ISOTOPICALLY ANOMALOUS ORGANIC MATTERS IN MURCHISON AND NORTHWEST AFRICA 801.
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Introduction: Recent studies reported extreme D- and ^{15}N-rich organic matters in the carbonaceous chondrites [1, 2]. The D- and ^{15}N-enrichment have been considered to be produced by chemical reaction in the cold molecular cloud and outer solar nebula [3, 4]. However, although both large D- and ^{15}N-enrichment has been predicted to produce by ion-molecule reaction at low-temperature, isotope imaging of the chondritic organic matters has shown that the largest D-enrichments and the largest ^{15}N-enrichments are not spatially correlated [1, 5]. Isotopic characteristics of individual isotopically anomalous organic matters in carbonaceous chondrites might provides us an important key to understand their origin and evolution. In this study, we survey organic matters with large D- and ^{15}N-enrichment in carbonaceous chondrites by in-situ analysis using isotope imaging.

Experimental: Polished thin sections of Murchison (CM2) and Northwest Africa (NWA) 801 (CR2) were used in this study. The thin sections were covered with a 30 nm thick carbon film for isotope and elemental analyses.

Hydrogen and nitrogen isotopes were measured on the thin sections by in situ quantitative isotope ratio imaging (isotopography) using HokuDai isotope microscope system (Cameca ims-1270 equipped with SCAPS [6]). The sample surface was homogeneously irradiated over a field area using a broad Cs^+ primary beam of ~60 µm in diameter. The primary beam was set to 20 keV and 1 nA. A typical incident electron gun was utilized for charge compensation of the analysis area. We acquired the following negative secondary ion images (isotopographs) for each analyzing field as a sequence of $^{12}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, $^{12}C^{14}N^-$, $^{12}C^-$, H^-, D^-, H^- and $^{12}C^-$, typically. A 150 µm contrast aperture (CA) was used for H-isotopes, and 50 µm CA for others. Lateral resolutions of the secondary ion images are ~0.3 µm for $^{12}C^{14}N^-$ and $^{12}C^-$, and ~1.1 µm for H^-. H isotopic composition of the matrix of Murchison and NWA 801 is normalized to a reported value of bulk composition for Murchison and phyllosilicate of Renazzo CR2 [7] for NWA 801, respectively. N isotopic compositions of matrix of Murchison and NWA 801 are normalized to bulk composition of Murchison and CR2 chondrites [8], respectively. The selection criterion for distinguishing isotopically anomalous matter is that one of their isotopic ratios is 2σ away from the 3σ the distribution of the surrounding matrix.

Isotopically anomalous spots were located in back-scattered electron (BSE) images using C elemental map obtained by FE-SEM-EDS system. (JEOL JSM-7000F, Oxford INCA Energy).

Results: Numbers of 17 and 11 isotopically anomalous carbonaceous spots were found in isotopographs (e.g. Fig. 1) of 44,400 µm^2 (12 matrix areas) and 76,600 µm^2 (25 matrix areas) for Murchison and NWA 801, respectively. Maximum of D- and ^{15}N-enrichments of the carbonaceous spots were δD = 2,920‰ and δ^{15}N = 2,620‰ for Murchison, and δD = 7,920‰ and δ^{15}N = 2,150‰ for NWA 801. Larger D-enrichments are not always associated with larger ^{15}N-enrichments in the carbonaceous spots (Fig. 2). Fractions of D-rich, ^{15}N-rich, and D- and ^{15}N-rich carbonaceous spots are shown in Fig. 3. Most of the isotopically anomalous carbonaceous spots found in Murchison were enriched in ^{15}N, whereas fraction of D-rich carbonaceous spots in NWA 801 are comparable to that of ^{15}N-rich carbonaceous spots.

Isotopically anomalous carbonaceous matters in Murchison and NWA 801 were identified by FE-SEM-EDS. They were sub-micron sized single globule or aggregated globules that are similar to our previous report from NWA 801 [2]. These carbonaceous matters showed no clear correlation between the morphology (single globules or aggregated globules) and the H and N isotopic compositions.

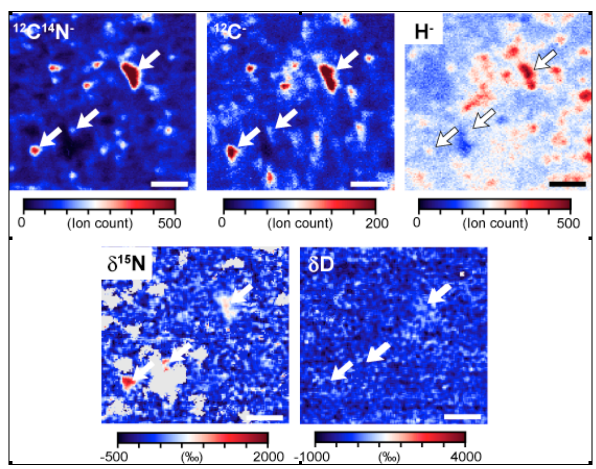

Fig. 1. Isotopographs of a ^{15}N-rich carbonaceous spots (indicated by white arrows) in matrix of Murchison. Gray masks correspond to area with low CN– or H– intensity. Scales show 5 µm.

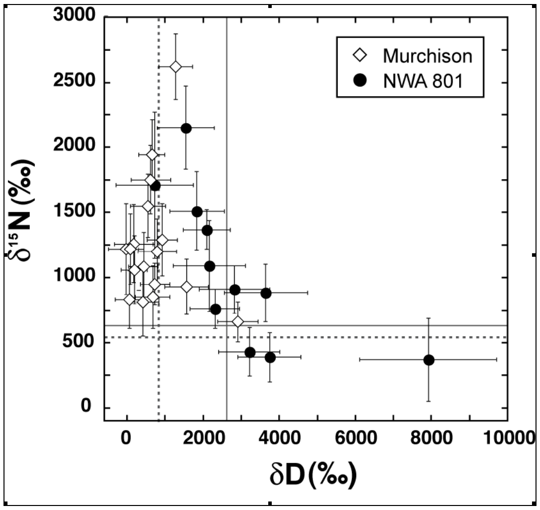

Fig. 2 H and N isotopic compositions of isotopically anomalous carbonaceous spots of Murchison and NWA 801. Gray line and dashed line show approximate lowest limit for isotope anomaly for NWA 801 and Murchison, respectively.

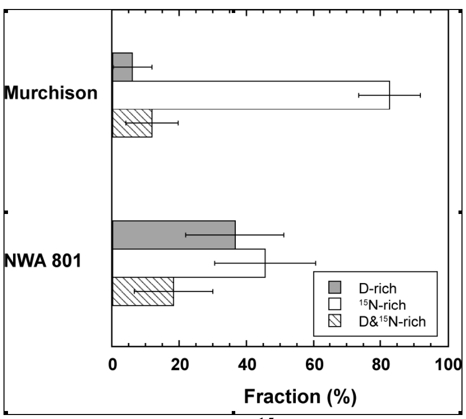

Fig. 3 Abundance of D-rich, ^{15}N-rich, and D- and ^{15}N-rich carbonaceous spots in Murchison and NWA 801.

Discussions: D- and ^{15}N-enrichment and association of nitrogen and hydrogen components suggest that the isotopically anomalous carbonaceous spots are corresponding to organic matters. Isotopic compositions of the isotopically anomalous organic matters found in this study (Fig. 2) can be classified into three groups: Extremely ^{15}N-rich but not associated with large D-enrichment (group A), extremely D-rich but not associated with large ^{15}N-enrichment (group B), and highly enriched in both D and ^{15}N (group C). Decoupled D- and ^{15}N-enrichment suggests their multiple origin.

Ion molecule reaction in the cold molecular cloud or perhaps in outer solar nebula could have produced organic molecules with group A, B, and C isotopic composition in gas-phase molecules or ice grain, if we consider spin dependence ion-molecule reaction suggested in most recent model [9]. In addition, D-rich molecules suggested to be produced at even 70 K in gas-phase molecules [3], whereas large ^{15}N fractionation suggested to occur at ~10 K [e.g. 4]. Ion-molecule reaction at 10 K < T < 70 K could also explain group B organic matters. Grain-surface reaction in the cold molecular cloud at ~10 K [10] can produce organic molecules with large D-enrichment (group B and C organic matters). Organic matters of group A or group C in this study seems to be attributed to results of self-shielding effects in outer solar nebula or perhaps in the edge of molecular cloud [e.g. 11, 12]. These isotopically anomalous molecules could have trapped in ice grain and been polymerized by chemical reaction, such as UV irradiation [13].

It is suggested that aqueous alteration on the parent body decreases D/H ratio of organic matters in carbonaceous chondrites [e.g. 14]. In addition, degree of aqueous alteration on typical CM2 chondrite has been suggested to be larger relative to CR2 chondrite [15]. Therefore, the less abundant D-rich organic matters in Murchison may have been attributed to loss of the isotopically heavy H by aqueous alteration.

Single or aggregated organic globules with D- and/or ^{15}N-enrichments in carbonaceous chondrites also were observed by previous studies [2, 16], suggesting that they were ubiquitous in early solar nebula. Although H isotopic compositions seemed to be affected by aqueous alteration, no clear correlation with the isotopic compositions and morphology (result of D-rich organic matters in NWA 801 is consistent with our previous report [2]). These results may suggest that organic matters with various morphology and various H and N isotopic compositions have been formed in the cold molecular cloud and/or outer solar nebula.

References: [1] Busemann et al. (2006) *Science* 312, 727-730. [2] Hashiguchi et al. (2011) Workshop on Formation of the First Solids in Early Solar System. (abstract #9012). [3] Millar et al. (1989) *ApJ* 340, 906-920. [4] Rodgers and Charnley (2008) *ApJ* 689, 1448-1455. [5] Briani et al. (2009) *PNAS* 106, 10522-10527. [6] Yurimoto et al. (2003) *Appl. Surf. Sci.* 203-204, 793–797. [7] Deloule and Robert (1995) *Geochim. Cosmochim. Acta.* 59, 4695-4706. [8] Pearson et al. *MAPS* 41, 1291-1303. [9] Wirström et al. (2012) *ApJ* 757, L11. [10] Watanabe (2006) Recent Successes and Current Challenges, Proceedings of the IAU symposium 231. pp. 415-426. [11] Chakraborty et al. (2012) *43rd LPSC* (abstract #2347). [12] Le Petit et al. (2002) *A&A* 390, 369-381. [13] Bernstein et al. (1999) *Sci. American.* 281, 42-49. [14] Herd et al. (2011) *Science* 332, 1304-1307. [15] Brearley (2006) In Meteorites and the Early Solar System II pp. 587-624. [16] Nakamura-Messenger et al. (2006) *Science* 314, 1439-1442.