A Common Origin for Organics in Meteorites and Comets: Was It Interstellar?

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Abstract. The insoluble organic material preserved in primitive chondritic meteorites shares many similarities with the refractory organic material in interplanetary dust particles and comets, suggesting that there is a genetic link between the organic matter in objects that formed between $\sim$3 AU and $\sim$30 AU from the Sun. These similarities include large D and ^{15}N enrichments in bulk and even more extreme enrichments in isotopic hotspots. The enrichments attest to formation in very cold environments, either in the outer Solar System or the protosolar molecular cloud. There are many properties of this organic material that are consistent with an interstellar origin, but a Solar System origin cannot be ruled out. Similar organic material is presumably an important component of most protoplanetary disks, and heating or sputtering of this material would be a source of PAHs in disks. The soluble organic matter was more heavily effected by processes on the chondritic parent bodies than the insoluble material. Amino acids, for instance, probably formed by reaction of ketones and aldehydes with NH_3 and HCN. The accretion of the relatively volatile NH_3 and HCN, presumably in ices, strengthens the chondrite-comet connection. However, unlike most comets the water in chondrites, when it was accreted, had D/H ratios that were similar to or depleted relative to Earth.

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1. Introduction

The three basic types of extraterrestrial material that are accreted by the Earth and survive atmospheric entry are classified according to size into: interplanetary dust particles (IDPs), micrometeorites (and the related fully melted cosmic spherules) and meteorites. IDPs and micrometeorites almost certainly have both cometary and asteroidal sources, although the proportions of cometary and asteroidal particles remain a matter of debate (Dermott *et al.* 2002; Nesvorny *et al.* 2010). The most recent dynamical arguments suggest that most come from Jupiter family comets (Nesvorny *et al.* 2010). With a few exceptions, those that come from the Moon and Mars, meteorites are fragments of main-belt asteroids (2-4 AU), with a strong bias towards inner belt asteroidal sources (Morbidelli *et al.* 2002). While there is an overall gradient of spectral classes in the asteroid belt (Gradie, Chapman & Tedesco 1989), there has been considerable mixing and it is likely that the meteorite collection has sampled many of these classes (Burbine *et al.* 2002).

Entry velocity, size, density and entry angle together determining the degree of frictional heating that a particle experiences during atmospheric entry and, therefore, the extent to which organics and other temperature sensitive materials are preserved. The IDPs that are collected in the upper atmosphere are small (typically <50 μm) and low

density, so that they decelerate relatively gently. Nevertheless, even the least heated of them probably experience temperatures of at least several degrees Celsius for several seconds. Denser particles from the same bodies as the IDPs would probably be destroyed during atmospheric entry, so it is unclear how representative of their parent bodies IDPs are. Micrometeorites (typically 100-1000 μm) are generally severely heated on atmospheric entry, and so most are unlikely to retain unmodified organic material. However, organics do survive in a rare group of C-rich particles that may have links to comets (Duprat *et al.* 2010). Evaporation, ablation and poor thermal conduction confine heating to the outer few millimeters of recovered meteorites.

The most primitive meteorites, the chondrites, are composed of materials that formed in the solar nebula or that even predate it. Chondrites can contain up to several weight percent of organic material. The complex suite of compounds that constitute this organic matter can have large D and ^{15}N enrichments that are usually interpreted to indicate that they or their precursors formed at very low temperatures. Similar enrichments are seen in IDPs (Messenger 2000; Aléon *et al.* 2003; Floss *et al.* 2006; Busemann *et al.* 2009) and Stardust particles returned from comet Wild 2 (McKeegan *et al.* 2006; Matrajt *et al.* 2008). Thus, it seems likely that there is a genetic link between the organics in chondrites and comets. It is still a matter of contention whether the organics formed in the presolar molecular cloud and/or in the early Solar System. A detailed understanding of the compositions of the various components of the chondritic organic matter may ultimately help resolve this debate.

Most chondrites also show evidence of having accreted water, presumably as ice, when they formed. It seems likely that the organics and water ice would have been intimately associated when they accreted, as they are in comets. In which case, the origins of the organics and water may be linked. Understanding the origin of the water in chondrites may also elucidate the origin of the water in the inner Solar System and transport processes in the solar protoplanetary disk (or solar nebula).

2. Meteorite Classification

Meteorites are broadly divided into two, the chondrites and achondrites (Krot *et al.* 2003). Only the most primitive types of meteorite, the chondrites, are generally thought to contain indigenous organic material. This is because achondrite meteorites come from parent bodies that experienced extensive melting, and even wholesale differentiation into silicate mantles and iron cores. Chondrites are comprised of three main components: refractory inclusions, chondrules and fine-grained matrix. Refractory inclusions and chondrules are high temperature (1400-1800°C) objects that formed in the solar nebula. Organics would not have survived the high formation temperatures of refractory inclusion or chondrule. Consequently, it is only in the matrix that cements the meteorites together that primary organic matter should be found. It is in the matrix that one also finds presolar circumstellar grains that formed around highly evolved stars, such as supernovae and asymptotic giant branch (AGB) stars (Nittler 2003; Alexander 2009), and were inherited from the protosolar molecular cloud.

Historically, the chondrites have been divided into three classes based on their compositions and mineralogies (ordinary, carbonaceous and enstatite). These in turn have been subdivided (Scott & Krot 2003; Weisberg, McCoy & Krot 2006) into a number of groups: ordinary chondrites into H, L and LL, carbonaceous chondrites into CI, CM, CR, CV, CO, CB, CH and CK, and enstatite chondrites into EH and EL. The name carbonaceous chondrite is a historical one and is a bit misleading since some ordinary and enstatite chondrites contain more C than some carbonaceous chondrites. The chondrite

classification scheme is still evolving as more meteorites are found - two new classes (R and K chondrites) have been identified, and a number of individual meteorites do not belong to any recognized group.

The CIs have bulk compositions that are essentially identical to that of the rock-forming component (excluding H, He, etc.) of the Sun (Lodders 2003). Because solar (or CI) is the starting composition from which all Solar System materials evolved, the compositional variations of chondrites and their components are generally expressed as deviations relative to CI. The deviations of the compositions of chondrites (and their components) from CI are presumed to be the results of their formation processes in the solar nebula.

After formation, the chondrites experienced secondary modification - protracted episodes of thermal metamorphism and aqueous alteration, and in some cases brief shock heating events - on their parent bodies. A petrographic classification scheme for secondary processes divides the chondrites into 6 types - types 3 to 6 reflect increasing extent of thermal metamorphism, and types 3 to 1 reflect increasing degrees of aqueous alteration. By convention, the chemical classification is followed by the petrologic one (e.g., CI1, CM2, CV3).

3. Organics in Chondrites

There have been a number of recent reviews of the organic matter in meteorites and IDPs (Botta & Bada 2002; Sephton 2002; Gilmour 2003; Sephton 2005; Pizzarello, Cooper & Flynn 2006). However, with the renewed interest in the subject, the introduction of new techniques, and new samples from Antarctica and the Stardust sample return mission to Comet 81P/Wild 2, the field is evolving rapidly. Here we focus on the most recent work. The organic matter is normally divided into solvent soluble (SOM) and insoluble (IOM) fractions, and consequently they are discussed separately. The abundances of IOM and the known components of the SOM are summarized in Table 1. Also included in Table 1 are the matrix volume percents because the organic matter would have been accreted by the chondrites in the matrix material.

3.1. *Insoluble Organic Matter*

The IOM shows tremendous variation in its elemental and isotopic compositions both within and between chondrite groups (Alexander *et al.* 2007b, 2010), but these variations are due, at least in large part, to processes that occurred on the asteroidal parent bodies of the chondrites (Alexander *et al.* 2007b; Alexander *et al.* 2010; Herd *et al.* 2011). In the meteorites (C1-2) that appear to have seen the most benign parent body conditions, the bulk composition of the IOM, normalized to 100 Cs, is $\sim C_{100}H_{70-79}N_{3-4}O_{11-21}S_{1-5}$ (Alexander *et al.* 2007b). This is remarkably similar to the average composition of the comet Halley CHON particles - $C_{100}H_{80}N_4O_{20}S_2$ - detected by the Vega 1 spacecraft (Kissel & Krueger 1987).

Even amongst the C1-2 chondrites there is considerable elemental and isotopic variation in their IOM. The chondrites that harbor the apparently most primitive IOM are the CRs. Not only are the bulk H and N isotopic compositions of the IOM in CRs more anomalous than IOM from almost any other chondrite, but their IOM also contains small ($\leqslant 1\ \mu$m) isotopic hotspots that are more numerous and more extreme than in other chondrites (Busemann *et al.* 2006). The D/H ratios of the hotspots can be up to ~ 40 times the terrestrial ratio, and $^{15}N/^{14}N$ ratios can be up to ~ 4 times the terrestrial ratio. The hotspot D and ^{15}N enrichments overlap with the range of gas phase molecules in the ISM, but the two isotope systems are not correlated in any simple way. The bulk CR IOM

Table 1. The abundances of insoluble and soluble organic compounds (in μg/g or ppm) found in carbonaceous chondrites. For the CMs, all data are from the Murchison CM2 meteorite, unless otherwise noted (updated from Botta & Bada 2002).

	CI	CM	CR	Tag. Lake
Matrix (vol%)	100	$\sim$50	$\sim$35	$\sim$80
IOM	$\sim$20,000	$\sim$10,000	$\sim$5,000	$\sim$18,000
Amino acids	$\sim$5[a]	14-71[d]	1-250[b]	0.04-5.6[c]
Aromatic hydrocarbons		3[d]	16[e]	
Aliphatic hydrocarbons		>35		
Monocarboxylic acids		>300	96[e]	165-448[c]
Hydroxy- and dicarboxylic acids		14-15	212[e]	
Purines and pyrimidines		1.3		
Basic N heterocycles		7		
Amines		8	103[e]	
Alcohols		11		
Aldehydes and Ketones		27		
Sulphonic acids		68		
Phosphonic acids		2		
Polyols		>8[f]		

Notes:
[a] Average for Orgueil and Ivuna (Ehrenfreund *et al.* 2001).
[b] Range from Martins *et al.* (2007).
[c] Herd *et al.* (2011).
[d] For Y-791198 (Naraoka *et al.* 1998).
[e] For GRA 95229 (Pizzarello *et al.* 2008).
[f] Lower limit of glyceric acid (Cooper *et al.* 2001).

isotopic compositions, and the range of hotspot compositions and sizes are very similar to those seen in the most primitive anhydrous chondritic IDPs (Messenger 2000; Aléon *et al.* 2003; Floss *et al.* 2006; Busemann *et al.* 2009), whose H and N isotopic compositions are dominated by those of their organics. The CR IOM H and N isotopic compositions are generally more anomalous than the compositions of organic particles identified in the Stardust mission samples (McKeegan *et al.* 2006; Matrajt *et al.* 2008). However, this could be because of modification during capture and, possibly, contamination.

The H/C ratios of the primitive IOM are not unlike those of a fairly mature coal. Thus, it is not surprising that the IOM is fairly aromatic. Nuclear Magnetic Resonance (NMR) spectroscopy suggests that $\sim$50% of the C in CR IOM is in small PAHs (one to a few benzene rings), that these PAHs are heavily substituted and are cross-linked by short, highly branched aliphatic chains and O functionality (Cody & Alexander 2005). IOM from CI and CM chondrites tend to be slightly more aromatic, but otherwise similar in structure to IOM in CRs (Gardinier *et al.* 2000; Cody, Alexander & Tera 2002; Cody & Alexander 2005; Cody *et al.* 2011). This confirms earlier work based on degradative chemistry (Hayatsu *et al.* 1977) and various pyrolysis techniques (Sephton, Pillinger & Gilmour 1999; Sephton & Gilmour 2001; Remusat *et al.* 2005; Sephton *et al.* 2005; Wang *et al.* 2005). The variations in aromatic C content are probably the result of parent body processes, and largely involved the conversion of aliphatic C to aromatic C and associated H loss (Herd *et al.* 2011). There also seems to be variable amounts of H

isotope exchange and/or preferential D loss during this process. This suggests that the D is preferentially concentrated in the aliphatic fraction, an inference that appears to be confirmed by recent pyrolysis (Remusat *et al.* 2006) and NMR measurements (Wang *et al.* 2011). Simple heating of IOM above a few hundred degrees Celsius in an O-free atmosphere (pyrolysis) releases a lot of small PAHs and leaves a char. Heating of IOM-like material would be one mechanism for producing the PAHs that have been seen in protoplanetary disks. Sputtering of IOM-like material by energetic particles would also release PAHs.

The isotopic hotspots in IOM are not abundant enough to account for the bulk D and ^{15}N enrichments. However, these hotspots are often associated with so-called globules or nanoglobules (Nakamura-Messenger *et al.* 2006). These globules are spherical to irregular in shape and often hollow (Nakamura *et al.* 2002; Garvie & Buseck 2004; Garvie, Baumgardener & Buseck 2008). Similar globules have now been found in IDPs and Stardust particles (Busemann *et al.* 2009; De Gregorio *et al.* 2010). Raman spectroscopy also suggests that the structure of the bulk of the organic material in the most primitive IDPs is similar to that of IOM from primitive chondrites, although on average it may be more disordered (Busemann *et al.* 2009). There is also a suggestion that the D in IDPs is largely associated with aliphatic material (Keller *et al.* 2004). However, based on IR spectra in the 3.4 μm C-H stretch region, higher CH_2/CH_3 ratios in IDPs than in chondritic IOM suggests that the aliphatic material in IDPs tends to be shorter and/or more branched (Flynn *et al.* 2003; Keller *et al.* 2004; Muñoz Caro *et al.* 2006; Kebukawa, Alexander & Cody 2011). Whether the greater disorder and higher CH_2/CH_3 ratios in IDPs is indigenous or was induced by irradiation in interplanetary space and atmospheric entry heating remains to be seen.

From the above, it is likely that there is a genetic relationship between the IOM and the organic matter in IDPs/comets, although the abundance of organic matter in IDPs and comets is much higher. The organic C contents are perhaps most usefully expressed in terms of the fractions of the bulk solar C. Based on Mg/C ratios, the percentage of solar C in CI chondrite IOM is $\sim$7%, it is $\sim$30% on average in IDPs and $\geqslant$30% in comet Halley CHON particles (Alexander *et al.* 2007a). Thus, if there is a genetic relationship between IOM in chondrites and IDPs/comets, IOM-like material seems to have been widely distributed in the solar nebula but it formed or was better preserved in the outer Solar System. This along with the structural and isotopic properties of the IOM places considerable constraints on the various formation scenarios that have been proposed for the IOM.

One often invoked formation mechanism is Fischer-Tropsch-type (FTT) synthesis in the solar nebula (Hayatsu & Anders 1981; Ferrante *et al.* 2000; Nuth, Hill & Kletetschka 2000). Typically, FTT synthesis takes place on catalytic mineral surfaces, but there is no systematic association of the IOM with any mineral in meteorites (Remusat *et al.* 2010). Also, FTT synthesis would be most efficient in a narrow zone in the warm inner Solar System (Kress & Tielens 2001). Hence it is unclear why IOM-like organics would be more abundant in the outer Solar System. Finally, FTT synthesis cannot explain the D and ^{15}N enrichments in IOM. It has been pointed out that the conditions in the outer Solar System would have been quite similar to those in the protosolar molecular cloud. Therefore, the D enrichments in the IOM could have formed by reaction of IOM-like material with H_2D^+ in the Solar System (Gourier *et al.* 2008; Remusat *et al.* 2009). However, if the conditions in the outer Solar System and the protosolar molecular cloud were so similar, this begs the question - what process destroyed the condensed organic C that appears to be so abundant in the diffuse and dense ISM, and then allowed organic C to reform so efficiently as IOM elsewhere in the Solar System? FTT synthesis also

does not explain why there is a fairly constant ratio of circumstellar grains to IOM in chondrites (Alexander *et al.* 2007a,b).

Based largely, but not solely, on the isotopic composition of the IOM, an ISM origin for the IOM has been invoked (e.g., Robert & Epstein 1982; Yang & Epstein 1984; Alexander *et al.* 2007b). An ISM origin is strengthened by the similarity of the IR 3.4 μm C-H stretch adsorption feature of IOM and of carbonaceous dust in the diffuse ISM (Ehrenfreund *et al.* 1991; Pendleton *et al.* 1994). Some proposed structures for the diffuse ISM carbonaceous dust invoke small, highly substituted PAHs and short, highly branched aliphatic chains (Jones, Duley & Williams 1990; Sandford *et al.* 1991; Dartois *et al.* 2005) and are remarkably similar to that of the IOM. On the other hand, Pendleton & Allamandola (2002) concluded that the PAHs in the diffuse ISM dust were large and that the dust contains few N or O heteroatoms. Oxygen isotopes suggest that much of the O functionality in chondritic IOM is probably the result of parent body processes (Alexander *et al.* 2007b), and it is not clear whether the N content of IOM is inconsistent with the spectroscopic constraints for diffuse ISM dust. It is also important to point out that the spectra Pendleton & Allamandola (2002) used is in fact a 600^oC sublimate from IOM and is, therefore, not representative of the bulk IOM. Nevertheless, this does not explain the absence of large PAHs in IOM. Pendleton & Allamandola (2002) concluded that the diffuse ISM dust probably formed in the outflows of C-stars. This too would be inconsistent with the IOM because the C-star outflows will be depleted in D and ^{15}N, and can have C isotopic compositions that are far from solar. Equally problematic to an interstellar origin for the IOM is that the 3.4 μm C-H stretch feature seen in the diffuse ISM dust and IOM is not seen in molecular clouds.

To overcome some of these problems, Alexander *et al.* (2008) suggested that in very cold molecular clouds cosmic ray irradiation of ice-coated diffuse ISM dust led to dehydrodgenation of aliphatic material and radiation damage of any large PAHs. Upon warming up, either as the dust enters a forming system or re-enters the diffuse ISM, the radicals in the damaged dust may react with radicals in the ice (e.g., H, OH, NH_2, CH_3, etc.) rather than reform their original bonds. Since the ice is likely to be D- and ^{15}N-rich, this process could explain both the heteroatom content, and D and ^{15}N enrichments in the IOM. Dust re-entering the diffuse ISM would have to loose its O functionality and remake any large PAHs, processes that would presumably have to be driven by the intense UV radiation field that exists there. This model should be testable experimentally. However, it does not explain the solar C isotopic composition of the IOM or the formation of globules. The C isotopes might be explained if in fact the typical lifetime of carbonaceous dust in the ISM is short compared to the production rate by C-stars (Serra Díaz-Cano & Jones 2008). In this case, there must be an efficient mechanism for making the dust in the ISM, and the bulk C isotopic composition of the dust that forms in the ISM is likely to have been close to the bulk isotopic composition of the ISM (i.e., solar) at that time. Nakamura-Messenger *et al.* (2006) suggested that globules could have formed by irradiation of ISM ices, but in their mechanism the wall thicknesses of the globules would reflect the penetration depth of the radiation (10s to a few hundred nanometers), which is too little for cosmic rays and probably requires unreasonably high C contents for the ice.

A quite different scenario for IOM formation is envisaged by Cody *et al.* (2008; 2011). They suggest that the IOM formed by polymerization of formaldehyde when accreted ice melted as meteorite parent bodies warmed due to the decay of short-lived radionuclides. This process naturally produces globule-like objects and can produce material with NMR spectra that resembles IOM on heating. If the ice formed in the ISM or outer Solar System, it and the formaldehyde it contained would probably be D-rich and contain ^{15}N-rich

N-bearing species that could be incorporated into the IOM. This model faces two hurdles. The first is whether there would have been enough formaldehyde in the ices to explain the abundances of IOM or IOM-like material in chondrites and, particularly, in IDPs and comets. This is especially problematic given that polymerization is an inherently inefficient process. The second is whether liquid water was present in cometary bodies, and whether the kinetics of the transformation of the initial polymer to more IOM-like material could take place at reasonable temperatures and over reasonable timescales for either comets or chondrites. The latter is experimentally testable, and the former has gained at least some recent support from the Stardust mission (Berger *et al.* 2011).

Ultimately, whether the organics in chondrites, IDPs and comets are solar or interstellar in origin may be determined not by the properties of the organics themselves, but rather by the abundance and origin of amorphous silicate material in IDPs and comets (Alexander *et al.* 2007a). Silicates in the ISM are essentially entirely amorphous. In IDPs and comets, on the other hand, crystalline silicates are a major component and must have formed at temperatures (>1000 K) that would have destroyed any interstellar organics. There is amorphous silicate material in primitive chondrites and IDPs, but there is an ongoing debate about whether the bulk of it is interstellar or not. Isotope analyses show that a few percent of the amorphous material in IDPs is circumstellar in origin. Given the short lifetime of circumstellar dust in the ISM, it seems likely that a significant fraction of the remaining amorphous material must be interstellar. Unfortunately, it is difficult to prove an interstellar origin and energetic Solar System processes (e.g., irradiation, impacts and condensation from a hot gas) can produce material with similar properties. Stardust samples do contain amorphous material, but it is hard to distinguish between indigenous material and that produced during capture. Comets are also known to contain amorphous silicates, but the results of the Deep Impact mission show that the grains being emitted by comets may not be representative of the bulk (Lisse *et al.* 2007). Nevertheless, one can roughly explain the abundances of organic C in IDPs and comet Halley if: (1) one assumes that all amorphous silicates in IDPs are interstellar and that ~50% of comet Halley silicates are amorphous and interstellar, and (2) adopt the range of abundances for carbonaceous dust and PAHs in the ISM inferred by Zubko, Dwek & Arendt (2004). Obviously, if a large fraction of the amorphous silicates proves to be solar in origin, then a proportional fraction of the organics must also be solar.

3.2. *Soluble Organic Matter*

The SOM in primitive chondrites is a complex suite of soluble compounds. The best characterized of these are summarized in Table 1. However, it seems likely that the bulk of the SOM has yet to identified (Schmitt-Kopplin *et al.* 2010). This poorly characterized material is composed of >46,000 compounds with masses of up to at least 1000 daltons and an approximate average composition of $C_{100}H_{155}N_3O_{20}S_3$ that resembles an IOM composition but with roughly twice the H content. Thus, it seems likely that the IOM and the uncharacterized SOM are related, but the uncharacterized SOM is presumably more aliphatic. Even within the classes of well-characterized SOM compounds there is tremendous structural diversity, although abundances tend to decrease significantly with increasing C number and extent of branching. The abundances of volatile compounds could also have been modified during the residence of the meteorites on Earth. Until we have a better understanding of the nature of the uncharacterized material, the work on the known soluble components probably presents a rather distorted picture of the origins of the SOM. Nevertheless, important features of the well-characterized SOM are briefly discussed below.

Even more than the IOM, the soluble organics are susceptible to modification (isotopic exchange, synthesis and destruction) during parent body processing. For instance, amino acid abundances decline dramatically within a chondrite group with increasing degree of alteration (Martins *et al.* 2007; Martins & Sephton 2009; Glavin *et al.* 2010; Herd *et al.* 2011). In the least altered chondrites, the amino acids are racemic within error. Surprisingly, the development of L enantiomeric excesses in amino acids like isovaline that do not easily racemize accompanies this decrease in abundance with increasing alteration (Glavin *et al.* 2010). Apparently, aqueous alteration either produced the enantiomeric excesses or amplified small excesses that already existed. The mechanism that produced or amplified these enantiomeric excesses is unknown, but one intriguing possibility is that it involves the IOM, which is known to possess chiral centers (Kawasaki *et al.* 2006).

The amino acids themselves are thought to be products of Strecker synthesis, the reaction of ketones and aldehydes with NH_3 and HCN. Presumably amino acid synthesis generally took place very early on in the alteration of the meteorites, but in the case of the Tagish Lake meteorite there may have been a second episodes of synthesis after alteration was fairly advanced (Herd *et al.* 2011). The fact that the relatively volatile NH_3 and HCN were in the ices that were accreted by the chondrites again suggests a link with comets. The HCN in comets is enriched in ^{15}N by roughly a factor of two over terrestrial (Shinnaka *et al.* 2011). The N isotopic composition in cometary NH_3 has not been measured, but in the ISM it is depleted in ^{15}N relative to terrestrial (Lis *et al.* 2010). The amino acids and NH_3 in two relatively unaltered CRs (GRA 95229 and LAP 02342) are only enriched in ^{15}N by about 10% over terrestrial (Pizzarello & Holmes 2009). In the Strecker synthesis, it is the N from the NH_3, not the HCN, that is inherited by the amino acid. The N from the HCN is converted into NH_3, which may eventually be incorporated into amino acids but only after significant dilution by pre-existing NH_3, which may explain the modest ^{15}N enrichments in NH_3 and amino acids.

The H isotopic compositions of amino acids have also been measured in one relatively unaltered CR (GRA 95229), and two more altered CMs (Murchison and Murray) (Pizzarello & Huang 2005; Pizzarello, Huang & Alexandre 2008). In a given meteorite, the D enrichment in straight chain amino acids tends to increase with increasing C number, and branched amino acids are more enriched than both the straight chain ones and the bulk IOM from the same meteorites. The amino acids in the more altered CMs are systematically less D-rich than in the less altered CR. The isotopic compositions of the putative precursor aldehydes and ketones are unknown, so it cannot be ruled out that some of the isotopic variations in the amino acids were inherited. Nevertheless, the patterns of isotopic variations are suggestive of isotopic exchange with the aqueous fluid during or after synthesis. Whatever the cause of the variations, the D enrichments (up to 8 times terrestrial) indicate that, like the IOM, the amino acids or their precursors formed in cold environments, either in the outer Solar System or the ISM. However, the C isotopic compositions of the amino acids are distinctly (>3-5%) more ^{13}C-rich than the IOM and are closer to those of the carbonate minerals that are present in aqueously altered chondrites (Engel, Macko & Silfer 1990; Pizzarello, Huang & Fuller 2004; Martins *et al.* 2007).

In the more altered CM Murchison, carboxylic acids rather than amino acids are the most abundant of the well-characterized SOM. In the Tagish Lake meteorite, in which a range of alteration is recorded, carboxylic acid abundances do seem to be a function of the extent of aqueous alteration (Herd *et al.* 2011). As with the amino acids, the H isotopic compositions of the straight chain carboxylic acids vary with C number, and the branched carboxylic acids are more D-rich (Huang *et al.* 2005; Herd *et al.* 2011). Again, the D enrichments of the carboxylic acids indicate that they or their precursors have a

cold chemistry heritage. It is tempting to invoke a simple conversion of amino acids to carboxylic acids, but the C isotopic compositions of the carboxylic acids are inconsistent with this. The ^{13}C abundances of the straight chain carboxylic acids in Murchison decrease with increasing C number down to isotopic compositions that resemble those of the IOM (Huang *et al.* 2005). Based on both the H and C isotopic compositions, it is possible that the carboxylic acids in Murchison and Murray are related to or were derived from the aliphatic component of the IOM (Huang, Alexandre & Wang 2007; Herd *et al.* 2011). The variation in C isotopic composition with chain length seen in Murchison and one Tagish Lake sample could reflect isotopic exchange with dissolved CO_2 with a composition like that of the carbonate minerals (Herd *et al.* 2011).

Comets contain simple alkanes and alkenes (Mumma & Charnley 2011). The same is true at least of the CM Murchison (Yuen *et al.* 1984). However, Murchison also contains CO and CO_2, several well-known mineral catalysts of FTT synthesis and would have generated considerable amounts of H_2 during alteration. Thus, at this stage it should not be ruled out that the simple hydrocarbons, as well as other components of the SOM are the products of FTT synthesis during alteration rather than being primordial.

4. Water in Chondrites

The O isotopic compositions of inner Solar System objects all appear to be more ^{16}O-poor than the composition of the Sun. UV self-shielding during the photodissociation of CO in the outer Solar System or near the surface of a molecular cloud can produce ^{16}O-poor water ice. Hence, the favored explanation for the O isotopic composition of the terrestrial planet region is that there was a massive influx of outer Solar System and/or interstellar water ice into the inner Solar System (Yurimoto & Kuramoto 2004; Lyons & Young 2005). This ice would have been accompanied by organic material and other primitive materials. Chondrites, except probably the enstatite chondrites, seem to have accreted water ice, indicating that they formed beyond the snowline. When they formed, all chondrites also contained circumstellar grains and, as argued above, organics that are genetically linked to organics in IDPs/comets. In comets, NH_3 and HCN are major volatile components. The fact that these relatively volatile compounds are needed for making the amino acids in chondrites strengthens the comet-chondrite connection.

The D/H ratio in water ice is expected to increase with radial distance from the Sun as temperatures and pressures decrease, and conditions approached those in molecular clouds. In most, but not all, comets the H isotopic compositions of the water are enriched in D by roughly a factor of 2 relative to terrestrial values (Mumma & Charnley 2011). Given the apparent relationship between chondritic and IDP/comet organics, one might expect that, as with comets, chondritic water would be similarly enriched in D.

The H isotopic composition of chondritic water is difficult to measure directly. This is because it is now primarily incorporated into hydrous silicates as OH^-. Heating of the meteorites does release the water, but also releases H from organics that will exchange/mix with the H from the hydrous silicates. The H isotopes of hydrated silicates can be measured at small scales (<30 μm) in materials that are free or organics or using techniques that preferentially measure H in hydrous minerals (Deloule, Robert & Doukhan 1998; Grossman *et al.* 2002; Bonal *et al.* 2011). The average H isotopic compositions of the water in some chondrites have also been estimated by subtracting the known organic materials that have been isolated from them (Robert 2002; Alexander *et al.* 2010).

From the range of D enrichments recorded in these kinds of measurements and estimates, it has been argued that the water in chondrites is composed of two components,

one that is much more D-rich than comets and may be interstellar, and another that formed at relatively high temperatures in the inner Solar System so that it has a H isotopic composition that is only slightly more D-rich than the solar composition (Deloule *et al.* 1998; Robert 2001; Robert 2002). More recently it has been suggested that the H isotopic composition of water in chondrites at all spatial scales has been enriched in D to varying degrees by two parent body processes (Alexander *et al.* 2010; Alexander *et al.* 2011; Bonal *et al.* 2011): (1) the oxidation of Fe by water and the consequent loss of H_2, and (2) by isotopic exchange with D-rich organics. If correct, none of the chondrites accreted water ice that was as D-rich as in most comets. The exact H isotopic compositions at the time of accretion are still uncertain, but in the CM and CI chondrites their D/H ratios were probably significantly below the terrestrial composition. Presumably the CM and CI water formed or re-equilibrated at smaller radial distances than typical cometary ices. How this can be reconciled with the presence of IDP/comet-like organics in chondrites, as well as NH_3 and HCN in the chondritic ices, remains to be seen.

While it is still not clear when the Earth and the other terrestrial planets accreted their volatiles, if it was at a late stage it would have been after parent body processes on the chondrites' parental asteroids had ceased. Thus, if the chondrites were the sources of the volatiles, their present bulk compositions (water and organics) should reflect what would have been accreted. Not only the H isotopes constrain the likely sources of the volatiles, but also the relative abundances and isotopic compositions of N and the noble gases. At present, no single chondrite group can explain all of these constraints.

5. Summary and Implications

Chondritic meteorites preserve a record of materials that were present in the first few million years of solar nebula evolution. These materials include demonstrably presolar circumstellar grains that were inherited from the protosolar molecular cloud. Most, if not all, chondrites also accreted organic matter when they formed, but generally this material has been heavily modified in the asteroidal parent bodies. In three chondrite groups (CI, CM, and CR) the organic matter has been reasonably well preserved, although it has been modification to varying degrees by hydrothermal alteration. The organic matter in the CI-CM-CR chondrites is broadly divided into solvent soluble and insoluble fractions.

The insoluble fraction (IOM) is a structurally complex, macromolecular material composed of small aromatic moieties that are cross-linked by short, highly branched aliphatic chains. It has a bulk elemental composition that is similar to the average of comet Halley CHON particles, and is dispersed in chondrite matrices as particles that are typically <1 μm across. In bulk, the insoluble material is significantly enriched in D and ^{15}N. Even more extreme isotopic enrichments can be found in localized (usually <1 μm across) hotspots, some of which are associated with so-called globules - spherical to irregular organic particles that are often hollow.

Similar globules, isotopic hotspots and/or bulk isotopic enrichments are found in the organic matter of chondritic interplanetary dust particles and comet 81P/Wild 2 samples. Thus, there is a genetic link between objects that formed between ∼3 AU and ∼30 AU from the Sun. The enrichments attest to formation in very cold environments, either in the outer Solar System or the protosolar molecular cloud. There are many properties of this organic material that are consistent with an interstellar origin, e.g., hotspot isotopic compositions overlap with those of gas-phase molecules in molecular clouds, a 3.4 μm IR adsorption feature resembles that of diffuse ISM dust and abundances relative to circumstellar grains are similar in all chondrites. However, at present a Solar System origin cannot be ruled out. Since the early Solar System does not appear to have been

particularly unusual and this organic material was so widespread in the solar nebula, presumably similar material is an important component of most protoplanetary disks. Heating or sputtering of this material would be a source of PAHs in disks.

The solvent-extractable organic material (SOM) is a complex suite of compounds. Many of these compounds show almost complete structural diversity for a given carbon number, and also have large enrichments in D and, if they contain N, in ^{15}N. The amino acids are thought to have formed by reaction of aldehydes and ketones with NH_3 and HCN very early in the aqueous alteration of the CI-CM-CRs. The fact that volatile NH_3 and HCN were accreted, presumably in ice, strengthens the chondrite-comet connection. Some amino acids in CI-CM-CR chondrites do not readily racemize exhibit 0-20% L-enantiomeric excesses. The L-enantiomeric excesses seem to increase with increasing hydrothermal alteration and decreasing amino acid abundances. Thus, the L-enantiomeric excesses appear to be the product of the alteration or the alteration has amplified small excesses that were inherited at the time of accretion.

Despite the links between chondrites and comets suggested by the organic matter, unlike most comets the water in chondrites, when it was accreted, had D/H ratios that were similar to or depleted relative to Earth. The water in chondrites seems to have formed or isotopically re-equilibrated with H_2 at the higher temperatures of the inner Solar System. How this can be reconciled with the preservation of primitive organics and accretion of volatiles like NH_3 and HCN remains to be seen.

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Discussion

IRVING: How are the enantiomeric excesses in some SOM compounds produced?

ALEXANDER: At this point, it is a complete mystery, but the answer obviously has tremendous astrobiological implications.

SARRE: It somewhat surprises me that PAHs are not seen in comets. Could it be that they are tied up in IOM-like material?

ALEXANDER: In meteorites there are small amounts of free PAHs, but the vast majority are tied up in IOM. So if, as seems likely, the organics in chondrites are related to those in comets, tying up most of the PAHs in IOM-like material seems a likely explanation for why PAHs are not seen in comets.

ELLINGER: Do you have structural information about the position of the D in the IOM and SOM?

ALEXANDER: In the IOM several lines of evidence suggest that the D is primarily associated with the aliphatic material. For the individual SOM compounds, there is not information about whether specific functional groups are more deuterated than others.