situ* analyses of N K-edge X-ray absorption near-edge structure ( $\mu$ -XANES) on the ALH carbonates.

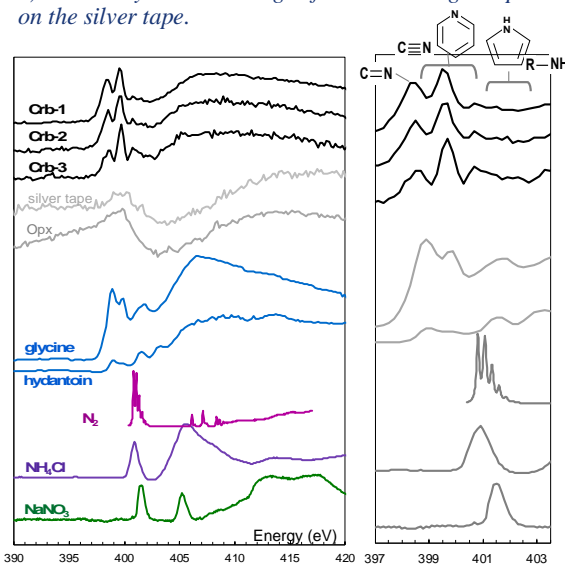
**Sample Preparations:** A rock fragment of ALH 84001, 248, was allocated from the Meteoritical Working Group, NASA. Brown-orange colored carbonate globules were observed under an optical microscope (Fig. 1) in a class 100 clean room at the Earth-Life Science Institute, Tokyo Institute of Technology. The carbonates were fragile and easily peeled off from the host rock by using a silver double-sticky tape (Nisshin EM Co., Ltd.). To reduce experimental contaminations, we did not use any conventional preparation tool (e.g., epoxy resin or polishing paste). The surfaces of the plucked carbonates were further sputtered for  $\sim 1$   $\mu$ m depth by a Ga ion beam using FIB-SEM (NX 2000, Hitachi Ltd.) at Extraterrestrial Sample Curation Center, JAXA. Silicate fragments from the same ALH rock (ALH Opx) were prepared in the same manner for the contamination check.

**Measurements:** Nitrogen  $\mu$ -XANES was conducted at BL27SU of SPring-8 synchrotron facility, Japan. Three N-bearing inorganic compounds ( $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{N}_2$  gas in air) and ten N-bearing organic compounds (amino acids, amines, and heterocyclic compounds) were analyzed as the references. X-ray beam was focused using a poly capillary lens to a final spot size of 25  $\mu$ m diameter or cut by closing slit to 10

$\mu$ m (V)  $\times$  30  $\mu$ m (H). To locate the targets, X-ray fluorescence (XRF) mappings of Si, Al, Mg, Fe, O and C of the samples were scanned at first with incident photon energy of 1900 eV. The energy range for the  $\mu$ -XANES measurement was 385–425 eV with an energy step of 0.2 eV. The spectra of the references were acquired in total electron yield (TEY) mode, whereas the others were in fluorescent yield (FY) mode using a single element silicon drift detector (Amptek).



**Fig.1.** a) Optical microscopic image of ALH carbonates. b) Secondary electron image of a carbonate grain plucked on the silver tape.



**Fig.2.** Nitrogen K-edge XANES spectra of ALH carbonates and the reference materials. L; whole spectra, R: Enlarged area of the absorptions.

**Results:** Nitrogen XANES spectra of ALH carbonates present two prominent absorptions at 398.9 eV and 399.9 eV with additional smaller peak(s) at 400.7–402 eV and a broader absorption at around 408 eV (Fig. 2). These features do not match those of  $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ , or  $\text{N}_2$ , but are consistent with the absorptions

of organic imino groups, nitrile groups, N-heterocyclic groups, and/or amino groups [4]. The XANES spectra indicate that ALH carbonates contain a variety of N-bearing organic compounds, whereas the contributions of inorganic N are insignificant. In contrast, N XANES spectra of ALH Opx and the silver tape do not present any significant features, suggesting that the possibility of our experimental contamination can be ignored.

#### Discussion:

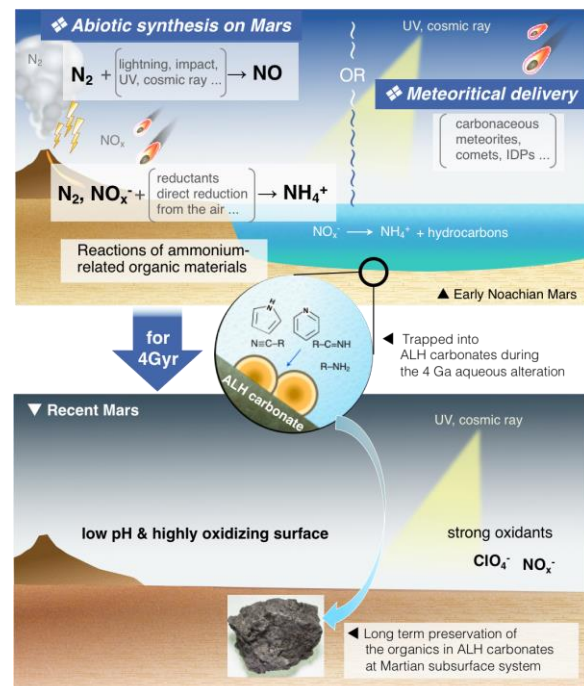
***Martian or terrestrial?*** When analyzing extraterrestrial organic matter, terrestrial contamination is always a serious concern. The experimental contamination was minimized by our careful preparations and examinations as described above. However, terrestrial carbon may have been incorporated into the meteorite through Antarctic ice meltwater. Bulk destructive studies reported the severe Antarctic contamination [e.g., 5,6]. Although it is difficult to exclude all possible contamination, our *in-situ* analyses reduce such risk by focusing on the fresh interiors of the individual grains.

***Long-term preservation of Martian organics.*** In the case of Martian origin, the N-bearing organics should have survived since early Noachian. Strong oxidants, such as perchlorate ( $\text{ClO}_4^-$ ) and nitrogen oxides ( $\text{NO}_x$ ) degrade organics. Perchlorate and  $\text{NO}_x$  were found both from present Martian regolith and Amazonian-aged young meteorites [7–10]. However, our ALH carbonates do not show the feature of  $\text{NO}_x$ , suggesting that the 4 Ga fluid, from which the carbonates precipitated on ALH host rock, was less oxidizing compared to the present Martian surface. This is consistent with an estimated Eh-pH range ( $\text{pH} = 8.7 - 11.3$ ,  $\text{Eh} = -0.46 - 0.76\text{V}$ ) [11]. Under this condition, the thermodynamically stable form of N in water is  $\text{N}_2(\text{aq})$  and/or  $\text{NH}_4^+$ . The N-bearing organics could have survived in the 4 Ga fluid, which was subsequently trapped and preserved in alteration minerals (i.e., ALH carbonates) at Martian subsurface system for billions of years.

***Origin for the N-bearing organics on early Mars.*** Possible origins for Martian organics are (a) *in-situ* synthesis and/or (b) meteoritical supply (Fig. 3). In the case (a), the fixation of N is required at first to produce N-bearing organic compounds, because atmospheric  $\text{N}_2$  is chemically inert.  $\text{NO}_x$  is formed on Mars by several mechanisms. Reduced N (e.g.,  $\text{NH}_3$  and  $\text{CN}$ ) has not been identified mainly due to their instability on the present Martian surface. However, some abiotic paths for  $\text{NH}_3$  and  $\text{CN}$  have been proposed for Hadean Earth [12], which might have occurred on early Mars as well. Once  $\text{NH}_3$  is formed, it behaves as an important starting chemical for more complex N-bearing molecules. (b) The meteoritic supply is also plausible. Carbonaceous chondrites contain a variety of insoluble

and soluble N-bearing molecules, such as amino acids, amines, amides, N-heterocyclic compounds, and macromolecular organic matter up to 100s ppm level. Comets and IDPs also contain various organic matter. It is possible that large amounts of them were supplied onto early Mars without degradation, although the influx rate is not determined quantitatively.

Whatever the origin, the presence of Martian organic and reduced forms of N indicates the importance of ‘Martian nitrogen-cycle’. If considerable amounts of organics are preserved at the subsurface of Mars over a geological time scale, they may evolve into more complicated compounds. 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.



**Fig.3.** Possible origins and history for the N-bearing organic components in ALH carbonates.

**References:** [1] Eigenbrode J. L. et al. (2018) *Science* 360, 1096–1101. [2] Steele A. et al. (2016) *Meteoritics & Planet. Sci.*, 51, 2203–2225. [3] Borg L. E. et al. (1999) *Science* 286, 90–94. [4] Leinweber P. et al. (2007) *J. Synchrotron Rad.* 14, 500–511. [5] Bada J. L. et al. (1998) *Science*, 279, 362–365. [6] Jull, A. J. T. et al. (1998) *Science* 279, 366–369. [7] Kounaves, S. P., et al. (2014) *Icarus* 232, 226–231. [8] Stern J. C. et al. (2015) *Proc. Natl Acad. Sci. USA.* 112, 4245–4250. [9] Kounaves, S. P., et al. (2014) *Icarus* 229, 206–213. [10] Jaramillo, E. A. et al. (2019) *Geophys. Res. Lett.* 46 3090–3098. [11] Kajitani, I. et al. (2020) *LPSC LI* (this conference). [12] Kitadai, N. et al. (2018) *Geoscience Frontiers* 9, 1117–1153.