

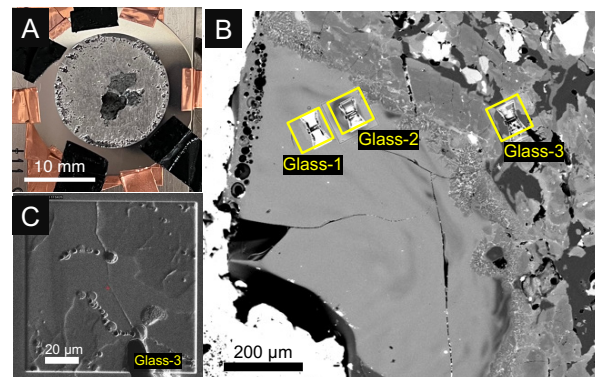
**IN-SITU NITROGEN SPECIATION OF SHERGOTTITE MARTIAN METEORITES AND TERRESTRIAL MARS ANALOG.** M. Koike<sup>1</sup>, A. Kurokawa<sup>1</sup>, K. Onishi<sup>1</sup>, R. Nakada<sup>2</sup>, Y. Sumiya<sup>1</sup>, T. Usui<sup>3</sup>, H. Sugahara<sup>3</sup>, and H. Amundsen<sup>4</sup>. <sup>1</sup>Hiroshima Univ. (Hiroshima, Japan; mizuhokoike@hiroshima-u.ac.jp), <sup>2</sup>KOCHI, JAMSTEC, <sup>3</sup>ISAS, JAXA, <sup>4</sup>CENSSS, Univ. of Oslo, Norway.

**Introduction:** Elucidation of past environment on Mars and its habitability is the hot topic. Nitrogen (N) is an essential element for terrestrial life, as well as an important environmental tracer for terrestrial planets. On Mars, no direct mechanism has been confirmed that fixes atmospheric N<sub>2</sub> into N-bearing compounds. However, recent explorations identified trace nitrate-bearing (NO<sub>3</sub>) salts from ~3.5 Ga sedimentary rocks at Gale crater [1, 2]. Martian meteorites also provide important clues. The 4.0 Ga Martian carbonate minerals in the Allan Hills (ALH) 84001 meteorite were reported to contain N-bearing organic matter [3]. Although origin of the organics has not been confirmed, it is likely that the N-bearing compounds were fixed and preserved at early Martian (near-)surface. On ancient Mars, “nitrogen-cycle” may have been active in atmosphere – geosphere – hydrosphere (plus, potential biosphere). To reveal the long-term evolution of Martian nitrogen-cycle and its relationship with the habitability, it is important to access geochemical records in the rock samples. Here, we conduct in-situ nitrogen speciation analyses of two young shergottite meteorites (Tissint and NWA 13367) and a terrestrial Mars analog.

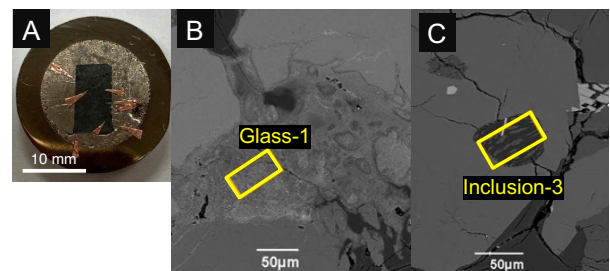
**Samples:** Two heavily shocked shergottites, Tissint and Northwest Africa (NWA) 13367, are selected for the nitrogen speciation. Tissint is an ~600 Ma olivine-phylic shergottite, observed to fall in Morocco in 2011. Abundant dark-colored shock-melted glassy areas (shock glass) in Tissint is known to concentrate Martian volatiles [4, 5]. NWA 13367 is a recently found peridotitic shergottite [6]. Its detailed mineralogy or geochemistry has not been reported. Our main targets are (i) the shock glasses in the two meteorites, where Martian atmospheric and topsoil components may have been trapped. In addition, (ii) magmatic inclusions of olivine phenocrysts in NWA 13367 might have contained Martian interior (mantle) volatiles.

To estimate early hydrous environments on Mars, we also focus on a terrestrial basaltic breccia from Bockfjord Volcanic Complex (BVC), Svalbard, Norway, regarding as potential analog for Noachian Martian altered rocks [7, 8]. Secondary carbonates and silicates in the BVC basalts have similarities to those in ALH 84001. Their alteration conditions are studied by the ongoing project [8]. In the present study, we aim to reveal (iii) the nitrogen chemical records in those carbonates and silicates.

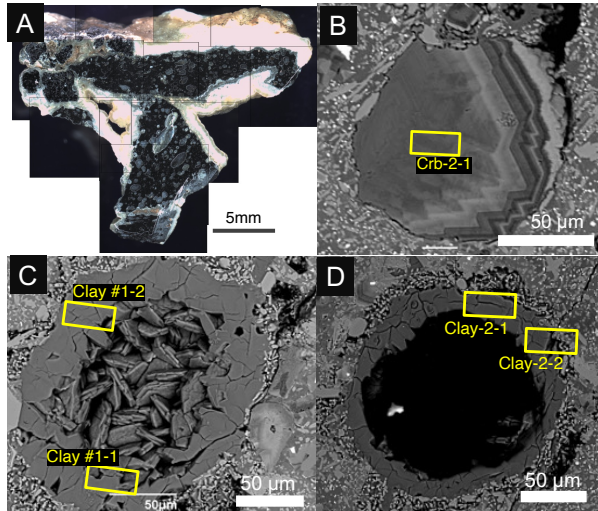
**Methods:** Thick sections of Tissint and NWA 13367 were pushed onto indium mounds (Fig. 1, 2). The two meteorites and a rock chip of the BVC basalt (Fig. 3) was polished using nitrogen-free Al<sub>2</sub>O<sub>3</sub> powder. All samples were then coated by carbon or osmium and observed by a SEM-EDS (JSM-6390) at Hiroshima. In Tissint, large bubble-rich glasses with pyroxene and plagioclase compositions are observed (Fig. 1B). NWA 13367 also has shock glassy areas, while they do not show observable-sized bubble (Fig. 2B). In addition to the shock glasses, magmatic inclusions in the sub-mm sized olivines are observed (Fig. 2C). In the BVC basalt, numerous carbonate globules with large chemical variations are identified (Fig. 3B). It also contains aggregates of zeolite-like clay minerals (Fig. 3C, D). After the SEM observation, the samples’ surfaces were additionally etched by Ga-ion beam using FIB (NX 2000 at JAXA) to reduce adhered contaminants before conducting the in-situ speciation.



**Fig.1.** Tissint. A) whole image of the In-mount. B) BSE image of the shock glassy areas. Yellow squares indicate the XANES targets. C) Enlarged SIM image of the bubble-rich areas at “Glass-3”.



**Fig.2.** NWA 13367. A) whole image of the In-mount. B, C) BSE images of the shock glass (B) and inclusion in olivine (C). Yellow squares indicate the XANES targets.



**Fig.3.** A) A whole image of the BVC basalt rock chip. B-D) BSE images of the carbonates (B) and the clay minerals (C-D). Yellow squares indicate the XANES targets.

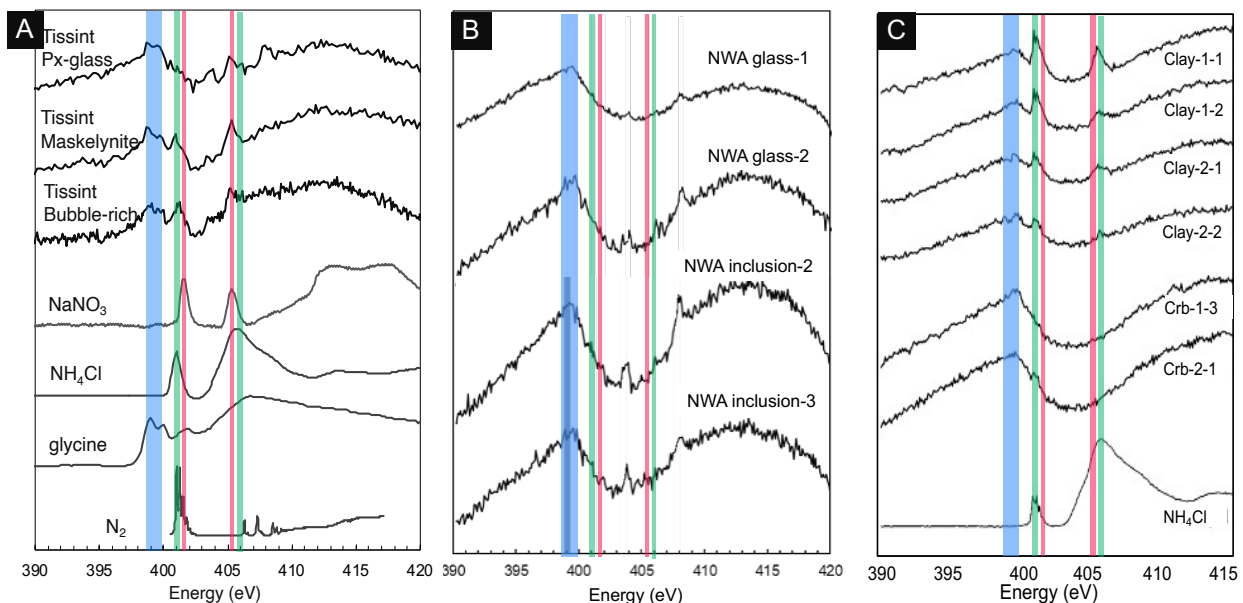
Nitrogen K-edge micro- X-ray absorption near edge structure ( $\mu$ -XANES) spectra of the samples were measured at BL27SU of SPring-8 synchrotron facility in Hyogo, Japan (from 2019 to 2021). The X-ray beam was cut by closing slit to spot size of 10  $\mu\text{m}$  (V)  $\times$  30  $\mu\text{m}$  (H) on the sample surface. For the  $\mu$ -XANES measurements, energy range was at 390 – 420 eV with a step of 0.2 eV. Fluorescent yield (FY) mode was applied to acquire trace N-related signals from the samples. The obtained spectra are then compared with the references [3] to identify N-related peaks if any.

**Results and Discussion:** For Tissint, XANES spectra of the shock glasses present the nitrate ( $\text{NO}_3$ )-

related peaks at 401.6 eV and 405.2 eV (Fig. 4A). The spectra also show broad peaks at  $\sim$ 399–400 eV related to N-bearing organics, although the possibility of terrestrial contamination cannot be ruled out. Contrary to Tissint, no N-related peak is observed from the shock glasses in NWA 13367 (Fig. 4B). XANES spectra of the inclusions show the sharp peaks at  $\sim$ 403 eV and 408 eV (Fig. 4B), which is interpreted as the Sc  $L_{\text{II}}$ ,  $L_{\text{III}}$ -edge absorptions. To summarize, Tissint contain Martian nitrates that may be trapped during the meteorite's ejection. The apparent absence in NWA 13367, in contrast, indicates that the nitrates and other N-related materials are heterogeneously distributed on Mars.

XANES spectra of the carbonates and the clay minerals in BVC basalt are summarized in Fig. 4C. While the carbonates do not show any N-related peak, the clay minerals present significant absorptions at 400.8 eV and 405.8 eV, related to ammonium ( $\text{NH}_4$ )-bearing salts. It is inferred that during the alteration of BVC, either hydrothermal or cryogenic process (e.g., [8]), the host basaltic rock may have been in contact the  $\text{NH}_4$ -bearing solution.

**References:** [1] Stern, J.C. et al. (2015) PNAS 112, 4245–4250. [2] Stern, J. C. et al. (2017) GRL 44, 2643–2651. [3] Koike, M. et al. (2020) Nature Comm. 11, 1988. [4] Chennaoui Audjehane et al. (2012) Science, 338, 785–788. [5] Chen, Y. et al. (2015) EPSL 425, 55–63. [6] Gattacceca et al. (2021) MaPS, 56, 1626–1630. [7] Amundsen, H.E.F. et al. (2011) LPSC XLII abstract #2223. [8] Wang, C. et al. (2023) LPSC LIV (this conference)



**Fig.4.** Nitrogen XANES spectra of A) Tissint shock glasses (upper three data) with N-reference materials (lower four), B) the shock glasses and inclusions of NWA 13367, C) the clay mineral (upper four) and carbonates (middle two) of BVC basalt. Color bars indicate the absorptions of nitrate ( $\text{NO}_3$ ): red, ammonium ( $\text{NH}_4$ ): green, and N-organics: blue, respectively.