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The existence of these dunes, their pristine appearance, and their superposition on other features tells us that in the geologically recent past, and quite probably the present, fine-grained and nonsticky (i.e., “dry”) material has been moved across Titan’s surface by wind. Because the net transport direction appears inclined at a small angle to eastward, it seems that if sand has migrated across large latitude ranges, the sand has circumnavigated Titan several times while doing so, apparently supporting a tidal wind model and arguing for an absence of standing liquids that would trap the sand [an absence of low-latitude lakes is also indicated by the lack of detection of specular reflections (25)]. The extent of the sand seas requires an origin for  $\sim 10^4$  to  $10^5$  km<sup>3</sup> of sand-sized material, considerably more than would be produced by impact ejecta (3). It may be that fluvial erosion of ice bedrock by liquid methane is able to produce this fine material. This would then somehow have to dry out, placing constraints on Titan’s meteorology. An alternative origin, perhaps supported by the optically dark appearance of the sand seas, is Titan’s stratospheric methane photochemistry, which over 4.5 billion years of solar system history may have produced up to  $10^6$  to  $10^7$  km<sup>3</sup> of hydrocarbons and nitriles, 10% of which would be solid (26). At issue is how this organic material is sorted and modified to produce the equivalent (in size and material properties) of sand.

Much work remains to fully characterize the distribution, morphology, and composition of these features in data already acquired and the much larger data sets anticipated in Cassini’s nominal and extended missions from RADAR

and from other instruments, and to relate the features to the windfield and planetary-scale cycles of sediment generation and transport. However, the morphology of these beautiful features, familiar to us from terrestrial arid regions, is a comforting sign that even though the environment and working materials on Titan are exotic, the physical processes that shape Titan’s surface (19) can be understood and studied here on Earth.

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22. Transport occurs when the wind’s friction speed  $U_*$  exceeds the threshold friction speed for saltation  $U_{*t}$ .  $U_*$  is a measure of wind stress that is related to the roughness-dependent drag coefficient  $C_d$  (typically 0.002 to 0.01) and the freestream windspeed  $U$  as  $(U/U_*)^2 \sim C_d$ ; thus, the freestream threshold speed is  $\sim 10$  to 25 times the friction speed. The optimum threshold speed has been estimated ( $I-3$ ), depending on assumed density, etc., as  $U_{*t} \sim 0.01$  to  $0.03$  ms<sup>-1</sup>, and thus dune formation requires freestream windspeeds of 0.1 to 0.7 ms<sup>-1</sup>. The corresponding Reynolds number range is 15 to 100.
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30. We gratefully acknowledge those who designed, developed, and operate the Cassini/Huygens mission. The Cassini/Huygens Project is a joint endeavor of NASA, the European Space Agency (ESA), and the Italian Space Agency (ASI) and is managed by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with NASA.

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## Interstellar Chemistry Recorded in Organic Matter from Primitive Meteorites

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Organic matter in extraterrestrial materials has isotopic anomalies in hydrogen and nitrogen that suggest an origin in the presolar molecular cloud or perhaps in the protoplanetary disk. Interplanetary dust particles are generally regarded as the most primitive solar system matter available, in part because until recently they exhibited the most extreme isotope anomalies. However, we show that hydrogen and nitrogen isotopic compositions in carbonaceous chondrite organic matter reach and even exceed those found in interplanetary dust particles. Hence, both meteorites (originating from the asteroid belt) and interplanetary dust particles (possibly from comets) preserve primitive organics that were a component of the original building blocks of the solar system.

Carbonaceous chondrites, the most primitive meteorites, and interplanetary dust particles (IDPs), primitive dust collected in Earth’s stratosphere, contain up to  $\sim 2$  and  $\sim 35$  weight percent C in organic matter, re-

spectively. This organic matter may represent an important source of prebiotic molecules that were essential for the origin of life on Earth (1). Most of the organic matter is insoluble in demineralizing acids and organic solvents, and

this proportion is probably macromolecular (1). Isotope anomalies in H and N suggest that this insoluble organic matter (IOM) is probably interstellar material that, like other presolar materials, has survived the formation of the solar system to be incorporated into planetesimals (2–6), but it may also include material that formed in the cold outer regions of the solar protoplanetary disk (7). Heating, mixing, and chemical reactions in the collapsing protosolar cloud, in the protoplanetary disk, and during accretion of the parent bodies of meteorites and IDPs could have altered—or erased—the initial isotope signatures of interstellar IOM. Aqueous alteration and thermal metamorphism on the parent bodies of meteorites and IDPs have further modified the organic carriers of these

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**Table 1.**  $\delta D$  and  $\delta^{15}N$  in carbonaceous chondrites, as measured by SIMS and NanoSIMS (13) (n.m., not measured). The hotspots are manually defined regions of  $\geq 1.3 \mu m$  ( $\delta D$ ) and  $\geq 500 nm$  ( $\delta^{15}N$ ), respectively. "Heterogeneity" has been parameterized with the fraction of automatically

created regions of interest [ROIs (13)] that are isotopically anomalous. We added up all ROIs with  $|\delta D_{ROI} - \delta D_{average}| > 3 \times \sigma_{ROI}$  and  $\sigma_{ROI} < 25\%$ . Note that all hotspot values are lower limits because their sizes are comparable to the spatial resolution of the imaging techniques.

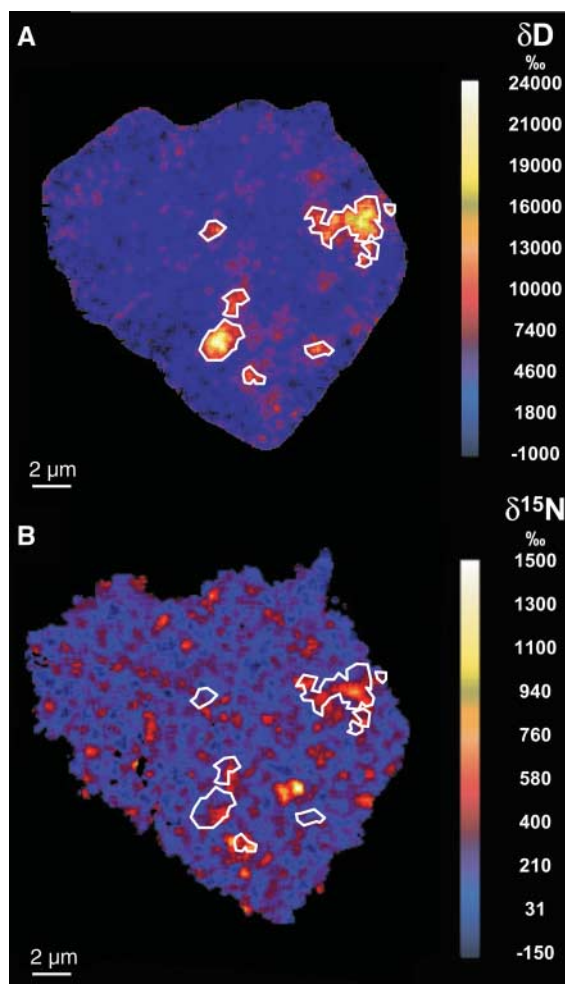
Meteorite	Class	$\delta D$				$\delta^{15}N$			
		Maximum, hotspot	Bulk IOM (14)	Analyzed area ( $\mu m^2$ )	Heterogeneity (area %)	Maximum, hotspot	Bulk IOM (14)	Analyzed area ( $\mu m^2$ )	Heterogeneity (area %)
<i>IOM</i>									
GRO 95577	CR1	19,400 $\pm$ 4,600	2973	11,780	0.6	1510 $\pm$ 240	233.2	1440	0.04
EET 92042	CR2	16,300 $\pm$ 2,100	3004	13,112	2.4	1770 $\pm$ 280	185.5	1937	1.0
Al Rais	CR2	14,300 $\pm$ 3,900	2658	6,261	0.3	1740 $\pm$ 350	146.3	3480	0.005
Murchison	CM2	1,740 $\pm$ 280	712	738	4.3	n.m.	n.m.	n.m.	n.m.
Bells	Anomalous CM2	9,700 $\pm$ 2,100	3283	5,702	0.3	3200 $\pm$ 700	415.3	2844	0.11
<i>Matrix</i>									
Al Rais	CR2	6,200 $\pm$ 650		867	6.2	2000 $\pm$ 200		637	0.03
Tagish Lake	Ungrouped C2	8,600 $\pm$ 1,000		3,963	2.9	410 $\pm$ 130		1234	0.10

isotope anomalies and exchanged them with isotopically normal matter. The detection of isotope anomalies indicates that the pristine character of the IOM has not been entirely lost.

Until now, the most extreme enrichments in D (8) and  $^{15}N$  (9) have been found in so-called hotspots (regions that are extremely isotopically enriched relative to the surrounding matter) in anhydrous cluster IDPs, which may originate from comets. In contrast, IOM from meteorites, whose parent bodies are in the asteroid belt, showed bulk isotope anomalies that were relatively small relative to those in IDP hotspots (6, 10). This difference was assumed to be the result of the more severe parent body alteration and possibly nebular processing [e.g., (11)] experienced by meteorites. However, very few analyses [e.g., (12)] on meteorites have been carried out on the same spatial scales as the IDP studies.

Here we report D and  $^{15}N$  hotspots in meteoritic IOM that are comparable to, or even exceed, those reported in IDPs. Thus, organic matter that is as primitive as that found in IDPs survives in some meteorites (Table 1), despite the more extensive alteration experienced by the meteorites on their parent bodies. This means that large samples of primitive organic matter can be prepared from meteorites for studies that would not be possible with IDPs, which typically have masses on the order of  $10^{-12}$  g.

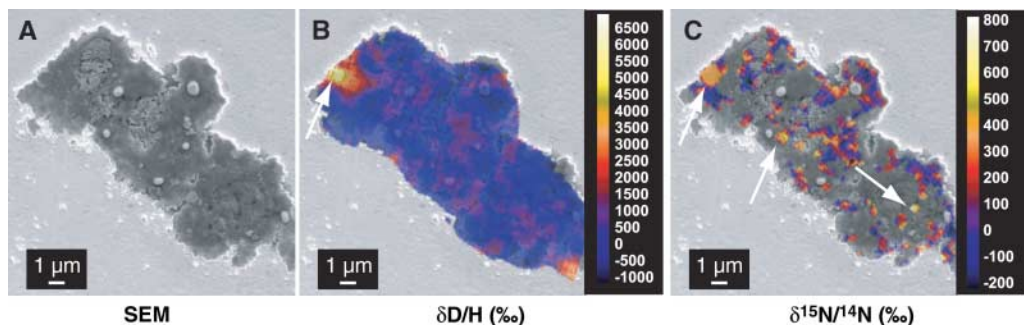
We analyzed matrix fragments from two carbonaceous chondrites (Al Rais and Tagish Lake) and IOM separates from five carbonaceous chondrites [Grosvenor Mountains (GRO) 95577, Elephant Moraine (EET) 92042, Al Rais, Murchison, and Bells] (Table 1) by imaging secondary ion mass spectrometry (13). All samples exhibited large isotopic heterogeneities [ $\delta D \sim 1700$  to  $19,400$  per mil (‰),  $\delta^{15}N \sim 400$  to  $3200$ ‰; the  $\delta$  notation gives measured isotopic ratios as deviations from terrestrial standards] on scales compara-



**Fig. 1.** Maps of (A)  $\delta D$  and (B)  $\delta^{15}N$  in a sample of IOM from the CR2 chondrite EET 92042. Most D and  $^{15}N$  hotspots in EET 92042 ( $\delta D$  up to  $16,300$ ‰ and  $\delta^{15}N$  up to  $1770$ ‰) are not spatially associated.

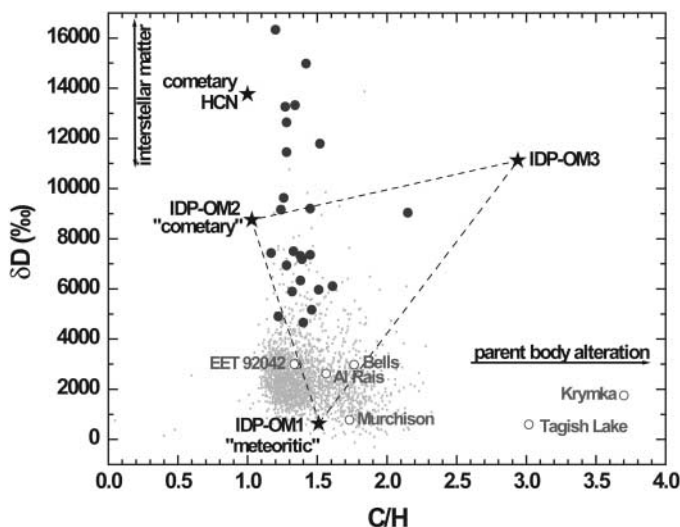
ble to the spatial resolutions of the instruments (Table 1) (13). The most extreme D/H values were found in pure IOM separates. Because the hotspots survive the chemical separation procedure and exhibit a range of compositions, the hotspots appear to be robust units that formed in a range of environments. Figure 1A is a D/H map of an IOM sample from EET 92042 (a Renazzo-type, or CR2,

chondrite recovered in Antarctica) that contains two large D hotspots and several smaller ones. The  $\delta D$  values for one of these ( $16,300 \pm 2100$ ‰) and for a similar hotspot in GRO 95577 ( $19,400 \pm 4600$ ‰) are the largest ever reported for meteoritic material. In total, D hotspots in EET 92042 IOM made up  $\sim 1.5\%$  of the area analyzed (Table 1). Note that the bulk IOM has a  $\delta D$  value of  $\sim 3000$ ‰ (14),



**Fig. 2.** (A) Scanning electron micrograph (secondary image) of a matrix fragment of Tagish Lake. (B) The overlaid  $\delta D$  map shows two D hotspots. (C) The overlaid  $^{15}N/^{14}N$  map shows hotspots with  $\delta^{15}N$  values up to  $\sim 400\text{‰}$  (arrows). The largest of these [at upper left, arrow in (B)] is also D-rich and is spatially related to a round carbonaceous region discernable in (A). These hotspots likely correspond to the “nano-globules” observed in this meteorite (13, 30).

**Fig. 3.**  $\delta D$  and C/H (atomic) in the IOM of EET 92042. The most D-rich regions (“hotspots,” solid circles) exhibit  $\delta D$  values between 4500 and 16,300‰. These values exceed those of suggested end members in the organic matter of IDPs (stars, OM1 to OM3) (28) and reach the  $\delta D$  value of cometary HCN ice (31). The average of automatically defined image subregions 2  $\mu m$  in diameter (gray dots) (13) is 2613‰, close to 3004‰ given for EET 92042 bulk IOM (open circle) (14), which indicates that sputtering equilibrium is reached and terrestrial contamination was not important for the EET 92042 measurements. Data from bulk IOM analyses of the same meteorites that are analyzed here are given for comparison (open circles) (14). Thermal alteration results in higher C/H values and ultimately homogeneous and low  $\delta D$  values.



and therefore these hotspots make only a small contribution to the bulk composition. This is true of all analyzed IOM. Regions that are highly D-enriched have also been found in matrix fragments of Al Rais and Tagish Lake (Fig. 2).

The meteoritic IOM and matrix fragments also exhibit substantial spatial heterogeneity in their N isotopic compositions (Fig. 1B). EET 92042 has a bulk  $\delta^{15}N$  of 185‰ (14) but has numerous regions with higher values up to  $\delta^{15}N = 1770 \pm 280\text{‰}$ . Bells IOM shows even larger enrichments in  $^{15}N$  than does EET 92042, both in bulk (415‰) and in several hotspots with extreme  $\delta^{15}N$  values between 2000 and 3200‰. These values are the highest ever reported for extraterrestrial material, except in presolar circumstellar grains (15). Note that the  $\delta^{15}N$  values are relative to terrestrial atmospheric N, but the Sun has isotopically lighter N [ $\delta^{15}N \leq -240\text{‰}$ , e.g., (16)]. The enrichments reported here are therefore even larger relative to the solar value (2100 to 5400‰). The  $\delta D$  values given here are relative to ocean water, which is also isotopically much heavier than was the initial solar H [ $\delta D \approx -870\text{‰}$  (17)].

There is no general spatial correlation between H and N isotopes in any of the measured samples (Fig. 1). Although some D hotspots are relatively  $^{15}N$ -enriched, the largest  $^{15}N$  enrichments of  $>1000\text{‰}$  are not spatially related to D hotspots; this indicates that the most extreme anomalies are generally in different molecular carriers and probably formed through different chemical pathways.

Our data show that highly anomalous matter survived essentially unaltered in the parent bodies of primitive meteorites.  $\delta D$  values of up to  $\sim 19,000\text{‰}$  and  $\delta^{15}N$  values above 3000‰ indicate that a complete homogenization of the pristine IOM did not occur. D enrichments comparable to those found in the IOM of the CR chondrites (Table 1) were previously observed only in two fragments of a cluster IDP (8, 18). Also, the highest observed  $\delta^{15}N$  hotspot values ( $\sim 2000$  to 3200‰ in Bells, 1770‰ in EET 92042) far exceed the highest value of  $1270 \pm 25\text{‰}$  found in IDPs (9, 19). The parent bodies of the cluster IDPs (possibly Kuiper Belt comets) have been assumed to contain the most primitive matter in solar system objects (8). The new results

imply that the parent bodies of both meteorites and IDPs acquired a comparably primitive assemblage of organic matter that survives in meteorites despite the more extensive processing that they experienced.

The largest D enrichment previously reported in a meteorite ( $\delta D \sim 8000\text{‰}$ ) was found by ion microprobe imaging of a matrix fragment of the CR2 chondrite Renazzo (12). We found comparable D enrichments in Al Rais (CR2) matrix, and even higher  $\delta D$  values ( $>14,000\text{‰}$ ) in IOM separates from three CR chondrites. These observations support the view, based on N isotopes in bulk samples, that CR chondrites are the carbonaceous chondrite group that preserved the most primitive organic matter (6). Bells IOM is even more isotopically anomalous than that of the CR chondrites, but Bells appears to be unique among the CM chondrites. The presence of D and  $^{15}N$  hotspots in the matrix of the ungrouped C2 chondrite Tagish Lake (Table 1) shows that primitive organics have survived in this meteorite, even though nuclear magnetic resonance studies (20) have revealed that bulk Tagish Lake IOM has been substantially altered by oxidation and is less primitive than the CR2 IOM. Microscopic analyses are necessary to fully understand the survival and alteration of pristine organics in meteorites; our micro-scale isotope examination of meteoritic components allows for the localization of these primitive organic components for further investigation.

The isotopic anomalies observed here must have originated either in cold interstellar clouds, where large  $\delta D$  values have been observed and large  $\delta^{15}N$  values have been predicted (2–6), or in the outer regions of the protoplanetary disk (7), where large D enrichments have been predicted for gas-phase molecules. Viable mechanisms for producing large  $\delta D$  and  $\delta^{15}N$  values in either environment are low-temperature ( $\sim 10$  K) ion-molecule reactions in the gas phase and catalytic processes on dust grains. An interstellar origin is supported by the similarity of the IOM infrared and ultraviolet (UV) spectra to interstellar medium features of refractory organics (21, 22). Moreover, the presence of circumstellar grains in meteorites and IDPs shows that interstellar

matter did survive the formation of the solar system. Finally, it has yet to be demonstrated that isotope anomalies formed in simple molecules in the outer protoplanetary disk could be transferred into the large amounts of complex organics eventually incorporated into the chondrite parent bodies. Therefore, we favor an interstellar origin. Regardless of where the anomalous material originated, the decoupled H and N systems indicate a variety of formation processes for the components of the organic matter.

The  $^{15}\text{N}$  enrichments observed here in the IOM of Bells and EET 92042 and in IDPs (9) far exceed the maximum model predictions for interstellar chemistry [ $\delta^{15}\text{N} \sim 800\%$  in certain molecules relative to the starting composition, (3, 4)]. A stellar, nucleosynthetic origin of these  $^{15}\text{N}$  enrichments is unlikely because, with one exception (13, 23), the C isotopic compositions of  $^{15}\text{N}$  hotspots did not exhibit the extreme anomalies indicative of nucleosynthesis ( $^{12}\text{C}/^{13}\text{C} \approx 0.01$  to  $100 \times$  solar ratio) typically found in meteoritic presolar grains (15). It is also unlikely that isotopically anomalous N from circumstellar grains has been redistributed into interstellar organic matter with essentially normal C isotopic composition. Likewise,  $^{13}\text{C}$  anomalies associated with  $^{15}\text{N}$  enrichments in IDPs are rare (9). Stellar sources of  $^{15}\text{N}$ -rich dust, such as novae, are only minor contributors to the dust in the Galaxy, and most (>90%) N-bearing circumstellar dust grains found in meteorites are enriched in  $^{14}\text{N}$  (15).

The  $\delta^{15}\text{N}$  values between 1000‰ and 3200‰ reported here require a new mechanism for enriching  $^{15}\text{N}$ . Elevated  $^{15}\text{N}/^{14}\text{N}$  values could have been produced by UV self-shielding in regions of the solar nebula (24) or protosolar cloud, where, because of the much greater abundance of  $^{14}\text{N}$ , the  $^{14}\text{N}_2$  UV absorption lines are saturated but not the  $^{15}\text{N}^{14}\text{N}$  and  $^{15}\text{N}_2$  lines. However, the potential magnitude of the enrichments that would ultimately be transferred to the IOM is unknown. Oxygen isotope anomalies in meteoritic minerals have been attributed to UV self-shielding, but these anomalies are only on the order of 50‰. Much larger O isotope anomalies measured in rare silica grains located in organic separates from Murchison (25) have been attributed to particle irradiation of matter by the early active Sun. However, such a scenario cannot explain the D enrichments in organic matter. This and the mostly uncorrelated occurrence of D and  $^{15}\text{N}$  hotspots suggest that different mechanisms were responsible for the isotope anomalies found in H, N, and O.

Whether the D and  $^{15}\text{N}$  enrichments in the IOM were established in the protosolar cloud or the protoplanetary disk, the presence of similar material in both meteorites and IDPs provides insights into the conditions that

prevailed during the formation of the asteroid belt. The parent bodies of the chondritic meteorites probably formed in restricted regions within the asteroid belt at  $\sim 3$  AU from the Sun. The organic molecules are much more fragile than the presolar circumstellar grains found in meteorites. The presence of organic C shows that the ambient temperature in the asteroid belt was low at the time of asteroid accretion, and that (i) the ambient temperature was always low, or (ii) the organics were introduced when the ambient temperatures in the asteroid belt were sufficiently low for their survival. The introduction of organic matter into the asteroid belt could be the result of continuing infall of interstellar material onto the protoplanetary disk, or transport of material from greater radial distances in the disk [e.g., through turbulent mixing (26)]. Radial mixing of organic matter into the asteroid belt would be consistent with the inference, based on the observation of crystalline silicates in comets, that such mixing was important in the early solar system [e.g., (26, 27)]. The cometary and asteroidal parent bodies of IDPs and primitive meteorites may have sampled to varying degrees the same reservoirs of presolar material (interstellar organic matter, amorphous silicates, and circumstellar grains) and crystalline silicate-dominated material that was processed in the inner solar nebula (13).

Although the IOM in primitive meteorites is isotopically very heterogeneous on a scale of  $\sim 0.1$  to  $1.5 \mu\text{m}$  (Fig. 1), as is the case for IDPs (8, 9), the most extreme D and  $^{15}\text{N}$  hotspots have C/H abundances that are typical of the bulk IOM (Fig. 3). However, isotopic imaging of IDPs has led to the suggestion that extraterrestrial organic matter is a mixture of three components (labeled OM1 to OM3) with distinct H and N isotopic compositions and C/H ratios [(28) and references therein]. These observations are not reproduced by meteoritic IOM (Fig. 3). The bulk IOM in many primitive meteorites is already much more D-rich [up to  $\delta\text{D} \sim 3000\%$  (14)] than the OM1 component in IDPs ( $\delta\text{D} \sim 630\%$ ) that has been suggested to resemble typical IOM in carbonaceous chondrites. All D hotspots show C/H ratios that are similar to those of the bulk IOM of the respective meteorites (Fig. 3). This is not the result of a more thorough mixing of the various organic phases in meteorites relative to IDPs, because the highest values for  $\delta\text{D}$  and  $\delta^{15}\text{N}$  in meteorites found here are more extreme than those of OM2 and OM3. IOM in meteorites is not represented by the three end-member components deduced from IDPs.

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#### Supporting Online Material

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Materials and Methods

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References

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