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Deuterium- and ^{15}N -signatures of organic globules in Murchison and Northwest Africa 801 meteorites

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Carbonaceous matter from the matrix of the Murchison (CM2) meteorite and Northwest Africa (NWA) 801 (CR2) meteorite that were extremely rich in deuterium (D) and ^{15}N was studied using in situ isotope imaging. The association of carbon, hydrogen, and nitrogen suggests that the carbonaceous matter was organic in nature, and the maximum magnitudes of D- and ^{15}N -enrichment in the organic matter were $\delta\text{D} = 2,880\text{\textperthousand}$ and $\delta^{15}\text{N} = 2,590\text{\textperthousand}$ in Murchison, and $\delta\text{D} = 7,500\text{\textperthousand}$ and $\delta^{15}\text{N} = 2,200\text{\textperthousand}$ in NWA 801.

The organic matter did not display a simple correlation between the magnitudes of D- and ^{15}N -enrichment, and the isotopically anomalous organic matter was classified into three types based on the H and N isotopic characteristics: extremely ^{15}N -rich without large D-enrichment (^{15}N -rich), extremely D-rich without large ^{15}N -enrichment (D-rich), and highly D- and ^{15}N -rich (D- ^{15}N -rich). The occurrence of isotopically anomalous organic matter was attributed to their origin in the molecular clouds and outer solar nebula, ion-molecule reactions at low temperatures, grain surface reactions at low temperatures, and self-shielding effects in gas phase molecules. However, the observed D- and ^{15}N -enrichment of the organic matter is much smaller than predicted by ion-molecule and grain surface reactions. This suggests a secondary modification of the H and N isotopic compositions of the organic matter in the solar nebula and in the parent body. In Murchison, the proportion of D-rich organic matter among the isotopically anomalous organic matter is smaller than in NWA 801, which presumably indicates that the D-enrichments are easily modified by aqueous alteration processes on the parent body.

Scanning electron microscopy revealed the morphology of the D- and ^{15}N -rich organic matter as aggregates of globules/particles or non-aggregated globules, where the size of each globule was $<1 \mu\text{m}$. Although there is no obvious correlation between the morphology of the organic matter and the H and N isotopic compositions, the result that Murchison contains more abundant globule/particle aggregates might suggests formation of aggregated nature due to aqueous activity.

Keywords: meteorites, isotope imaging, H and N isotope anomalies, organic matter, aqueous alteration

INTRODUCTION

Carbonaceous chondrites are the most primitive of the known meteorites, and their parent bodies were formed by the accretion of several discrete components from the early solar system, including organic carbon (up to ~4 wt%; Grady *et al.*, 2002; Sephton, 2002). Most of the organic carbon (75–99%) is present as complex macromolecular organic materials (Gilmour, 2003). The macromolecular organic materials can be extracted by acid demineralization as the residue and is defined as insoluble organic matter (IOM). IOM from carbonaceous

chondrites exhibits various hydrogen (H) and nitrogen (N) isotopic compositions (Busemann *et al.*, 2006), some of which have significant deuterium (D) and ^{15}N -enrichment, which is possibly related to their origins in the cold molecular cloud and/or in the outer solar nebula (Busemann *et al.*, 2006; Nakamura-Messenger *et al.*, 2006; Alexander *et al.*, 2007, 2010; Messenger *et al.*, 2008; Briani *et al.*, 2009; Bonal *et al.*, 2010; Remusat *et al.*, 2010; Zega *et al.*, 2010; Hashiguchi *et al.*, 2013).

Significant ^{15}N -enrichment could have been produced by ion-molecule reactions in cold molecular clouds at 10 K (Terzieva and Herbst, 2000; Charnley and Rodgers, 2002; Rodgers and Charnley, 2008), and such reactions could also produce large D-enrichment (Millar *et al.*, 1989; Roberts *et al.*, 2003). It has also been suggested that large hydrogen isotope fractionation occurred by grain-surface reactions in the molecular cloud (Watanabe, 2006; Watanabe and Kouchi, 2008). D- and ^{15}N -

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enrichments can also be produced by a self-shielding effect in the early solar nebula, and in the molecular cloud (e.g., Le Petit *et al.*, 2002; Lyons, 2009, 2010; Lyons *et al.*, 2009; Aléon, 2010; Chakraborty *et al.*, 2012). The large isotope anomaly in chondritic organic matter has been explained by these phenomena in the parent molecular cloud and in the outer protoplanetary disk of the early solar system.

The various isotopically anomalous compositions of chondritic organic matter seem to result from their different histories. The isotopic compositions and morphology of D-rich organic matter in Northwest Africa (NWA) 801 meteorites (CR2) have been investigated (Hashiguchi *et al.*, 2013), and their formation processes at low temperatures in molecular clouds and outer solar nebula were discussed. Therefore, combination studies of H and N isotopic compositions of the organic matter could provide further insights into their origin and evolution history, and address the possibility of secondary alteration of organic matter on the parent body by aqueous alteration (Sephton *et al.*, 2003; Alexander *et al.*, 2007; Yabuta *et al.*, 2007; Oba and Naraoka, 2009).

In this study, the H and N isotopic compositions of organic matter in the Murchison (CM2) and NWA 801 meteorites (CR2) were determined by *in situ* analysis, and their morphology was investigated. The origin and evolution of organic matter in space and on their parent bodies with respect to the isotopic compositions and morphology of individual organic matter are also discussed here.

EXPERIMENTAL METHODS

Sample preparation

The samples used in this study were polished thin sections of Murchison (CM2) and NWA 801 (CR2). The same thin section of NWA 801 analyzed by Hashiguchi *et al.* (2013) was used, but the areas analyzed in this study were different. The thin sections were covered with a 30 nm thick carbon film for isotope and elemental analyses, mounted in epoxy resin (BUEHLER CastoLite Resin), and polished using alumina paste. While the resin filled the cracks, penetration of the epoxy resin into the sample bodies was not observed.

Isotope ratio imaging (isotopography) for hydrogen and nitrogen

H and N isotopes on the thin sections were measured by *in situ* quantitative isotope ratio imaging (isotopography), using an isotope microscope system consisting of a secondary ion mass spectrometer (Cameca ims-1270) equipped with a stacked CMOS-type active pixel sensor (SCAPS) apparatus (Yurimoto *et al.*, 2003; Nagashima *et al.*, 2004; Kobayashi *et al.*, 2005;

Hashiguchi *et al.*, 2013).

The sample surface was homogeneously irradiated over a field area of diameter $\sim 60 \mu\text{m}$, using a broad Cs^+ primary beam set to 20 keV and 1 nA. A normal incident electron gun was utilized for charge compensation. Stigmatic images of negative secondary ions from each analysis field were acquired in the sequence $^{12}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^-$, H^- , D^- , H^- and $^{12}\text{C}^-$, and the total sputtering time for one field was typically 25 min. The exposure time was typically 5 s for $^{12}\text{C}^{14}\text{N}^-$, 100 s for $^{12}\text{C}^{15}\text{N}^-$, 5 s for H^- , 400 s for D^- , and 5 s for $^{12}\text{C}^-$, with repetition of the sequence. Lateral resolutions of the secondary ion images were different ($\sim 0.3 \mu\text{m}$ for $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^-$, and $\sim 1 \mu\text{m}$ for H^- and D^-) due to the use of different contrast aperture sizes. To reduce the consumption of D and/or ^{15}N , acquisition of the D^- and/or $^{15}\text{N}^-$ isotopographs was stopped when the image was clearly observed using the nondestructive monitoring mode, which is a significant characteristic of the SCAPS detector (Takayanagi *et al.*, 2003).

Identification of isotopically anomalous materials

Isotopographs of the H- and N-isotopes were obtained by calculating the D^-/H^- and $^{15}\text{N}^-/\text{H}^-$ intensity ratios for each pixel, respectively. The results are reported in the δ -notation, which expresses the deviation in parts per thousand from the terrestrial standard, which is the SMOW (standard mean ocean water) value for D/H, and the atmospheric value for $^{15}\text{N}/^{14}\text{N}$. To calculate the δ -values, the average values of the matrix areas in the isotopographs are assumed to correspond to bulk H and N isotopic compositions of CR2 chondrites or Murchison (Alexander *et al.*, 2012). The reported δD and $\delta^{15}\text{N}$ values for bulk Murchison are -61.7 and $45.6\text{\textperthousand}$, respectively. For NWA 801, averaged δD and $\delta^{15}\text{N}$ value of bulk CR2 chondrite ($696.22\text{\textperthousand}$ and $173.43\text{\textperthousand}$, respectively) are used. Although clay minerals could occur in the matrix of Murchison and NWA 801, the difference of matrix effect between clay minerals and organic matter could be ignored, because the difference of instrumental isotopic fractionation factors between clay minerals and organic matter (Deloule and Robert, 1995; Bonal *et al.*, 2010) were within the errors of this study.

Digital image processing using a moving average with 3×3 pixels was applied to the δD and $\delta^{15}\text{N}$ isotopographs to reduce random error caused by the low signal intensities of individual pixels. The image processing did not decrease spatial resolution of the image, because one pixel size corresponded to one third of the spatial resolution.

The abundance of D- or ^{15}N -rich materials was parameterized in several regions of interest (ROIs). For the identification of D-rich materials, all ROIs were summed as $[\delta\text{D} \text{ (or)} \delta^{15}\text{N}_{\text{ROI}} - \delta\text{D} \text{ (or)} \delta^{15}\text{N}_{\text{matrix}}] > (2\sigma_{\text{ROI}} + 3\sigma_{\text{matrix}})$. It is to be noted that all δD or $\delta^{15}\text{N}$ values for

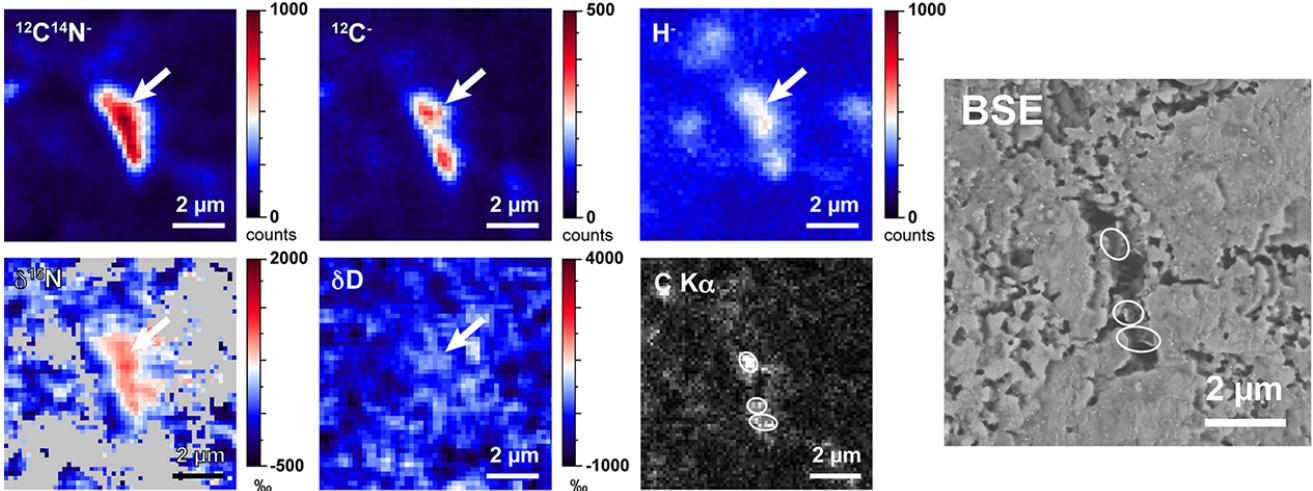


Fig. 1. Isotopographs, BSE image, and X-ray C K α map of ^{15}N -rich carbonaceous matter from M04-2 embedded in the Murchison matrix. Scale bars indicate secondary ion counts for the $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^-$, and H^- isotopographs, and permit for the $\delta^{15}\text{N}$ and δD isotopographs. The BSE image and X-ray C K α map were obtained from the approximate matrix region corresponding to the isotopographs. Gray masked areas in the $\delta^{15}\text{N}$ image indicate regions with insufficient signal of $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ for statistically significant analysis. Elongated carbonaceous matter was associated with high $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ secondary ion intensities and with large ^{15}N -enrichment relative to the surrounding matrix. The X-ray C K α map shows three C intense spots indicated by arrows, which correspond to the $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ intense regions in the isotopographs.

D- or ^{15}N -rich materials were the lower limits, as their sizes were expected to be comparable to the spatial resolution for imaging and the high D/H or $^{15}\text{N}/^{14}\text{N}$ ratio would be diluted by the low D/H or $^{15}\text{N}/^{14}\text{N}$ ratios of the surrounding matrix materials. D- or ^{15}N -rich organic matter in carbonaceous chondrites have been found as sub-micron size particles (Nakamura-Messenger *et al.*, 2006; Messenger *et al.*, 2008; De Gregorio *et al.*, 2010; Remusat *et al.*, 2010; Zega *et al.*, 2010; Hashiguchi *et al.*, 2013), as a result of which δD and $\delta^{15}\text{N}$ values of the isotopically anomalous materials were determined by the highest δD or $\delta^{15}\text{N}$ pixel (corresponding to $0.6 \times 0.6 \mu\text{m}^2$) in the processed isotopographs.

Counting statistics were employed towards error calculation of the D- or ^{15}N -rich material, and standard deviations were employed for the surrounding matrix. The error for the D- or ^{15}N -rich material was calculated by following equation:

$$10^3 \cdot \frac{R_{\text{sample}}}{R_{\text{matrix}}} \sqrt{\frac{1}{C_1} + \frac{1}{C_2}}$$

where R_{sample} and R_{matrix} are the isotope ratios (D/H or $^{15}\text{N}/^{14}\text{N}$) of D- or ^{15}N -rich material calculated by secondary ion counts/s, respectively; C_1 and C_2 are the total ion counts of D (or ^{15}N) and H (or ^{14}N) in the highest δD or $\delta^{15}\text{N}$ pixel, respectively. The standard deviation of the surrounding matrix was calculated from the pixels, and

used for normalization to calculate the δ -values. Typical errors for the D- or ^{15}N -rich materials were approximately the same as the surrounding matrix (590‰ for δD of NWA 801, 300‰ for δD of Murchison, 200‰ for $\delta^{15}\text{N}$ of NWA 801 and 240‰ for $\delta^{15}\text{N}$ of Murchison). The larger errors for δD value of matrix in NWA 801 than in Murchison might be the result of heterogeneity of H isotopic composition of the matrix minerals.

Morphological observation of isotopically anomalous carbonaceous matter

The D-rich and ^{15}N -rich carbonaceous matter analyzed in δD and $\delta^{15}\text{N}$ isotopographs, were subsequently observed in secondary electron (SE) images, back scattered electron (BSE) images and X-ray elemental maps acquired using a field emission scanning electron microscope (FE-SEM; JEOL JSM-7000F) equipped with an energy dispersive X-ray spectrometer (EDS; Oxford INCA Energy). High-resolution SEM and BSE images were obtained at 5 kV and 0.5–1 nA, with a spatial resolution of 50 nm. The elemental map of C was collected with an electron beam at 3–5 nA and an acceleration voltage of 5 kV.

The positions of isotopically anomalous materials were determined by comparison of the δD or $\delta^{15}\text{N}$ and $^{12}\text{C}^-$ isotopographs and C elemental maps (Figs. 1 and 2), followed by detailed morphological observations using BSE images at high magnification. The method used for the identification of isotopic anomalous carbonaceous matter is described elsewhere (Hashiguchi *et al.*, 2013).

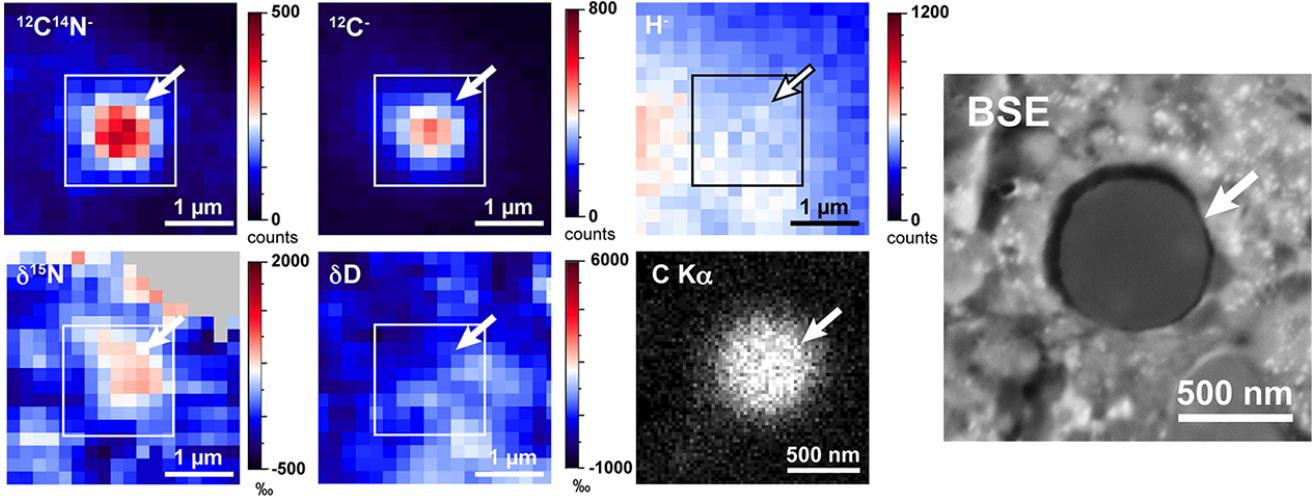


Fig. 2. Isotopographs, BSE image and X-ray C K α map of ^{15}N -rich carbonaceous matter from 081-1 embedded in the NWA 801 matrix. Scale bars indicate secondary ion counts for the $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^-$, and H^- isotopographs, and permit for the $\delta^{15}\text{N}$ and δD isotopographs. Gray masked areas in the $\delta^{15}\text{N}$ image indicate regions with insufficient signal of $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ for statistically significant analysis. The BSE image and X-ray C K α map were obtained from the region indicated by white or black squares in the isotopographs. Round-shaped carbonaceous matter was observed at the area associated with high $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ secondary ion intensities and with high $\delta^{15}\text{N}$ relative to the surrounding matrix.

RESULTS

Carbonaceous spots with hydrogen and nitrogen isotope anomalies

A total of 28 isotopically anomalous spots associated with high $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ secondary ion intensities were determined from the surveyed areas in Murchison and NWA 801 thin sections. Their isotopic compositions are listed in Table 1 and plotted in Fig. 3. BSE images of all carbonaceous matter observed in this study are shown in Supplementary Fig. S1.

Isotopically anomalous organic matter were surveyed from a total area of $\sim 44,400 \mu\text{m}^2$ in the Murchison matrix, corresponding to 12 fields. Seventeen isotopically anomalous carbonaceous spots (e.g., Fig. 1) were identified from the 12 fields, with maximum $\delta\text{D} = 2,590\text{\textperthousand}$ and $\delta^{15}\text{N} = 2,880\text{\textperthousand}$.

For the NWA 801 matrix, a total of 11 carbonaceous spots associated with isotopically anomalous signatures (e.g., Fig. 2) were observed in 25 fields of isotopographs ($\sim 76,600 \mu\text{m}^2$), with maximum $\delta\text{D} = 7,500\text{\textperthousand}$ and $\delta^{15}\text{N} = 2,220\text{\textperthousand}$. The variations of isotopic anomalies for ^{15}N was similar in Murchison and NWA 801, but not for D (Fig. 3).

The degree of D-enrichment in the carbonaceous matter is not simply associated with the degree of ^{15}N -enrichment (Fig. 3). Therefore, the isotopically anomalous carbonaceous matter were classified into three groups based on the isotopic compositions as follows: highly ^{15}N -rich, but not enriched in D (^{15}N -rich); highly D-rich, but

not enriched in ^{15}N (D-rich); enriched in both D and ^{15}N ($\text{D-}^{15}\text{N}$ -rich). The fractions of D-rich, ^{15}N -rich and $\text{D-}^{15}\text{N}$ -rich carbonaceous spots within the extremely isotopically anomalous carbonaceous matter in Murchison and NWA 801 are shown in Fig. 4. The ^{15}N -rich carbonaceous spots were dominant in Murchison (82%), whereas D-rich carbonaceous spots were less abundant (6%). In contrast, the abundance of ^{15}N -rich carbonaceous spots and D-rich carbonaceous spots were comparable for NWA 801. The fractional abundance of $\text{D-}^{15}\text{N}$ -rich carbonaceous spots was small in both samples.

Morphology of isotopically anomalous carbonaceous matter

The morphologies of carbonaceous matter associated with isotopic anomalies were observed using FE-SEM-EDS, with the exception of one (Murchison) and two carbonaceous spots (NWA 801). These spots are listed as “not located” in Table 1 and were probably consumed during isotope microscope measurements.

Hashiguchi *et al.* (2013) classified the morphology of carbonaceous matter in NWA 801 as globule aggregate, round globule, irregular-shaped globule, and ring globule. All the four types were identified in the carbonaceous matter of NWA 801 in this study. However, the ring globule structure observed in NWA 801 in this study had a void in the center without any inorganic materials (Fig. 5). This ring structure is similar to organic nanoglobules reported in many carbonaceous chondrites (Nakamura-Messenger *et al.*, 2006; Messenger *et al.*, 2008; De

Gregorio *et al.*, 2010; Matsumoto *et al.*, 2013), but was not observed by Hashiguchi *et al.* (2013). Globule aggregate, round globule, and irregular-shaped globule structures were identified in the isotopically anomalous carbonaceous matter of Murchison, whereas the ring globule type was not observed. Aggregated carbonaceous

matter probably contain some non-globular particles that are unable to be distinguished by FE-SEM. Thus we refer the aggregate “globule/particle aggregate” in this study. Typical characteristics of petrology surrounding the carbonaceous matter were not identified.

The fractions of globule/particle aggregates and non-aggregated globules (i.e., round globule, irregular-shaped globule, and ring globule) in Murchison and NWA 801 are shown in Fig. 6. Most of the isotopically anomalous carbonaceous spots in Murchison (~70%) occur as globule/particle aggregates with sizes of 0.7–3.2 μm , while

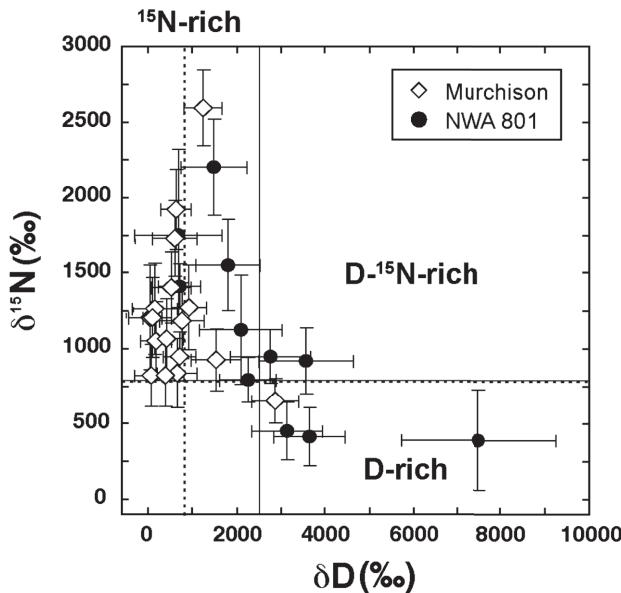


Fig. 3. Hydrogen and nitrogen isotopic compositions of isotopically anomalous carbonaceous matter from Murchison (open diamonds) and NWA 801 (solid circles). The solid and dashed lines indicate the approximate lowest limits for the detection of D- or ^{15}N -enrichment for NWA 801 and Murchison, respectively. The isotopic compositions have no positive correlations. The plots were classified into three groups based on the detection limit lines calculated from typical error of $[2\sigma_{\text{ROI}} + 3\sigma_{\text{matrix}}]$, i.e., ^{15}N -rich, D-rich, and D- ^{15}N -rich.

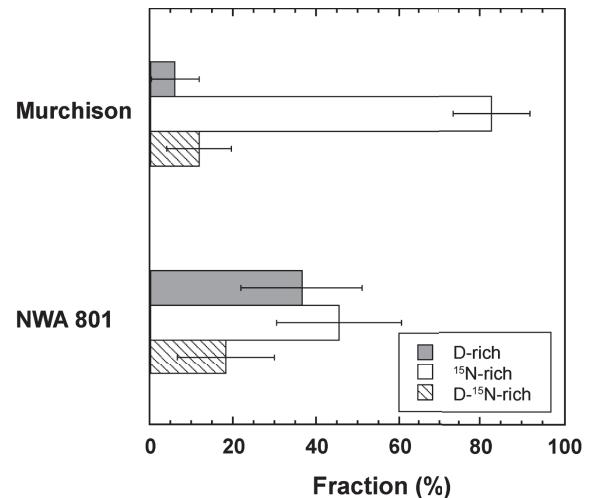


Fig. 4. Fraction (%) of D-rich organic matter (gray), ^{15}N -rich organic matter (white), and D- ^{15}N -rich organic matter (diagonal line), in Murchison and NWA 801. Fraction of D-rich organic matter refers to the (whole number of the D-rich organic globules)/(whole number of isotopically anomalous organic globules) found in each of the meteorites. Error bars are one standard deviation (1σ) calculated by number statistics.

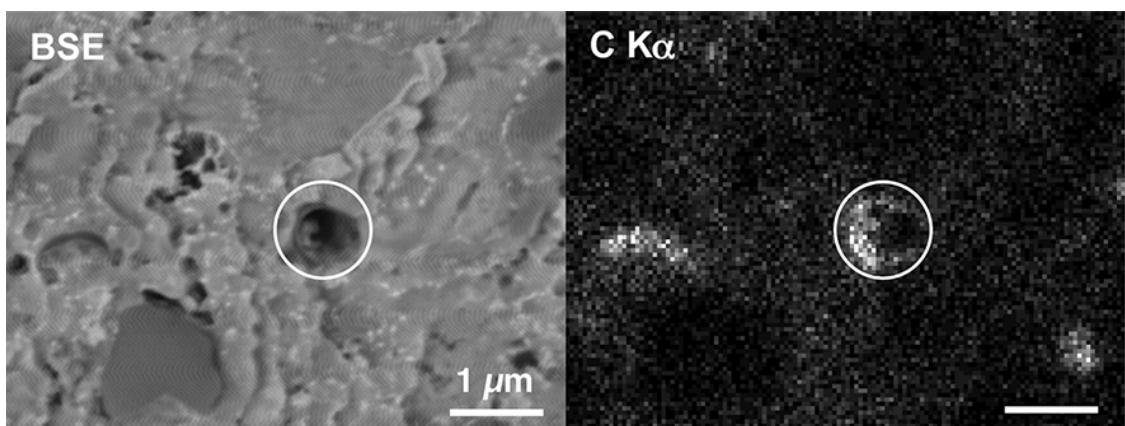


Fig. 5. BSE image and X-ray C K α map of a D-rich ring globule (090-1) embedded in the NWA 801 matrix.

Table 1. Hydrogen and nitrogen isotopic compositions, shapes and sizes of the isotopically anomalous carbonaceous spots in Murchison and NWA 801

	δD (‰)*			$\delta^{15}\text{N}$ (‰)*			Enrichment	Morphology	Size (μm)
Murchison									
M02-3	1,250	±	440	2,590	±	250	D, ^{15}N	Globule aggregate	3.2
M03-1	650	±	450	830	±	230	^{15}N	Irregular-shaped globule	0.5
M03-2	60	±	370	820	±	210	^{15}N	Not located**	—
M03-4	400	±	420	820	±	210	^{15}N	Irregular-shaped globule	0.4
M04-1	170	±	340	1,050	±	260	^{15}N	Irregular-shaped globule	1.1
M04-2	720	±	380	940	±	160	^{15}N	Globule aggregate	2.4
M04-3	600	±	520	1,730	±	250	^{15}N	Globule aggregate	0.9
M04-5	420	±	380	1,060	±	270	^{15}N	Globule aggregate	2.4
M04-6	910	±	400	1,270	±	280	^{15}N	Round globule	0.5
M04-7	-40	±	470	1,200	±	350	^{15}N	Globule aggregate	0.7
M05-3	770	±	500	1,180	±	250	^{15}N	Globule aggregate	1.7
M06-1	530	±	460	1,400	±	240	^{15}N	Globule aggregate	2.4
M06-3	160	±	500	1,260	±	300	^{15}N	Globule aggregate	3.1
M10-1	90	±	210	1,200	±	270	^{15}N	Globule aggregate	1.6
M11-1	640	±	340	1,920	±	270	^{15}N	Globule aggregate	1.7
M12-1	2,880	±	530	650	±	150	D	Globule aggregate	1.6
M12-3	1,540	±	570	920	±	210	D, ^{15}N	Irregular-shaped globule	0.7
NWA 801									
078-2	3,640	±	800	410	±	190	D	Round globule	0.5
078-3	2,760	±	920	940	±	180	D, ^{15}N	Not located**	—
078-4	3,130	±	790	450	±	190	D	Globule aggregate	0.5
078-5	2,100	±	940	1,120	±	360	^{15}N	Not located**	—
079-2	720	±	490	1,410	±	150	^{15}N	Irregular-shaped globule	0.2
079-3	2,250	±	640	790	±	150	D, ^{15}N	Irregular-shaped globule	0.2
081-1	1,790	±	710	1,550	±	300	^{15}N	Round globule	0.7
084-1	7,500	±	1,770	390	±	330	D	Globule aggregate	1.6
085-1	690	±	990	1,750	±	570	^{15}N	Globule aggregate	0.5
090-1	3,560	±	1,060	910	±	220	D	Ring globule	0.8
093-1	1,490	±	740	2,200	±	320	^{15}N	Globule aggregate	1.4

*Errors are two standard deviation (2σ) calculated from the H and D or ^{14}N and ^{15}N ion counts.

**Carbonaceous matter that could not be observed by X-ray carbon mapping.

the sizes of non-aggregated globules were in the range of 0.4–0.7 μm . On the other hand, the fraction of non-aggregated globules was larger (~55%) in NWA 801, the sizes of which were distributed from 0.2 to 0.7 μm , and the sizes of globule/particle aggregates were in the range of 0.5–1.6 μm . In both meteorites, no correlation between H and N isotopic compositions and the size of isotopically anomalous carbonaceous matter was found.

There are morphological differences between the globule/particle aggregates in Murchison and NWA 801. The globule/particle aggregates in Murchison are densely packed with several types of carbonaceous matter (e.g., Fig. 1), whereas those of NWA 801 are composed of submicron carbonaceous matter that are distributed separately within an area of $\sim 1 \mu\text{m}^2$.

Figure 7 shows the relationship between the H and N isotopic compositions and the morphology of the organic matter in Murchison and NWA 801. Any clear correlation was not revealed between the isotopic compositions and the morphology of the organic matter.

DISCUSSION

Characteristics of D-rich and ^{15}N -rich carbonaceous matter in Murchison and NWA 801

The large D- and ^{15}N -enrichments found in Murchison and NWA 801 were associated with high secondary ion intensities of $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ (e.g., Figs. 1 and 2), suggesting that the carbonaceous matter is organic. The H and N isotopic compositions obtained in this study, ex-

cept H isotopic compositions of organic matter in NWA 801, are roughly comparable with previous results on CM and CR chondrites (Fig. 8). However, range of the δD value of organic matter in NWA 801 seems to be lower than those in other CR2 chondrites (Fig. 8).

There are potential issues of contamination by the epoxy resin used in this study for modification of isotopic compositions of extraterrestrial organic matter, although penetration of epoxy was not observed in the samples used. On the other hand, in the previous studies, there

are potential issues of modification of isotopic compositions due to the chemical extraction procedures used. The agreement of isotopic distribution between the previous and current studies suggests that both the methods of sample preparation did not significantly affect their isotopic compositions. The H and N isotopically anomalous carbonaceous matter found in this study exhibits δD or $\delta^{15}\text{N}$ values which are similar to those reported from D- and ^{15}N -rich organic spots in IOM or matrix fragment of CR2 chondrites and Murchison (Fig. 8).

The δD or $\delta^{15}\text{N}$ value of isotopically anomalous organic matter in both meteorite would not be diluted by surrounding matrix in isotopography, because no correlation between the size and H or N isotopic composition of organic matter was found. Leitner *et al.* (2012) revealed that NWA 852, that is paired with NWA 801, contains O-anomalous presolar grains in concentrations comparable to other more primitive meteorites. This result and identification of highly D- and/or ^{15}N -rich organic matter in NWA 801 in this study suggest that NWA 801 have experienced little terrestrial alteration. Thus, their δD value of organic matter in NWA 801 would not be affected by terrestrial alteration. Heterogeneous nature of CR chondrites have suggested by their petrology (Weisberg *et al.*, 1993) and oxygen isotopic composition (Schrader *et al.*, 2011). Therefore, lower range of δD value in NWA 801 might be resulted from heterogeneous nature of CR chondrites or unique nature of NWA 801.

The bulk abundance of total organic matter in these chondrites was calculated from the areas with high H- and C⁻ intensity, from all the isotopographs. For this calculation, it was assumed that the area% corresponded to a vol% and those of the matrices in Murchison and NWA

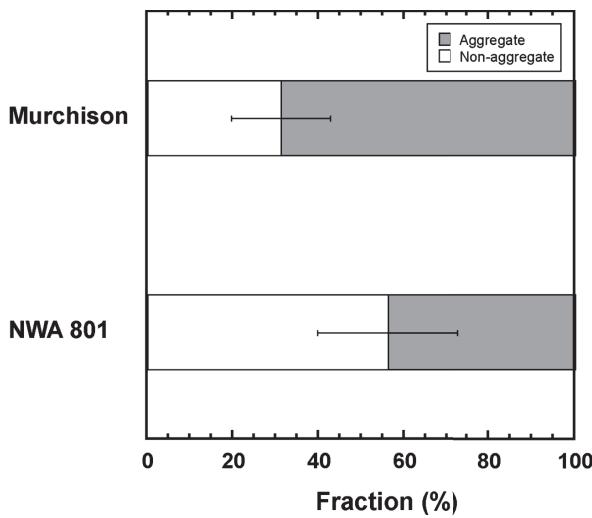


Fig. 6. Fraction (%) of isotopically anomalous organic matter in globule/particle aggregates (gray) and non-aggregated globules (white) of Murchison and NWA 801. Error bars are one standard deviation (1σ).

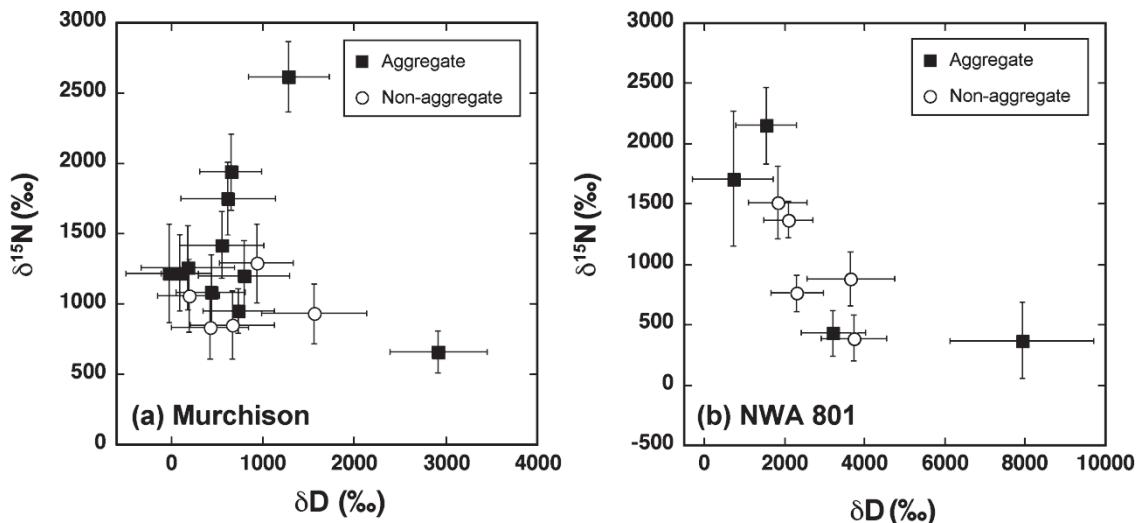


Fig. 7. Hydrogen and nitrogen isotopic compositions of globule/particle aggregates (solid squares) and non-aggregated globules (non-aggregate) (open circles) from (a) Murchison and (b) NWA 801.

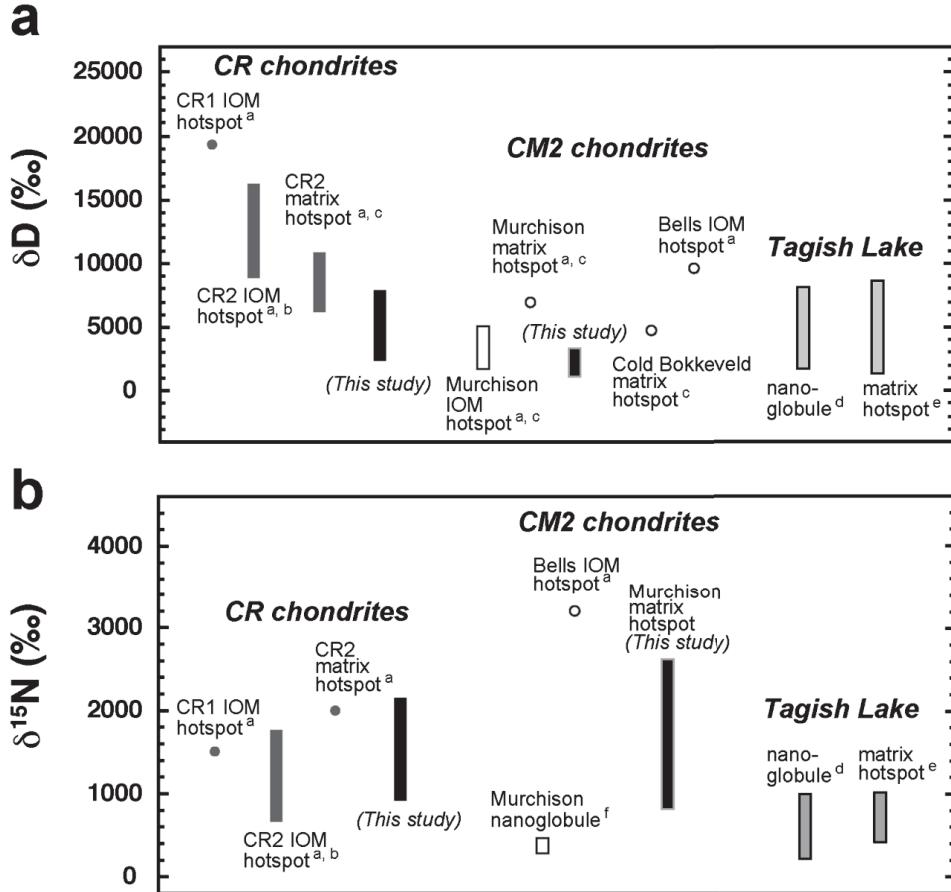


Fig. 8. Distributions of (a) δD and (b) $\delta^{15}\text{N}$ for hotspots observed in the IOM and matrix of CR, CM chondrites and the Tagish Lake meteorite. These data were taken from: ^aBusemann et al. (2006), ^bHashizume et al. (2011), ^cRemusat et al. (2010), ^dNakamura-Messenger et al. (2006), ^eZega et al. (2010), ^fDe Gregorio et al. (2010).

801 were 70 and 30 vol%, respectively (Weisberg *et al.*, 2006). The bulk abundances of organic matter were calculated to be ~4 and 2 area% in Murchison and NWA 801, respectively (Table 2). The density of the organic matter was assumed to be similar to kerogen (~1 g/cm³; Boyer *et al.*, 2006), and that of the chondrite matrix is ~3 g/cm³. Hence, the organic matter in Murchison and NWA 801 was estimated to be 1.3 and 0.7 wt%, respectively (Table 2). The calculated abundances of total organic matter determined in this study are equivalent to the IOM abundances in Murchison and in CR chondrites (~0.8 wt% for Murchison, <0.1–1.3 wt% for CR chondrites: Alexander *et al.*, 2007).

The fractions of isotopically anomalous organic matter were calculated using isotopography, by counting the pixels of ROIs with $[\delta\text{D} \text{ or } \delta^{15}\text{N}_{\text{ROI}} - \delta\text{D} \text{ or } \delta^{15}\text{N}_{\text{matrix}}] > (2\sigma_{\text{ROI}} + 3\sigma_{\text{matrix}})$. The total pixels of all the ROI with H or ¹⁵N isotope anomaly relative to total pixels of high H⁻ and C⁻ intensity were calculated, which corresponds to the organic matter described above.

The fractions of D-rich organic matter and ¹⁵N-rich organic matter relative to total organic matter in NWA 801 (0.06 and 0.22 area%, respectively) are approximately consistent with abundances for D or ¹⁵N hotspots of the IOM from CR2 chondrites previously reported (0.3–2.4 area% for D hotspot, 0.005–1.0 area% for ¹⁵N hotspot: Busemann *et al.*, 2006). On the other hand, the fraction of D-rich organic matter in Murchison in the present study (0.13 area%) is much smaller than that previously reported for the IOM (4.3 area%: Busemann *et al.*, 2006). The difference in the abundance of D-rich organic matter may be attributed to different criterion for the D isotopic anomalies between this study and that reported by Busemann *et al.* (2006). This study used the H isotopic composition of the matrix was used as a criterion for the isotopic anomaly, while Busemann *et al.* (2006) used the H isotopic composition of the IOM. Upon using their criteria ($[\delta\text{D}_{\text{IOM_ROI}} - \delta\text{D}_{\text{average}} > 3\sigma_{\text{IOM_ROI}}]$), the abundance of D-rich organic matter in Murchison found in this study increased to ~1 area%, which shows better agreement with

Table 2. Abundances of organic matter and isotopically anomalous carbonaceous matter

Meteorite	Organic matter*		Isotopically anomalous carbonaceous matter/whole organic matter (area%)	
	area%	wt%	D-rich	^{15}N -rich
Murchison	4.4	1.3	0.1	1.0
NWA 801	2.0	0.7	0.1	0.2

*Abundance of the organic matter was bulk-normalized value.

Busemann *et al.* (2006). The fraction of ^{15}N -rich organic matter relative to the total organic matter in Murchison is ~ 1 area%, and is reported here for the first time. Most of organic matter in carbonaceous chondrites occur as fine-scaled mixture with minerals, such as phyllosilicate or sulfides (Zega *et al.*, 2010; Le Guillou and Brearley 2014). Therefore, our estimation of abundance for organic matter is possibly overestimated. This would lead to underestimate for abundance of isotopically anomalous organic matter, because abundance of isotopically normal organic matter is much higher than isotopically anomalous organic matter. However, our estimation approximately consistent with reported value from IOM study (Busemann *et al.*, 2006), thus, the underestimate due to mixing organic matter with minerals would not be significant.

Formation processes for D- and ^{15}N -enrichment in the organic matter of Murchison and NWA 801

Complex refractory organic matter accompanied by D- and/or ^{15}N -enrichment could have formed as a result of UV irradiation on ice grains condensed from gas molecules in cold molecular clouds (Bernstein *et al.*, 1999; Greenberg, 2002), and in the early solar nebula (e.g., Schutte *et al.*, 1992; Allamandola *et al.*, 1988; Greenberg *et al.*, 1995; Ciesla and Sandford, 2012). Three processes have mainly been discussed to explain such large isotopic enrichments of D and ^{15}N observed in the organic matter of meteorites: 1) ion-molecule reactions in cold molecular cloud and in the outer protoplanetary disk, 2) grain-surface reactions in cold molecular clouds, and 3) self-shielding in molecular clouds and in the outer protoplanetary disk.

Ion-molecule reactions at ~ 10 K in cold molecular cloud and in the outer protoplanetary disk of the solar system could produce organic matter extremely rich in ^{15}N (up to $\sim 9,000\text{\textperthousand}$; Terzieva and Herbst, 2000; Charnley and Rodgers, 2002; Rodgers and Charnley, 2008) and with large D-enrichment (up to $\sim 6 \times 10^6\text{\textperthousand}$; Robert *et al.*, 2003). Thus, the organic matter with D- ^{15}N -rich isotopic compositions shown in Fig. 3 could have originated from ion-molecule reactions at ~ 10 K. Organic matter with large D-enrichment would also have been formed by ion-molecule reactions at slightly warmer temperatures of 10 K

$< T < 70$ K (Millar *et al.*, 1989). However, large ^{15}N -enrichment would not be expected to occur at such warm temperatures. Therefore, ion-molecule reactions at 10 K $< T < 70$ K could have formed the organic matter with D-rich isotopic compositions shown in Fig. 3. The ^{15}N -rich organic matter in Fig. 3 is difficult to form by simple ion-molecule reactions. However, if spin-dependent ion-molecule reactions involving the ortho/para ratio of H₂ in the cold molecular clouds were considered, then organic molecules with ^{15}N -rich isotopic composition could be formed (Wirström *et al.*, 2012). The variations of D- and ^{15}N -enrichment shown in Fig. 3 could originate from nitriles or ammonia, by various spin-dependent ion-molecule reactions in the molecular cloud. Aikawa and Herbst (1999) and Aikawa *et al.* (2002) suggest that D fractionation occurs by similar processes in the protoplanetary disk and cold molecular clouds. D fractionation in the protoplanetary disk in the early solar system was also suggested by H isotope measurements of organic matter in chondrites (Remusat *et al.*, 2006, 2010).

Molecules that were D- and ^{15}N -enriched could have been trapped in ice grains and changed to D- and ^{15}N -rich complex organic matter by UV irradiation. However, D- and ^{15}N -enrichment formed by ion-molecule reactions is expected to be much larger than that observed in this study (Fig. 9); therefore, it was concluded that the D- and ^{15}N -enrichment in organic matter formed by ion-molecule reactions was decreased by secondary processes.

Organic molecules with significant D-enrichment could also have been produced on the surfaces of ice grains via quantum mechanical tunneling at ~ 10 K (Watanabe, 2006; Watanabe and Kouchi, 2008), although large ^{15}N -enrichment has not been predicted by such processes. Organic matter with D-rich isotopic compositions could be produced via the grain-surface reactions in cold molecular cloud (Fig. 9) and the ice grains would be changed to organic matter by UV irradiation (e.g., Bernstein *et al.*, 1999; Greenberg, 2002; Ciesla and Sandford, 2012).

D-enrichment produced by grain-surface reaction is predicted to be significantly larger (e.g., $\sim 10^6\text{\textperthousand}$; Watanabe, 2006; Watanabe and Kouchi, 2008) than that

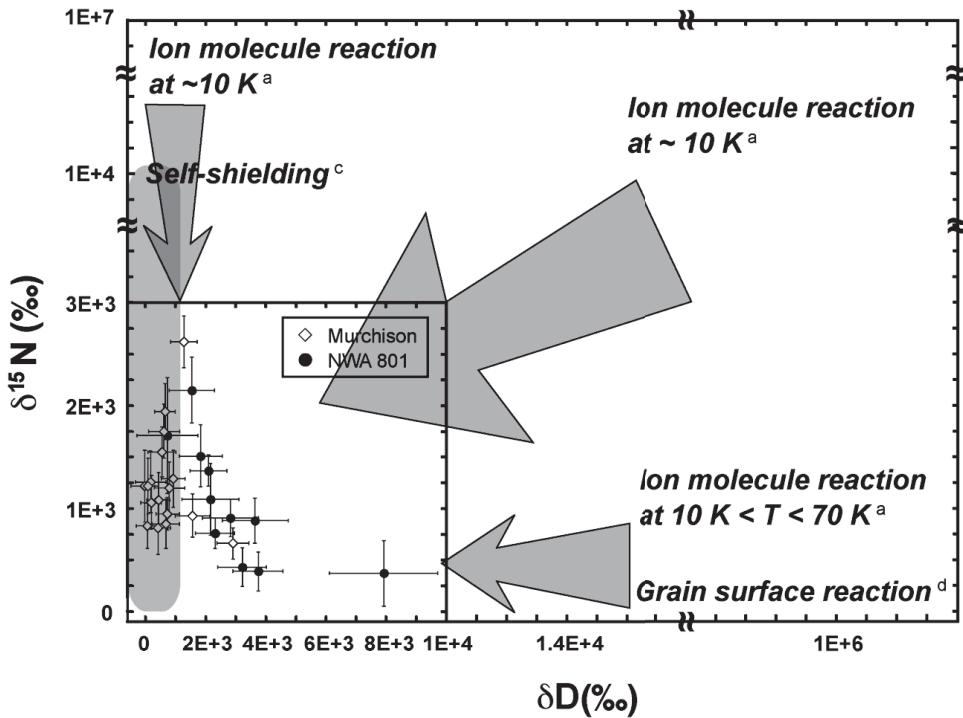


Fig. 9. Isotopic compositions of organic matter from Murchison and NWA 801 compared with isotopic compositions inferred by organic matter isotope fractionation models of organic matter in space. Trends by secondary modification D- and ^{15}N -enrichments of organic matter are indicated by arrows. Self-shielding effects form isotopic compositions comparable to those of organic matter plotted in this diagram, and the range of the isotopic composition is shown by the gray rectangular area. ^aMillar *et al.* (1989), Rodgers and Charnley (2008), Wirström *et al.* (2012). ^bWatanabe (2006), Watanabe and Kouchi (2008). ^cLe Petit *et al.* (2002), Lyons (2009), Lyons *et al.* (2009), Lyons (2010), Chakraborty *et al.* (2012).

observed for the organic matter in Murchison and NWA 801. Therefore, the decrease of D-enrichment in the organic matter could be explained by secondary processes.

Self-shielding in the outer protoplanetary disk and molecular clouds of the solar system by UV photodissociation, has been suggested for the mechanism of D and ^{15}N fractionation observed in organic matter of carbonaceous chondrites (e.g., Le Petit *et al.*, 2002; Lyons, 2009, 2010; Lyons *et al.*, 2009; Aléon, 2010; Chakraborty *et al.*, 2012). Experimental N-isotopic fractionation due to isotope self-shielding by vacuum UV (VUV) photodissociation at wavelengths $<95\text{ nm}$ produced large ^{15}N -enrichment ($\delta^{15}\text{N} = \text{up to } \sim 2,500\text{\textperthousand}$) in NH_3 (Chakraborty *et al.*, 2012), and H_2 self-shielding could produce moderate D-enrichment ($\delta\text{D} < \sim 900\text{\textperthousand}$; Le Petit *et al.*, 2002). Thus, the organic molecules with D- and ^{15}N -enrichment produced may have been trapped in ice grains and complex organic matter with ^{15}N -rich and D- ^{15}N -rich isotopic compositions (Fig. 3) could have been produced.

Previous calculations (Le Petit *et al.*, 2002) showed that the D-enrichment produced by self-shielding effect is smaller than that observed in the D-rich organic matter

examined in this study (Fig. 9). Hence, the D-rich organic matter seem to inherit isotope anomalies formed as a result of ion-molecule and grain-surface reactions rather than those formed by the self-shielding effect.

Time of incorporation of isotopically anomalous organic matter into CM or CR parent bodies

Murchison contains a higher fraction of ^{15}N -rich organic matter (and a lower fraction of D-rich organic matter) than NWA 801. If the ^{15}N -rich organic matter had been transferred, from region of its formation, at a different time from the D-rich organic matter, one might expect that the abundance of ^{15}N -rich/D-rich organic matter was dependent on the accretion age of chondrites. It is expected that the CM parent body was accreted within $\sim 1\text{ Ma}$ of CAI formation ($4567.2 \pm 0.6\text{ Ma}$ for formation age of CAI in the CV chondrite Efremovka: Amelin *et al.*, 2002), by estimation of timescales for alteration of CMs (Brearley *et al.*, 2001). Absolute ages for the CR chondrules have been reported as $4564.7 \pm 0.6\text{ Ma}$ (Amelin *et al.*, 2002, 2004), thus CR parent body would be younger than CMs.

The model of spin-dependent ion-molecule reactions

suggests that gaseous nitriles or ammonia can exhibit a wide range of fractionation, for both ^{15}N and D in dense cloud cores, at different times of core age (Wirström *et al.*, 2012). For example, nitriles that are ^{15}N -rich but moderately enriched in D can be formed in less than about 2×10^5 years, whereas highly D-rich ammonia can be produced within $\sim 2 \times 10^5\text{--}10^6$ years (Wirström *et al.*, 2012). Both D-rich and ^{15}N -rich organic molecules can be produced within $\sim 10^6$ years of core age, which is within the age of CAI formation (e.g., Amelin *et al.*, 2004). Therefore, it is unlikely that the variation of ^{15}N -rich/D-rich organic matter between these chondrites originated by differences of transportation time into the solar nebula from the dense core, and differences of incorporation time of various isotopically anomalous organic matter onto chondrite parent bodies, because the duration of the chondrite parent body formation is longer than the duration for the formation of isotopically anomalous organic matter.

The N_2 self-shielding effect can also result in an excess of ^{15}N in molecules such as HCN in first $10^3\text{--}10^4$ years of the solar system (Lyons *et al.*, 2009). These ^{15}N -rich molecules could evolve into ^{15}N -rich organic matter by UV irradiation onto ice grains (for instance), and be transferred into the region of formation of chondrite parent bodies. Because accretion in the CM parent body occurred $\sim 1\text{--}2$ Ma earlier than in the CRs (Brearley *et al.*, 2001; Amelin *et al.*, 2002, 2004), larger amounts of ^{15}N -rich organic matter (with ^{15}N excess produced by self-shielding process) could be accreted into CM parent body, resulting in a larger fraction of ^{15}N -rich organic matter in Murchison than in NWA 801. In this case, it is expected that a larger abundance of ^{15}N -rich organic matter was incorporated into the chondrite parent body with older accretion age. However, a larger fraction of ^{15}N -rich organic matter (without D-enrichment) than in CR, and CM chondrites, has been reported in the Isheyev CH/CB chondrite (Briani *et al.*, 2009; Bonal *et al.*, 2010) which is younger than the CR chondrites (Amelin *et al.*, 2004; Krot *et al.*, 2005). Consequently, the time of ^{15}N excess production by the self-shielding effect does not appear to affect the different fractions of ^{15}N -rich organic matter in Murchison and NWA 801.

Pizzarello and Holmes (2009) suggested the late stage of star-forming region for distinct environment of ^{15}N -rich organics in carbonaceous chondrites. Aléon (2010) also argued the late addition of ^{15}N -enrichments to organic matter in extraterrestrial materials. If ^{15}N -rich organic matter in this study have been formed late stage of star formation in early solar nebula, abundance of ^{15}N -rich organic matter and the age of meteorites should show anti-correlation like suggested in Aléon (2010). However, their abundance is Murchison > NWA 801 that is correlated with the age (CRs is younger than CMs as discussed

above). Therefore, ^{15}N -rich organic matter found in Murchison and NWA 801 would be attributed to chemical reaction in ISM or outer solar system than the same process in late stage of star formation.

Modification of the isotopic compositions in isotopically anomalous organic matter

Fraction of D-rich organic matter identified in Murchison was lower than that in NWA 801 (Fig. 4). This result could be attributed to the modification of the H isotopic composition by secondary processes in the solar nebula or on the parent bodies.

Remusat *et al.* (2010) proposed mixing processes between D-rich organic matter produced in outer edge of solar nebula and moderately D-rich organic matter from the mid-plane, resulting in a reduction of the D-enrichment. Modification of isotopic compositions of the organic matter would depend on the time they spend in the outer and inner solar nebula. Although the distances of chondrite parent bodies from the Sun are uncertain, more water-rich chondrites have been assumed to be formed further from the Sun, namely CIs > CMs > CRs (e.g., Alexander *et al.*, 2007). Therefore, transportation of D-rich organic matter from outer edge of solar nebula to CM parent body would require a shorter distance than to the CR parent body. Moreover, the parent body of CM chondrites has been suggested to be older than CRs. The time spent by the D-rich organic matter, in between the inner nebula and the outer edge, for incorporation into CM parent body is shorter than that for the CR parent body, and thus D-rich organic matter accreted into Murchison would be less affected by the mixing process, than that of NWA 801. Therefore, while some degree of modification of D-rich organic matter would have occurred by the mixing processes, the different abundances of D-rich/ ^{15}N -rich organic matter between Murchison and NWA 801 are not attributed to it.

D-rich organic matter has also been suggested to be modified by aqueous alteration on the parent body (e.g., Herd *et al.*, 2011). Although both CM2 and CR2 chondrites exhibit evidence of various degrees of alteration, most CR chondrites have experienced significantly less alteration than Murchison, which is one of the typical CM2 chondrites (Brearley, 2006). The δD value of water in the early solar system has been reported to be less than that of the D-rich organic matter found in this study (<1,000‰: Robert, 2006). Hydrous pyrolysis experiments of the IOM in CM chondrites decreased the hydrogen isotopic compositions. Oba and Naraoka (2009) experimentally demonstrated a decrease of the δD value for IOM in Murchison (e.g., from 986‰ to 307‰ at 270°C). Similar results were observed for the IOM of the Murray meteorite (CM2) (from 792‰ to -41‰ at 300°C: Yabuta *et al.*, 2007). Therefore, the lower amount of D-

rich organic matter in Murchison than in NWA 801 suggests that modification of H isotopic composition occurred during aqueous alteration on the parent body of Murchison. Similar D-enrichment decreasing processes have been considered to occur in the Tagish Lake meteorite (Herd *et al.*, 2011), in which the IOM from a less altered fragment has not only a higher average D/H ratio, but also a much higher abundance of very D-rich sub-micrometer-sized isotopic hot spots, than the IOM from a more altered fragment.

A decrease of ^{15}N -enrichment in the IOM of carbonaceous chondrites by aqueous alteration has also been previously suggested (e.g., Sephton *et al.*, 2003; Yabuta *et al.*, 2007). Sephton *et al.* (2003) showed that the labile components in IOM are enriched in ^{15}N , and these components are released from the IOM by hydrous pyrolysis. Significant ^{15}N -enrichment was observed in the organic matter of Isheyev clasts and the isotopic anomaly was less abundant in more altered clasts, which suggests modification of the ^{15}N -enriched organic matter by aqueous alteration (Bonal *et al.*, 2010). However, a solid-state ^{15}N nuclear magnetic resonance (NMR) study on Orgueil IOM indicated that nitrogen is mainly involved in heterocyclic units such as pyrroles ($\text{C}_4\text{H}_5\text{N}$) (Derenne and Robert, 2010). The C-H bond (bond energy <120 kcal/mol: e.g., Remusat *et al.*, 2006) in the IOM would have been released more easily than N-C or N=C bonds (bond energy >6,000 kcal/mol: e.g., Cao *et al.*, 2000), which indicates that a disturbance in D-enrichment is more likely than in ^{15}N -enrichment. Thus, the ^{15}N -rich organic matter in this study could be attributed to not only spin dependent ion molecule reaction discussed above but also a preferential decrease of the D-enrichment from organic matter that was originally enriched in both ^{15}N and D.

It is noteworthy that the IOM of Orgueil (CI) showed a very high D-enrichment despite a high degree of alteration of CI chondrite (Remusat *et al.*, 2010) (Fig. 8). Therefore, whole D-rich organic matter in carbonaceous chondrites must not modified by aqueous alteration, however, some degree of modification of the isotopic composition of organic matter in carbonaceous chondrites must have occurred by aqueous alteration on the parent bodies.

Morphology of the isotopically anomalous organic matter

The isotopically anomalous organic matter analyzed in this study was found to be sub-micron scale non-aggregated organic globules or aggregates of several organic globules that may contain some organic particles (Fig. S1). The morphologies of the globules in NWA 801 have been described in our previous report (Hashiguchi *et al.*, 2013), and were also partly described for the CI, CM, CR chondrites (Garvie and Buseck, 2004; De Gregorio *et al.*,

2010; Remusat *et al.*, 2010), Tagish Lake (e.g., Garvie and Buseck, 2004; Nakamura-Messenger *et al.*, 2006; Matsumoto *et al.*, 2013), and the Bells meteorite (Messenger *et al.*, 2008). Therefore, the common globular morphology of organic matter associated with D- and ^{15}N -enrichment suggests a ubiquitous distribution in the early solar nebula.

Organic matter could have been formed by ultraviolet (UV) irradiation onto ice grains in the molecular cloud (Greenberg, 2002) and in the outer disk of the early solar nebula (Ciesla and Sandford, 2012). Saito and Kimura (2009) suggested that nanometer sized organic globules could be formed by irradiation of plasma particles such as protons and He^+ around evolved stars. If the organic globules identified in this study were formed from plasma particles, then their isotope anomalies of D and/or ^{15}N would be obtained after formation of the organic globules, because significant D- and ^{15}N -enrichment of organic matter is not expected around evolved stars.

The globular shape can be produced by fluid activity (Dworkin *et al.*, 2001; Cody *et al.*, 2011; De Gregorio *et al.*, 2013; Kebukawa *et al.*, 2013). In addition, recent studies showed variety of globule morphologies in CR, CM (Changela *et al.*, 2012, 2013; De Gregorio *et al.*, 2013) and CI, CO carbonaceous chondrites (De Gregorio *et al.*, 2013), and suggested modification of the morphology of organic nanoglobule during aqueous alteration on the parent body. Therefore, the morphology of organic matter (aggregated globules and/or particles and non-aggregated globules) in Murchison and NWA 801 might record the effect of aqueous alteration.

The relationship between the H and N isotopic compositions and the morphology of the organic matter in Murchison and NWA 801 (Fig. 7) does not reveal any clear correlation. Hashiguchi *et al.* (2013) reported a similar result for the D-rich organic matter in NWA 801. This study has clarified that this result can be expanded to N isotopic characteristics for the both chondrites, i.e., isotopic characteristics of organic matter are not correlated with their morphology. Murchison, that would be more altered than NWA 801, contains more abundant aggregated organic globules/particles. This results suggest the nature of the aggregated organic globule/particles may have been resulted from the aqueous activities in the parent body, although no relationship between isotopic composition and morphology was identified. Assuming that ^{15}N -rich organic matter is attributed to preferential decrease of D during aqueous alteration, there may be a correlation between organic morphology and isotopic compositions.

CONCLUSIONS

D-rich and ^{15}N -rich carbonaceous matter was identi-

fied from the matrix of the Murchison and NWA 801 meteorites using *in situ* isotope imaging. Large D-enrichment (up to $\delta D = 7,500\text{\textperthousand}$), ^{15}N -enrichment (up to $\delta^{15}\text{N} = 2,590\text{\textperthousand}$), and the association of hydrogen, carbon, and nitrogen suggest that the carbonaceous matter corresponds to organic matter.

Most of the D-enrichment of organic matter is not positively correlated with the ^{15}N -enrichment in both meteorites. The organic matter exhibit three groups of hydrogen and nitrogen isotopic compositions: highly ^{15}N -rich without large D-enrichment (^{15}N -rich), highly D-rich without large ^{15}N -enrichment (D-rich), and enriched in both D and ^{15}N (D- ^{15}N -rich). D-rich organic matter is less abundant in Murchison than in NWA 801, which presumably indicates a decrease of D-enrichment from the organic matter of Murchison by aqueous alteration rather than by different time of incorporation of the D-rich or ^{15}N -rich organic matter into CM and CR parent bodies, or by a mixing process between D-rich organic matter and moderately D-rich organic matter in early solar nebula. In addition, portions of the ^{15}N -rich organic matter of Murchison and NWA 801 can probably be attributed to a preferential decrease of D-enrichment from originally D- ^{15}N -rich organic matter.

The organic molecules associated with D- and ^{15}N -enrichments could have been formed by the ion-molecule reaction in molecular clouds and in the outer solar nebula at temperatures $<70\text{ K}$. Although the formation of ^{15}N -rich organic molecules without D-enrichment by simple ion-molecule reaction is difficult, this can be explained if we consider the spin dependent reaction mechanisms. D-rich organic molecules could have also been produced by grain-surface reaction in cold molecular clouds. These D- and ^{15}N -rich organic molecules could have evolved to complex organic matter by UV irradiation on ice grains in cold molecular clouds and in the outer solar nebula. Self-shielding in molecular clouds and in the early solar nebula was also considered to explain the formation of ^{15}N -rich and D- ^{15}N -rich organic molecules.

The D- and ^{15}N -enrichment produced by ion-molecule and grain-surface reactions is much larger than that observed in this study, therefore, the D- and ^{15}N -enrichments of organic matter found in this study have been decreased, most likely by secondary processes in the solar nebula or on the parent body.

The morphologies of the isotopically anomalous organic matter in Murchison and NWA 801 are classified as globule/particle aggregates and non-aggregated globules. No clear correlation between the morphology and isotopic compositions was observed. However, the fraction of globule/particle aggregates in Murchison is larger than that in NWA 801. This result suggests that aggregated structure of the organic matter may have been caused by aqueous activity.

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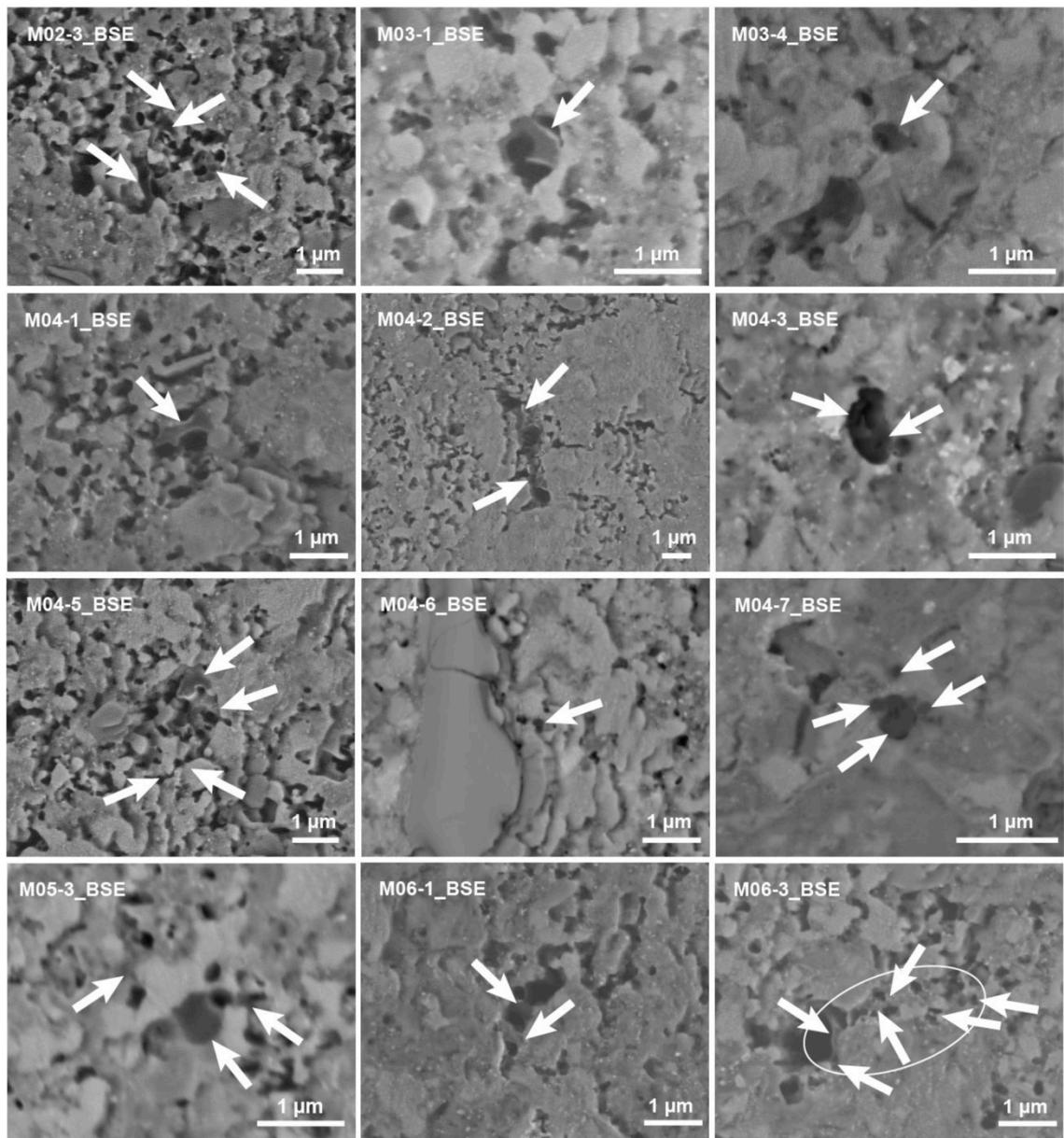
SUPPLEMENTARY MATERIALS

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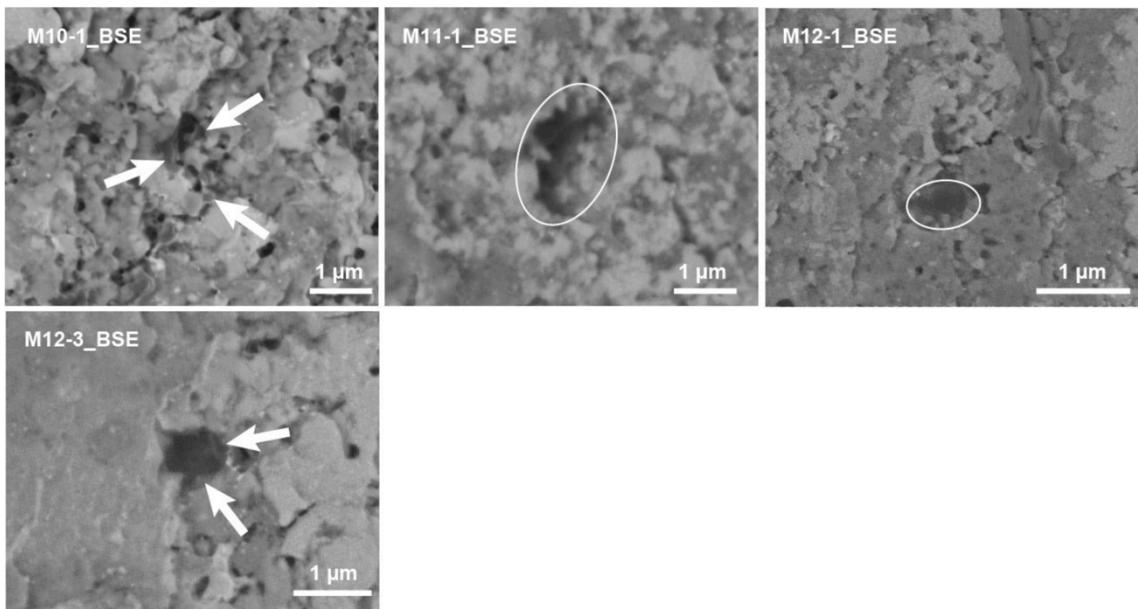
Figure S1

Supplementary Figure S1.

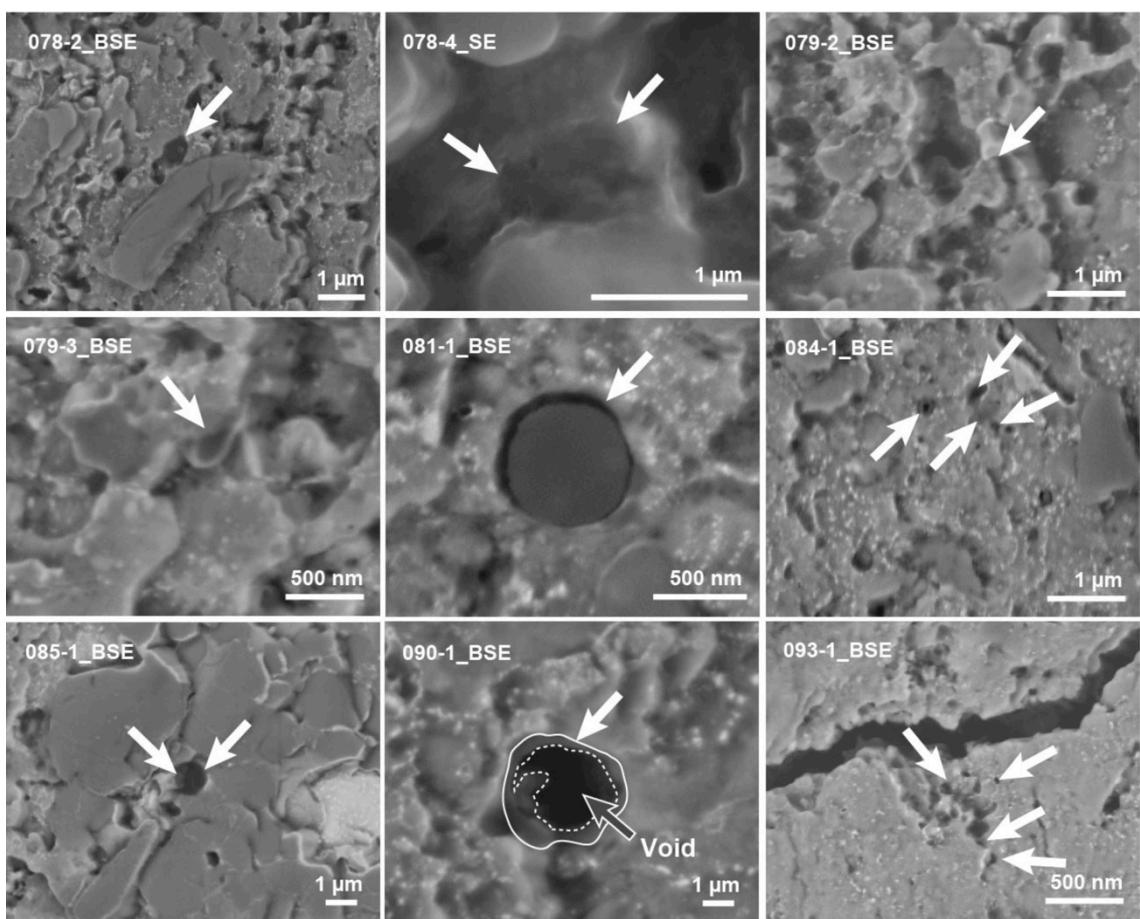
(a)



(a) (continued)



(b)



Supplementary Figure S1. BSE and SE images of organic matter from (a) Murchison and (b) NWA 801. Arrows and circles indicate locations of the organic matter. The sample numbers shown in each image correspond to those in Table 1.