

## *In situ* preservation of nitrogen-bearing organic matter in carbonates from ancient Mars

Mars was once warm enough to maintain persistent liquid water around 4-billion-years ago (Ga), where by the surface environment would have been favorable to sustain life [1]. Thus, the question of “life on Mars” has driven intensive studies of the Red Planet. In the late 1970s, NASA’s Viking lander reported organic matter for the first time. More recently, in the 2010s, NASA’s Curiosity rover detected various C- and S-bearing molecules from 3.5 Ga mudstones at Gale crater. Such findings strongly indicate the importance of organic matter in Martian near-surface systems. However, little is known about its origin, distribution, preservation and evolution, as well as its possible relationship to biological activity. The international Mars science community has set a long-term goal toward achieving Mars sample return (MSR) to search for biosignatures/biomarkers. Yet, the success of MSR must be awaited until the mid-2030s. Along with planetary explorations, laboratory analyses of Martian meteorites also provide important insights. In particular, a unique Martian meteorite named Allan Hills (ALH) 84001 is known to contain carbonate minerals that precipitated from aqueous fluid at 4 Ga Mars. In our latest study [2], we found that these carbonates preserved indigenous nitrogen-bearing organic matter, thanks to our recently developed analytical technique for high-spatial-resolution *in situ* nitrogen speciation.

Nitrogen (N) is one of the essential elements for life on Earth. In addition, N is a useful geochemical tracer to reveal the co-evolution process of the atmosphere–hydrosphere–lithosphere–biosphere of the planets. On Mars, chemical/isotopic signatures of N are not well understood because of analytical difficulties. Most previous studies relied on destructive analyses of bulk rock of Martian meteorites, whereby severe contamination from the environments is a serious possibility.

We conducted an *in situ* N *K*-edge micro-X-ray absorption near-edge structure ( $\mu$ -XANES) analysis at SPRING-8 BL27SU, which enabled the near-contamination-free measurement of micrometer-scale N species in the carbonates from ALH 84001 [2]. Since the target carbonate grains are small ( $\leq \sim 100 \mu\text{m}$  in diameter; Fig. 1), the X-ray beam was focused using a polycapillary lens to a final spot of  $25 \mu\text{m}$  diameter or cut by closing slits  $10 \mu\text{m}(\text{V}) \times 30 \mu\text{m}(\text{H})$ . Furthermore, to reduce experimental contamination, we did not use any conventional preparation tool (e.g., epoxy resin or polishing paste). The surfaces of the

carbonates were sputtered to  $\sim 1 \mu\text{m}$  in depth using a FIB-SEM Ga ion beam at Extraterrestrial Sample Curation Center, JAXA.

Nitrogen XANES spectra present two prominent absorption peaks at 398.9 and 399.9 eV with a broader absorption peak at around 408 eV (Fig. 1). Several smaller peaks are also seen between 400.7 and 402 eV. Such spectral shapes do not match XANES spectra of dinitrogen ( $\text{N}_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), or ammonium chloride ( $\text{NH}_4\text{Cl}$ ). On the other hand, they are consistent with the absorptions of organic imino and nitrile groups. Pyridinic N-heterocyclic groups also have peaks in a similar energy range. The peaks between 400.7 and 402 eV may correspond to pyrrolic N-heterocyclic, amide, and/or amino groups. Our XANES data indicate that the carbonates in ALH 84001 contain various N-bearing organic components. The plausible groups are the imino, nitrile, N-heterocyclic, amide, and/or amino groups. The contributions from inorganic N (e.g.,  $\text{N}_2$ , nitrate, or ammonium salt) are negligible.

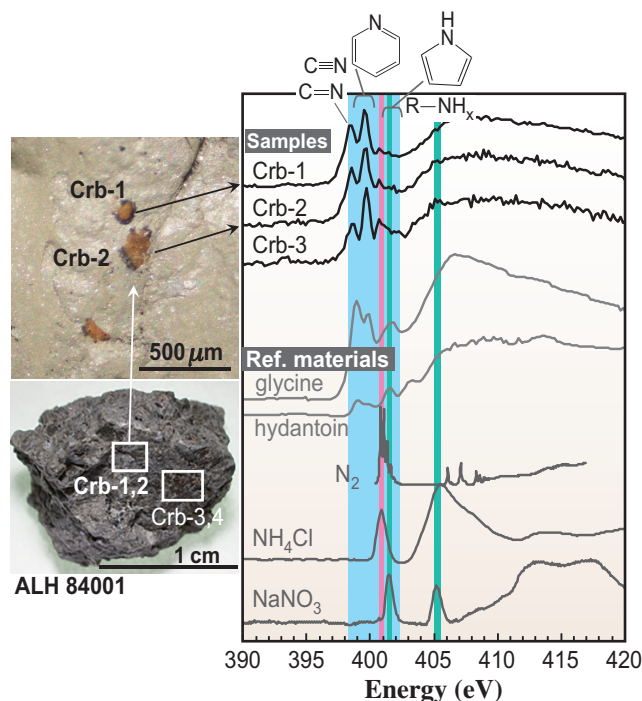


Fig. 1. Nitrogen *K*-edge XANES spectra (right) of the carbonate grains (upper left) acquired from the host rock of ALH 84001 (lower left) along with the XANES spectra of the selected reference N-bearing compounds. The significant absorption energies for  $\text{N}_2$  (400.8 eV; magenta),  $\text{NaNO}_3$  (401.4 and 405.2 eV; green), and N-bearing organics (398–402.5 eV; light blue) are highlighted. Images modified after [2].

The N-bearing organics found in the ALH 84001 carbonates are expected to have survived in the Martian near-surface system since 4 Ga. The 4-Ga aqueous fluid, from which these carbonates precipitated, must have provided nondestructive environments for the organics (i.e., moderate conditions of pH, oxidation-reduction potential (Eh), UV, and cosmic-ray irradiation). Strong oxidants, such as chlorine oxides ( $\text{ClO}_x$ ) and nitrogen oxides ( $\text{NO}_x$ ), are known to exist in the current Martian near-surface system and to degrade its organics. In contrast, our N-XANES results suggest the absence of nitrogen oxides of the ALH 84001 carbonates. Our on-going sulfur K-edge study of the same samples proposes moderate oxidation to a neutral condition for the 4-Ga Martian fluid (pH = 6–9 and Eh =  $-0.25$ – $0$  V). The coexisting N in that fluid should be in the form of  $\text{N}_2$  (aq) and/or  $\text{NH}_4^+$ . It is inferred that early Mars had a less oxidizing surface than that of today, at least locally and temporally. Our finding further implies that the organic matter could have survived in the carbonates (and other alteration minerals) on Mars over a long geological time.

Possible origins of the Martian organics are (1) *in situ* synthesis and/or (2) meteoritic supply (Fig. 2). In Case 1, chemically inert atmospheric  $\text{N}_2$  should first be fixed into accessible forms.  $\text{NO}_x$  could have

been produced on early Mars via thermal shock by volcanic lightning, meteorite impacts, and/or solar/cosmic X-ray irradiations. Moreover, reduced N (e.g., ammonia and hydrogen cyanide) has not been identified on Mars. However, several abiotic paths for the formation of reduced N species are proposed for ancient Earth's environment, such as the reduction of  $\text{NO}_x$  by metallic iron and/or aqueous solutions, as well as the photochemical reduction of atmospheric  $\text{N}_2$ . Similar processes could have occurred on early Mars. In Case 2, the meteoritic supply of organic compounds is also a plausible source. Carbonaceous chondrites are known to contain various insoluble and soluble N-bearing organic groups at sub-ppm to  $10^2$ -order ppm levels. Interplanetary dust particles and comets also contain various components. The previous detection of organic matter in a much younger Martian meteorite may reflect such an extra-Martian origin.

Whatever the origin, the organic and reduced forms of N in ancient Mars indicate the presence of a "Martian N-cycle." If considerable amounts and variations of organic compounds were produced, delivered, and preserved in the Martian near-surface system over geological time scales, they may have had a chance to evolve into more complex forms. It is expected that additional hidden records of the Martian N-cycle will be acquired by future investigations, including a sample return mission from the Martian moons (Martian Moons eXploration; MMX) [3], MSR missions [4], and exploration of the Martian subsurface, as well as further advanced studies of Martian meteorites.

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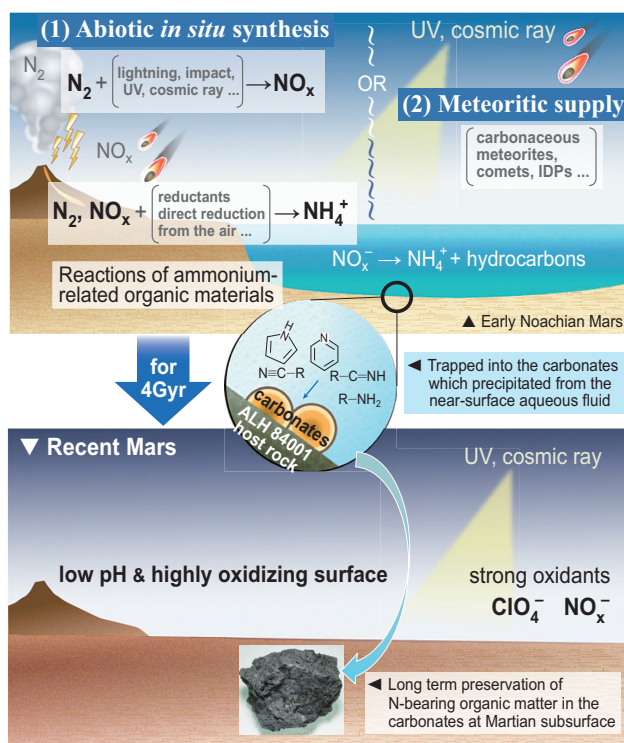


Fig. 2. Schematic image of the 4 Ga and current Martian near-surface systems. The ancient N-bearing organics were trapped and preserved in the carbonates over geological time scales. Images modified after [2].