In-situ characterization of carbonaceous materials in the Northwest Africa 7034

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Introduction: Martian basaltic breccia Northwest Africa 7034 (hereafter, NWA 7034) has the high contents of bulk carbon (2080 ± 80 ppm) and water (6190 ± 620 ppm) [1]. The bulk-rock composition of NWA 7034 is similar to that of Martian surface collected by orbital satellites and rovers, thus the NWA 7034 becomes a direct linkage between Martian meteorites and Martian surface materials [1]. Many alteration related products (for example, organic carbon, carbonate and ferric hydroxides) exist between basaltic mineral fragments as matrix in NWA 7034 [1]. It is implied that the alteration products, which are akin to the near-surface materials of the Mars, occurred by hydrothermal alteration induced by magmatic activities [1, 2]. It is also suggested that the alteration products were formed by fluid discharged from meteoroids when the meteoroids collided on the Mars during early Amazonian epoch (2.1 billion years ago: crystallization period of NWA 7034) [1, 2]. A few kinds of carbonaceous materials are reported from Martian meteorites and Martian surface materials; 1) reduced macromolecular carbon (MMC) formed through magmatic mineral crystallization process in shergottites, 2) δD-rich carbon vein/grain formed by Martian surface fluid in shergottites, 3) siderite-bearing alteration products (iddingsite) in nakhlites, and 4) chlorobenzene-like carbon in the Martian sub-surface soil (mudstone) verified by curiosity rover observation [*e.g.,* 3-6]. In this study, we work on characterizing the functional groups distribution/composition, textures, and isotpic signatures of the carbonaceous materials in NWA 7034 using our STXM based multi-probe *in-situ* microscopic techniques to clarify the origin of these carbonaceous materials.

Sample and Experiments: NWA 7034 (0.0583 g) was crushed into a powder. We used the powder to determine bulk-rock constituent of NWA 7034 by Rigaku XRD MultiFlex at Hiroshima University. Carbon concentration in the powder was measured by combustion analysis using Flash EA1112 (Thermo Finnigan) at Kochi Core Center, Kochi University. A polished chip sample of NWA 7034 (7×10 mm) was prepared through dry polishing process for our STXM based TEM/NanoSIMS microscopic *in-situ* analysis, apart from bulk analysis. Fine-textures of carbon-rich portions in the polished sample were observed using FE-SEM/EDS (JEOL JSM-7100F) at NIPR. A laser micro-Raman spectroscope (Renishaw inVia) was employed for verifying the carbonaceous materials (G-band width/ G-band center) at NIPR. The ultra-thin foils of selected carbon-rich portions were prepared by a FIB system (Hitachi SMI3200, and SMI4050) at Kochi Institute for Core Sample Research JAMSTEC and KEK-Photon Factory for STXM, FE-TEM/STEM and NanoSIMS analyses. FIB-assisted STXM analysis was conducted for C-, N-, O-, Na-, and Fe-NEXAFS at PF BL13A (compact STXM). TEM/STEM observation using JEOL JEM-2100F was conducted for fine textural observations at Tohoku University after the STXM measurements. Finally, C, O, and D isotope imaging using CAMECA NanoSIMS was conducted to obtain their isotopic characteristics at the Kochi Institute for Core Sample Research, JAMSTEC.

Results: Bulk-rock constituent of NWA 7034 studied here (plagioclase: 37.4 ± 1.3%, low-Ca pyroxene: 18.3 ± 4.1%, iron oxides: 22.7 ± 2.5%, Ca pyroxene 16.2 ± 1.7% and alkali-feldspar: 5.5 ± 1.5%) was consistent with previous study [1]. Bulk-rock carbon content was 400 ± 10 ppm, which is smaller than previous studies (~ 2080 ± 80 ppm) [1], although the measured amount is several ten timse higher than thoes of SNC meteorites [3]. Raman D/G band ratios (G-band width (FWHM) range: 90–150, G-band center range: 1565–1595 cm^{-1}) were consistent with those of Martian carbonaceous materials [3, 7].

STXM C-, N- and O-NEXAFS indicated that there were two different types of carbonaceous materials in NWA 7034; i.e., a) N-rich and b) N-poor carbonaceous materials. N-rich and N-poor carbonaceous materials are distributed in the matrix and mineral fractures, respectively. N contents in the N-poor carbonaceous materials are below the detection limit of STXM transmission mode (below sub percent order). From C-, N- and O-NEXAFS, N-rich carbonaceous materials have C*=C (aromatic C), C=C-C*=O (vinyl-keto bond), C*≡N (nitrile), NHx (C*=O)C (amidyl) and OR(C*=O)C (carboxylic C). In contrast, N-poor carbonaceous materials have aromatic C, vinyl-keto bond, carboxylic C, and accompany Ca (or Ca-Mg) carbonate. Although C-NEXAFS study for Matrian carbonaceous materials is very limited, the presence of aromatic C, vinyl-keto bond, and carboxylic C peaks are similar to the C-NEXAFS features of opaque rim materials of carbonates in ALH 84001

[8]. In addition, C-NEXAFS features of both N-rich and N-poor carbonaceous materials is different from terrestrial organic matters but broadly consistent to extraterrestrial organic matters [9, 10].

TEM observations revealed that both N-rich and N-poor carbon in NWA 7034 is amorphous and partly be foamed, which may be suggestive of thermal metamorphism. Fine-grained secondary minerals (*e.g.,* calcite and halite) were embedded both into the N-rich and N-poor carbonaceous materials. Although TEM images and Fe-NEXAFS imply the presence of clay minerals in the carbonaceous materials, we could not take adequate their SAED patterns because they were too fine-grained.

$\delta^{13}C$ of several carbonaceous materials were determined by NanoSIMS analysis. $\delta^{13}C$ values for N-rich and N-poor regions of carbonaceous materials were 9.58 ± 8.13 ‰ and 28.03 ± 11.9 ‰, respectively. Both of them are different from the $\delta^{13}C$ values of the carbonaceous materials enclosed in minerals as inclusions in NWA 7034 (-23.4 ± 0.73 ‰). The $\delta^{13}C$ value of N-rich carbonaceous materials is broadly consistent with that of bulk-rock NWA 7034 (-3.0 ± 0.16 ‰, [1]) within analytical error. However, the $\delta^{13}C$ values for N-rich and N-poor regions are consistent not only with those for Martian atmosphere but also those for Martian carbonate which may reflect atmospheric value of their precipitation periods [11, 12]. This result implies that the possibility of not only the contribution of magmatic components ($\delta^{13}C$ = -20 to -30 ‰), but also that of atmospheric component (enriched in $\delta^{13}C$) to the carbonaceous materials in NWA 7034. The δD value of the N-rich carbonaceous material was 373 ± 68 ‰ is slightly above of upper limit of Martian mantle value (275 ‰) [13]. The $\delta^{13}C$ and $\delta^{18}O$ of carbonate mineral adjacent to the N-rich carbonaceous materials was 5 ± 20 ‰ and 17 ± 6 ‰ respectively, which is similar to carbonate that could form from modern Martian atmosphere rather than match with those of Martian carbonate [11, 12].

Discussion: It is considered that the N-poor carbonaceous materials occurring in the mineral fractures of NWA 7034 are similar to MMC based on their occurrences and Raman D/G band ratios [3]. It is unlikely that the N-rich carbonaceous materials occurring in the matrix originate from terrestrial materials, because representative terrestrial organic matter (such as humic substances and soil organic matter) has only C=C, C-OH, O=C-OH, and no C≡N [*e.g.,* 14, 15] although the C-and N-NEXAFS obtained from the N-rich carbonaceous materials indicate the existence of C≡N bond. The δD value of the N-rich carbonaceous material was 373 ± 68 ‰ (partly near 1000 ‰) which is slightly higher than that of Martian mantle value (275 ‰) but lower than that of typical Martian surface water [13]. It is noted that the measured δD values are also similar to the maximum bulk-rock step heating value: $\delta D_{heating\ 804C^{o}}$ = +319 ‰ and $\delta D_{heating\ 1014C^{o}}$ = +327 ‰ of NWA 7034 [1]. These bulk-rock step heating value are lower than Martian atmospheric water and atmospheric exchangeable near-surface water (δD > 3000 ‰) but agree with surficial water mixed reservoir such as subsurface ice and hydrated crust on Mars (δD = 275 to 1500 ‰) [13, 16]. This observed δD value in N-rich carbonaceous materials implies that Martian surface water [13, 16] might be marginally involved during the formation of the carbonaceous materials. The presence of the fine clay minerals in the N-rich carbonaceous materials also supports this implication. STXM-TEM/STEM supported positive isotopes results implied that the carbonaceous materials in NWA 7034 include Martian surface component (high $\delta^{13}C$ and δD), and this high temperature positive value carbonaceous material is one of the distinct Martian origin reservoirs.

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