

CHAPTER IV

The Origin and Evolution of Organic Matter in Carbonaceous Chondrites and Links to Their Parent Bodies

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Abstract

The nature of organic matter in meteorites reveals information about early solar system chemistry and the histories of parent bodies as recorded in the effects of physical and chemical processes that occurred over the past 4.5 billion years. Asteroids and their fragments impact the Earth with ~40 million kg of material each year and contributed to the inventory of organics available for the origin of life. Analyses of primitive carbonaceous chondrites over the last five decades have revealed a major insoluble organic component, as well as a complex and highly diverse suite of soluble organic molecules that includes aliphatic and aromatic hydrocarbons, carboxylic acids, hydroxy acids, N-heterocycles, polyols, amino acids, amines, and many other molecules that have not yet been identified. Thermal and aqueous alteration in primitive asteroids played an important role in the formation and destruction organics, including amplification of L-amino acid and D-sugar acid enantiomeric excesses that may have contributed to the origin of homochirality in life on Earth.

4.1. Introduction

The organic contents of carbonaceous meteorites reflect a long and diverse history (Fig. 1), beginning with the formation of the Solar System in a molecular cloud in which low temperature radiation-driven chemistry and isotopic fractionation could occur in both the gas phase and on ice and mineral grain surfaces (Albertsson et al., 2014; Ehrenfreund and Charnley, 2000; Fegley, 1993; Zinner, 1988). Some of this molecular cloud material was incorporated into planetesimals, including asteroids and comets where additional chemical reactions and processing took place as these objects grew in size and experienced secondary (post-accretion) alteration events. Radiogenic decay of short-lived radionuclides (*e.g.* ^{60}Fe and ^{26}Al), impact shocks, and other processes heated the planetesimals (Dyl et al., 2012; Weiss and Elkins-Tanton, 2013), resulting in a range of thermal metamorphism and aqueous alteration conditions. These alteration conditions could both drive the formation of complex organics from interstellar precursors as well as their destruction and transformation. The nature of organic matter in meteorites reveals information not only about early solar system chemistry but also about the histories of parent bodies as recorded in the effects of physical and chemical processes and timescales from nucleosynthesis and circumstellar dust formation, through Solar System formation and protoplanetary disk dynamics to planetesimal and planet formation that occurred over the past 4.5 billion years.

Asteroids, comets, and their fragments including meteorites, micrometeorites and interplanetary dust particles (IDPs) also serve as delivery vehicles for organic matter. At present $\sim 4 \times 10^7$ kg of extraterrestrial material, ranging in size from meter sized meteorites down to micron sized IDPs, rains down on the Earth every year (Love and Brownlee, 1993). On average IDPs contain about 12 wt% carbon (Thomas et al., 1993; Thomas et al., 1994), approximately half of which is organic matter (Flynn et al., 2004). Carbonaceous chondrites contain a wide range of carbon abundances from ~ 0.1 wt% for CK chondrites up to ~ 5 wt% carbon for the CI chondrites which is present in both organic and inorganic form (Pearson et al., 2006). The flux of exogenous organic matter delivered to the early Earth by IDPs and carbon-rich meteorites ~ 4 billion years ago may have been orders of magnitude higher than the present rate with estimates of up to 10^9 kg per year of organic carbon (Jenniskens et al. 2000). Therefore, exogenous delivery may have been an important source of organic carbon on the early Earth including complex prebiotic molecules available for the origin of life.

Early studies of meteoritic organics beginning in the 1960s focused primarily on a few well-known, large carbonaceous chondrite falls including the CM2 meteorites Murchison and Murray and the CV3 Allende (Cronin and Moore, 1971; Degens and Bajor, 1962; Kvenvolden et al., 1970a; Kvenvolden et al., 1971a; Lawless et al., 1971; Oró et al., 1971). Over the last five decades, an increasing supply of meteorite samples from other carbonaceous chondrite groups, the majority of which have been collected in Antarctica by the Antarctic Search for Meteorites (ANSMET) program (Corrigan et al., 2014), has led to a dramatic increase in our understanding of organics in primitive meteorites. Analyses of carbonaceous chondrites have revealed a major insoluble organic component consisting of $> 70\%$ of the total organic carbon (Alexander et al., 2007), as well as a complex and highly diverse suite of soluble organics (Pizzarello et al., 2006a; Schmitt-Kopplin et al., 2010; Sephton, 2002) including aliphatic and aromatic hydrocarbons, carboxylic acids, hydroxy acids, nucleobases, polyols, amino acids, amines, and others, the vast majority of which have not yet been identified. The structural, isotopic, and enantiomeric compositions of organic compounds in meteorites can be signatures of their formation mechanisms and processing

histories. For example, large isotopic anomalies in many elements of both soluble and insoluble organic fractions may indicate that they or their precursors formed in the interstellar medium where D and ^{15}N (Busemann et al., 2006; Elsila et al., 2012a), particularly, can be enriched in organic molecules via ion-molecule processes and a number of other processes. Subsequent parent body aqueous and thermal processing in asteroids played an important role in the formation and destruction of amino acids and other soluble organics, including amplification of enantiomeric excesses observed in some meteorites.

With a few exceptions, including the Moon and Mars (Fig. 1), meteorites are fragments of Main Belt asteroids (~2-4 AU). While some may be extinct comets, the vast majority of asteroids are the last vestiges of the planetesimal swarm from which the terrestrial planets formed. Some meteorites, the achondrites, come from asteroids that extensively melted and even differentiated into silicate mantles and iron cores. While they often saw elevated temperatures, the chondritic meteorites never melted. They are aggregates of components (e.g., chondrules, refractory inclusions, and matrix) that largely formed in the solar protoplanetary disk, but also contain a small amount of protosolar molecular cloud material. Interplanetary dust particles (IDPs) are small <100 μm diameter particles and are, if anything, even more primitive than the chondrites. IDPs are thought to come from both asteroids and comets. Most of what is known about comets has been obtained by remote sensing and some *in situ* observations, but IDPs and the NASA Stardust comet sample return mission from Wild 2 and the ESA Rosetta mission to comet 67P/C-G have allowed us to begin developing a more detailed understanding of the mineralogy of comets and their volatile and organic constituents.

In this Chapter, we provide an overview of what is currently known about the distribution, abundance, isotopic composition, and chirality of organic matter in carbonaceous chondrites and interplanetary dust particles, and their potential links to asteroid and comet parent bodies. We also discuss the role and importance of past and future small body sample return missions in our further understanding of the formation and evolution of organics in the Solar System.

4.2 Classification of Chondrites and IDPs and Post-Accretion Parent Body Alteration

4.2.1 Classification

Meteorites are divided into three overall categories (Fig. 2) based on whether they are dominated by rocky material (stony meteorites), metals (iron meteorites), or a mixture of the two (stony-iron meteorites). There are at least 45 recognized meteorite groups based on differences in their elemental, isotopic, and mineralogical compositions (Weisberg et al., 2006). More than 90% of all meteorite falls are stony meteorites that are further subdivided into chondrites, groups of meteorites that escaped melting, and achondrites, groups of meteorites that have a complex history involving asteroidal or planetary melting and differentiation. The chondrites are sub-divided into three major classes (ordinary, carbonaceous and enstatite) based on their elemental and isotopic (primarily O and Cr) compositions, and physical features. Chondrites in turn have been subdivided into a number of groups (Krot et al., 2014): ordinary chondrites (OCs) into H, L and LL; carbonaceous chondrites (CCs) into CI, CM, CR, CB, CH, CV, CO and CK; and enstatite chondrites (ECs) into EH and EL. The carbonaceous chondrite class represents roughly 4% of all meteorite falls. The classification scheme for chondrites is still evolving as more meteorites are found.

The bulk compositions and physical features of the chondrites were established during accretion of their parent asteroids. After formation, they experienced so-called secondary modification by thermal metamorphism and aqueous alteration. A petrographic classification scheme for secondary processes divides the chondrites into 6 types - types 3 to 6 reflect increasing thermal metamorphism, and types 3 to 1 reflect increasing degrees of aqueous alteration. The type 3s have been further subdivided into 3.0-3.9, with 3.0 being the most primitive petrologic type. By convention, the chemical classification is followed by the petrologic one (e.g., CI1, CM2, CV3).

Chondrites are often referred to as cosmic sediments because they are made up of diverse materials that formed in the solar nebula. These materials are dominated by three components – refractory inclusions and chondrules, both of which were formed by high temperature processes (~1700-2100 K), are embedded in a fine-grained (<5-10 μm) matrix. It is in the matrix that any primordial organics would have been accreted because the organics would not have survived chondrule and refractory inclusion formation.

While there are variations, the bulk elemental compositions of the chondrites are fairly similar to that of the solar photosphere (excluding H, C, N, O, and the noble gases). This is particularly true for the CI chondrites that are indistinguishable from the non-volatile composition of the solar photosphere. Much of the compositional variations (fractionations relative to solar) amongst chondrites appear to be largely controlled by the volatility of the elements. The volatility of an element is normally expressed as its calculated 50% thermodynamic equilibrium condensation temperature from a gas of solar composition at a total pressure of 10^{-4} bars (e.g. Lodders, 2003). Other compositional variations seem to be the result of physical processes, such as metal-silicate fractionation.

Chondritic IDPs, those with roughly chondritic bulk compositions, can be divided into two broad categories (Bradley, 2014): compact hydrated particles, and porous nominally anhydrous particles that are often referred to as chondritic porous (CP) IDPs. The hydrated particles share many mineralogical similarities with the CM and CI chondrites, although there are also important differences. The anhydrous particles do not seem to have a clear affinity to any known meteorite group. Based on their very fine grain size, disequilibrium assemblage of minerals and amorphous silicates, and abundant presolar materials, the CP-IDPs are thought to be the most primitive Solar System objects found to date. All IDPs will have experienced at least some brief heating during atmospheric entry, as well as irradiation by solar wind, etc. while in interplanetary space.

4.2.2 Metamorphism and Aqueous Alteration

Whether the dominant secondary mineralogy is anhydrous (thermally metamorphosed) or hydrated (aqueously altered) probably reflects the initial water/rock ratio of the meteorite, as well as the peak temperature it experienced. The dominant heat source that drove alteration and metamorphism is thought to have been the decay of the short-lived radionuclide ^{26}Al ($t_{1/2}\approx 0.7$ Ma). However, heating associated with impacts may also have played some role.

4.2.2.1 Aqueous alteration

The type 1-3.0 chondrites exhibit a wide range in the extent of aqueous alteration that they experienced, from essentially complete alteration (type 1s) to incipient alteration in the finest-grained matrix (near the boundary between types 2 and 3). The degree and style of alteration, as

well as secondary mineral compositions (Table 1), vary within and between chondrite groups, reflecting differing conditions. As a result, the compositions and relative proportions of the secondary minerals changed with progressive alteration, forming the basis for several alteration classification schemes that are based on a range of different criteria (Alexander et al., 2013; Harju et al., 2014; Howard et al., 2015; Rubin et al., 2007).

Metal and sulfides in the matrix are likely to have been amongst the first materials to react with the fluid upon melting of the ice. This will have produced H₂, H₂S, magnetite and Fe, Ni ions in solution. The amount of H₂ that was generated will have depended on the initial abundance of Fe in metal and sulfide, as well as the water/rock ratio, but could have been substantial (Rosenberg et al., 2001; Wilson et al., 1999). Indeed, estimates suggest that so much H₂ could have been generated that if it was unable to escape to space asteroids could have experienced catastrophic disruption (Wilson et al., 1999). Other volatiles that would have been present, such as CO, CO₂ and CH₄, are also likely to have been partially lost at the same time. Because of the reduced nature of the gases being lost, the meteorites will have become progressively more oxidized. Once the silicates began to alter, the alteration probably proceeded in a similar manner to terrestrial serpentinization of basic (Mg-rich and Si-poor) igneous rocks.

Table 1. The major secondary minerals produced in the alteration of the CI, CM and CR chondrites and the ungrouped C2 carbonaceous chondrite Tagish Lake (TL) (Brearley, 2003; Brearley, 2006; Brearley and Jones, 1998).

Mineral	Formula	Occurrence
<u>Serpentines</u>		
chrysotile/lizardite/antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄	CI,CM,CR,TL
cronstedite	Fe ₂ ²⁺ Fe ³⁺ (SiFe ³⁺)O ₅ (OH) ₄	CI,CM,TL
<u>Smectite clays</u>		
saponite	(Ca/2,Na) _{0.66} (Mg,Fe ²⁺) ₆ (Si,Al) ₈ O ₂₀ (OH) ₄	CI,CR,TL
<u>Other</u>		
tochilinite	6(Fe,Ni) _{0.9} S ₅ (Fe,Mg)(OH) ₂	CM,CR
epsomite	MgSO ₄ .7H ₂ O	CI
gypsum	CaSO ₄ .2H ₂ O	CI
calcite/aragonite	CaCO ₃	CI,CM,CR,TL
dolomite	CaMg(CO ₃) ₂	CM,CR,TL
siderite	FeCO ₃	TL
magnetite	Fe ₃ O ₄	CI,CM,CR,TL
pyrrhotite	Fe _{1-x} S (x=0-0.17)	CI,CM,CR,TL
pentlandite	(Fe,Ni) ₉ S ₈	CM,CR,TL

Despite this progressive alteration and varying conditions, the number of major minerals produced by the alteration is fairly limited (Table 1). Serpentine in its various forms, often interlayered with saponite, is the most widespread secondary mineralogy. The unusual mineral tochilinite is most common in the CM2 chondrites, and is much less common in CM1s and CRs than CM2s. It appears to have formed during alteration of metal and sulfide under relatively reducing conditions and low temperatures (<120 °C). Temperatures and water/rock ratios during alteration have been estimated for various chondrites based on their mineral assemblages and isotopic systematics within and between their minerals (Table 2). It is important to realize that

these estimates generally assume thermodynamic equilibrium, which is by no means certain in these meteorites.

The potential for synthesis, modification and/or destruction of organics during aqueous alteration will have to be borne in mind when discussing the origins of the organic material in these meteorites. For instance, the generation of H₂ and catalytic minerals like magnetite, chromite, awaruite, pyrrhotite and pentlandite in the presence of CO/CO₂ could have led to Fischer-Tropsch-type (FTT) synthesis (e.g., McCollom and Seewald, 2007). The presence of water, NH₃ and H₂S, may have made a more diverse chemistry possible than is typical of FTT synthesis. Synthetic pathways for producing amino- and hydroxy-acids, such as the Strecker-cyanohydrin type synthesis, are also possible. The presence of smectite clays can also facilitate synthetic pathways (Williams et al., 2005). However, to date there has been no quantitative or even qualitative work on the influences of fluid composition, secondary mineralogy and temperature on the organic contents of chondrites.

Table 2. Estimated temperatures and water/rock ratios during aqueous alteration of chondritic meteorites. The water rock ratio is based on the atomic proportions of O and is roughly the volume ratio.

	Temperature (°C)	Water/Rock Ratio
CI1	50-150, 100-150	1.1-1.2
CM1	~120	0.3
CM2	0, 1-25, 20-71 ^a , 80	0.3-0.6
CR	50-150	0.4-1.1
C2 (Tagish Lake)	<200-350	

All but one of the sources are given in reviews by Brearley (2006) and Krot et al. (2006). ^aGuo and Eiler (2007).

4.2.2.2. *Metamorphism*

As temperatures rose, the diverse mineral assemblages in chondrites would have begun to equilibrate. This process of adjustment, thermal metamorphism, causes: (1) thermodynamically stable minerals to grow and chemically equilibrate with one another, (2) destruction of thermodynamically unstable minerals, (3) crystallization of amorphous material in chondrules and matrix, (4) destruction or transformation of organic matter, and (5) loss of volatiles like H, N and the noble gases. The extent to which chondrites were transformed will have depended on the conditions and duration of metamorphism.

The effect of metamorphism on both soluble and insoluble organic (IOM) material in meteorites can be profound. For instance, in the very reduced ECs, there is progressive graphitization of the IOM in the type 3s and into the type 4s. Free C is essentially absent from the type 5-6 ECs. In the more oxidized OCs and CCs, there is competition between graphitization and destruction of the IOM. The destruction is presumably driven by oxidation of the IOM, perhaps by water and Fe-oxides, and is essentially complete in OCs by type 3.6-3.7. The IOM persists, albeit in significantly reduced amounts, in the highest type COs and CVs (3.6-3.8). Despite its progressive destruction, the structural reorganization of the IOM during metamorphism as measured by Raman

spectroscopy has proved to be a very useful classification tool for type 3 chondrites (Bonal et al., 2007; Bonal et al., 2006; Quirico et al., 2011; Quirico et al., 2003).

The peak temperatures experienced during metamorphism are somewhat uncertain, particularly amongst type 3s. Mineralogical and other indicators suggest that temperatures ranged from $\leq 250^{\circ}\text{C}$ for type 3.0s to $\sim 700^{\circ}\text{C}$ at the type 3-4 boundary (Huss et al., 2006b; Kessel et al., 2007; Wlotzka, 2005). Spectroscopy of IOM has also led to estimates of the peak temperatures during metamorphism that are to first order consistent with the mineralogical indicators (Busemann et al., 2007; Cody et al., 2008b; Huss and Lewis, 1994), although inconsistencies between these studies do call into question their accuracy (Bonal et al., 2016; Quirico et al., 2011).

4.3. Organics in Carbonaceous Chondrites, Comets, and IDPs

Extraction Methodologies. Most of the detailed organic analyses published to date have focused on the solvent soluble and insoluble fractions of the organic matter in carbonaceous chondrites (Botta and Bada, 2002; Pizzarello et al., 2006a). The structure and isotopic composition of the refractory organic matter in IDPs (Clemett et al., 1993; Flynn et al., 2008; Starkey et al., 2013) and cometary grains returned by Stardust (Sandford, 2008; Sandford et al., 2006a) have also been studied, however much less is known about their soluble organic composition due to low concentrations and the limited amount of sample mass available for study. The majority of carbon in primitive chondrites is present as insoluble organic matter (IOM, $> 50\%$ of total organic carbon), a structurally complex aromatic macromolecule that is obtained after HCl/HF or CsF/HF demineralization of the bulk meteorite (Alexander et al., 2007; Cody et al., 2002). The structure and isotopic composition of the IOM found in carbonaceous chondrites and refractory organic matter in IDPs will be discussed in Section 4.3.1. The soluble organic component found in carbonaceous chondrites and micrometeorites can be extracted by heating crushed samples in solvents of different polarities such as water, formic acid, hydrofluoric acid, methanol, hexane, benzene or mixtures. For amino acid analyses, the water extracts are typically also hydrolyzed using hydrochloric acid to determine the total abundance of bound or acid-labile compounds (Glavin et al., 2006). These current extraction methodologies have largely remained unchanged for the last five decades since a protocol for the extraction of amino acids was used to study the Murchison meteorite (Kvenvolden et al., 1970a). Solvent extracts of Murchison and other carbonaceous chondrites have been found to contain a diverse and complex mixture of soluble organics including amino and diamino acids, imino acids, aliphatic amines and amides, aliphatic and aromatic hydrocarbons, alcohols, aldehydes, ketones, carboxylic and dicarboxylic acids, hydroxy acids, N-heterocycles, alkyl sulfonic and phosphonic acids, polyols and others (Botta and Bada, 2002; Pizzarello et al., 2006a; Sephton, 2002) that will be discussed in Section 4.3.2.

4.3.1. Insoluble Organic Matter (IOM)

In this Section, we focus on what is currently known about the elemental, molecular and isotopic compositions of insoluble organic matter in primitive chondrites. The chemical variations observed in IOM among the different meteorite groups and petrologic types in relation to the meteorite parent body processes will also be discussed.

4.3.1.1. *Elemental and molecular compositions*

Insoluble organic matter extracted from primitive chondrites is a polyaromatic hydrocarbon with a structure and composition similar to that of terrestrial kerogen. A model of the molecular structure of IOM in types 1 and 2 carbonaceous chondrites is shown in Figure 3 which was based on the results obtained by destructive methods (e.g., pyrolysis, chemical degradation, and thermochemolysis) and non-destructive analyses (e.g. ^{13}C and ^{15}N NMR, FTIR, XANES, and EPR) (Derenne and Robert, 2010). Solid state ^{13}C NMR studies suggested that polycyclic aromatic rings with aliphatic substituents are predominant in the structure of IOM from CM and CI chondrites (Cody et al., 2002; Cronin et al., 1987; Gardinier et al., 2000). Cody et al. (2002) further made quantitative correction and concluded that that IOM is composed of small ring ($< \text{C}_{20}$)-aromatic network ($\sim 60\%$) crosslinking with short-branched aliphatic chains ($\sim 20\%$) and various oxygen ($\sim 20\%$) functional groups (e.g., ether, carbonyl groups). Elemental compositions of IOM in the most primitive meteorites (in terms of H/C, aromaticity and isotopic composition) are estimated as $\text{C}_{100}\text{H}_{70}\text{N}_3\text{O}_{12}\text{S}_2$ (Hayatsu et al., 1977), $\text{C}_{100}\text{H}_{48}\text{N}_{1.8}\text{O}_{12}\text{S}_2$ (Zinner, 1988), $\text{C}_{100}\text{H}_{52.7}\text{N}_{2.9}\text{O}_{25}$ (Cody et al., 2002), and $\text{C}_{100}\text{H}_{58.8}\text{N}_{3.3}\text{O}_{18.3}$ (Alexander et al., 2007).

The chemical structure of IOM drawn by NMR is consistent and complementary with those suggested by the degradative analyses of IOM. Pyrolysis of IOM or powder of carbonaceous chondrites yielded 1 to 6 ring-polycyclic aromatic hydrocarbons (PAHs) and O-, N-, S- bearing aromatic compounds, as building blocks of IOM (Holzer and Oro, 1979; Komiya et al., 1993; Levy et al., 1973; Sephton et al., 2004). Dichromic acid ($\text{H}_2\text{Cr}_2\text{O}_7$) oxidation, which selectively cleaves aliphatic bonds of a macromolecule, yielded 1 to 4 ring-PAHs from IOM (Hayatsu et al., 1977). Alkaline copper oxide (CuO) oxidation IOM from a CM2 chondrite yielded aromatic acids such as hydroxybenzoic acid, indicating that of phenolic and aryl aromatic moieties are ether linked (Hayatsu et al., 1980). Tetramethylammonium hydroxide (TMAH) thermochemolysis detected methyl and dimethyl esters of aromatic acids and diacids and dimethoxy benzoic acid methyl esters, revealing the occurrence of ester and ether bridges between aromatic units in the IOM of CM Murchison and CI Orgueil chondrites, respectively (Remusat et al., 2005). Ruthenium tetroxide (RuO_4), a selective oxidant that converts aromatic units into CO_2 and yields aliphatic and aromatic acids (Remusat et al., 2005), yielded short chain dicarboxylic acids, hydroxyl acids, polycarboxylic aromatic acids (Remusat et al., 2005) and short chain monocarboxylic acids. These results indicated that IOM contain short alkyl chains ($\text{C}_1\text{-C}_9$).

As other features, diamagnetic diradicaloids having a quinoidal structure were identified in IOM from CM Murchison and CI Orgueil chondrites by electron paramagnetic resonance (EPR), based on the heterogeneous distribution and temperature-dependent behavior of the organic radicals (Binet et al., 2004).

Interestingly, molecular asymmetries (**R** configuration) were determined in IOM from CM Murray and even CV Allende chondrites by using of the asymmetric autocatalytic Soai reaction (Soai et al., 1995) although asymmetry was not found in the hydrothermal treated IOM (Kawasaki et al., 2006).

4.3.1.2. *Isotopic compositions*

The IOM in the primitive carbonaceous chondrites exhibit large but variable enrichments in D and ^{15}N (Alexander et al., 2007; Kerridge et al., 1987; Robert and Epstein, 1982; Yang and Epstein,

1983, 1984). Alexander et al. (1998) suggested that meteoritic IOM were divided into more than two fractions; a labile ^{15}N - and ^{13}C - rich fraction and a refractory ^{15}N - and ^{13}C - depleted fraction (Alexander et al., 1998). In the hydrous heating experiments of IOM from CM2 chondrites, $\delta^{15}\text{N}$ values were remarkably depleted after heating compared to $\delta^{13}\text{C}$ (Sephton et al., 2003; Yabuta et al., 2007), it is likely that a major part of ^{15}N in IOM is present as hydrolysable and/or oxidisable functional groups (Sephton et al., 2003), one of which could be nitrogen-bearing aliphatic moieties (Yabuta et al., 2007). Pizzarello et al. (2011) observed the release of abundant free NH_3 ($\delta^{15}\text{N} = +223\text{‰}$) by hydrothermal treatment of IOM from weakly altered CR2 GRA 95229 at 300°C for 6 days, which was higher than water soluble NH_3 ($\delta^{15}\text{N} = +134\text{‰}$) from the same meteorite (Pizzarello and Groy, 2011). On the other hand, it is the only 15% of total nitrogen content that was decomposed by hydrous heating of IOM, indicating that most of the nitrogen still remains as refractory portion (Yabuta et al., 2007). According to solid-state ^{15}N -NMR of Orgueil IOM, it is suggested that nitrogen is mainly involved in heterocyclic units such as pyrroles within the aromatic network (Derenne and Robert, 2010). The recent combined work by using solid-state ^{15}N -NMR and N-XANES has updated the N-speciation of $\sim 3\%$ imine, $\sim 4\%$ nitrile, $\sim 12\%$ pyrrole, $\sim 0\%$ primary amine, $\sim 30\%$ secondary amine (N-H), $\sim 30\%$ tertiary amine (N), and $\sim 21\%$ nitro (NO_2) groups (Code and Alexander, 2017).

It has been isotopically indicated that some kind of soluble organic compounds were generated from IOM. Carbon isotopic compositions of 1 and 2 ring-PAHs from solvent extracts of CM2 Murchison meteorite powder ($\delta^{13}\text{C} = -28.8$ to -5.8‰) and from hydrous pyrolyzed Murchison IOM ($\delta^{13}\text{C} = -24.6$ to -5.6‰) were shown to be very similar, respectively (Sephton et al., 1998). They concluded that the free PAHs were likely produced from the labile portion of macromolecular IOM. Considering that the more labile portion of the Murchison IOM is enriched in D ($\delta\text{D} \geq +1165\text{‰}$) (Kerridge et al., 1987), the free PAHs and labile portion of IOM were thought to be interstellar origin. The large kinetic isotope effects ($> 20\text{‰}$) in $\delta^{13}\text{C}$ for C_6 to C_{20} PAHs (Sephton and Gilmour, 2000) are regarded as the carbon isotopic fractionation specifically occurred in the cold environments such as interstellar medium (Langer et al., 1984). Huang et al. (2007) determined the carbon and hydrogen isotopic ratios of individual monocarboxylic acids produced by RuO_4 oxidation Murchison IOM and showed that hydrogen isotopic ratios ($\delta\text{D} = 600$ - 1200‰) of the IOM aliphatic side chains and water-soluble monocarboxylic acids in Murchison are similar, suggesting the common precursors for these components. However, the carbon isotopic ratios are lower in RuO_4 -derived monocarboxylic acids ($\delta^{13}\text{C} = -57.9$ - 0.4‰) than in water-soluble monocarboxylic acids ($\delta^{13}\text{C} = -15.9$ - 11.3‰).

Of the typical values from the types 1 and 2 carbonaceous chondrites ($\delta\text{D} \approx 100$ - 1000‰ and $\delta^{15}\text{N} \approx -8$ to 30‰), the IOM from the CR chondrites and the anomalous CM2 Bells (Fig. 4) contain the largest bulk D and ^{15}N enrichments ($\delta\text{D} \approx 3000\text{‰}$ and $\delta^{15}\text{N} \approx 160$ - 400‰) (Alexander et al., 2007). These enrichments are comparable to the bulk compositions of chondritic porous (CP)-IDPs (Aléon et al., 2001; Messenger, 2000). In particular, aliphatic carbon (and carboxyls) is considered as D-rich carrier from the studies of IDPs (Keller et al., 2004) and anhydrous Antarctic micrometeorites (Noguchi et al. 2017). Depletion of both aliphatic carbon and δD in the chondritic IOM with the progress of aqueous alteration may support the hypothesis that aliphatic carbon is enriched in D (Section 4.3.1.3) (Alexander et al., 2007; Cody and Alexander, 2005; Yabuta et al., 2007), but depletion of δD also involves hydrogen isotopic exchange with water.

An even more striking similarity is the presence of isotopic hotspots in the IOM and CP-IDPs that can be hugely enriched in D and ^{15}N (δD up to $50,000\text{‰}$ and $\delta^{15}\text{N}$ up to 3000‰) (Busemann et al., 2006; Messenger, 2000) (see Fig. 5). At least some of these hotspots are associated with so-

called organic nanoglobules (De Gregorio et al., 2013; Garvie et al., 2008; Matsumoto et al., 2013; Nakamura-Messenger et al., 2006) that are spherical and often hollow, irregular components of the IOM. The organic nanoglobules have diverse morphologies (De Gregorio et al., 2013; Hashiguchi et al., 2013; Matrajt et al., 2012). De Gregorio et al. comprehensively surveyed the morphology, organic functional chemistry, and isotopic composition of 184 nanoglobules in IOM from 7 primitive CI1, CM2, CR1, CR2, and CO3.0 carbonaceous chondrites (De Gregorio et al., 2013). They concluded that ¹⁵N-rich aromatic nanoglobules were likely formed in cold molecular cloud or outside of solar nebula, although the morphologies do not directly record the information of precursors but are reflected by parent body aqueous alteration (De Gregorio et al., 2013). D-rich organic nanoglobules bearing silicate and oxide inclusions were first discovered in the CR2 chondrite NWA 801 (Hashiguchi et al., 2013). These nanoglobules were suggested to have formed in the outer solar system rather than in the presolar environment, because of lack of oxygen isotopic anomalies of the silicates and oxides.

4.3.1.3. Chemical variations of IOM among different meteorite groups and petrologic types

The chemical histories of meteorites are likely to play a role on the variations of elemental, molecular, and isotopic compositions of organic molecules in meteorites. Different chondritic groups have different asteroidal parent body and/or solar nebula histories, which include processes such as aqueous alteration, thermal metamorphism, and impact-induced dehydration (see Chapter 2 and Section 4.2). If all the chondritic IOM had a common origin, then any variations in the IOM composition and structure within and between chondrite classes should be understandable in terms of parent body and, perhaps, nebular processing.

Aqueous alteration. Solid-state ¹³C NMR investigation of IOM from different carbonaceous chondrite groups revealed that fractional concentration of aliphatic carbon ($F_{\text{CH}_x} = \text{\%aliphatic carbon}/100\% \text{ carbon}$) decreased in the order of CR2 EET 92042 ($F_{\text{CH}_x} = \sim 0.2$) > CI1 Orgueil ($F_{\text{CH}_x} = \sim 0.1$) > CM2 Murchison ($F_{\text{CH}_x} = > 0.1$) > Tagish Lake ($F_{\text{CH}_x} = \sim 0.03$) as well as H/C (Alexander et al., 2007), while those of carbonyl carbon slightly increased in the same order (Cody and Alexander, 2005). This trend was thought to reflect the different degrees of parent body aqueous alteration, which petrologic indicators suggest is lowest in the CR chondrites. It is suggested that low temperature chemical oxidation with the progress of aqueous alteration converted aliphatic moieties into carbonyl carbon (Cody and Alexander, 2005). An intense oxidation of Tagish Lake would also be consistent with its very low abundance of soluble organics, especially amino acids (Pizzarello et al., 2001). It has been reported that the weakly-altered CM2.8 Paris IOM shows a quite high aliphatic/aromatic carbon ratio with H/C=0.7 compared to Murchison IOM (Vinogradoff et al., 2015).

It has been suggested that the Tagish Lake meteorite is an ungrouped C2 meteorite derived from a D-type asteroid (Hiroi et al., 2001). This meteorite is thought to have experienced a unique aqueous alteration history compared to CM2 and CI1 chondrites (Zolensky et al., 2002), and is composed of several lithologies that experienced different alteration conditions (Herd et al., 2011; Zolensky et al., 2002). The IOM in these lithologies exhibit ranges of H/C ratios and functional group chemistries from CR/CM-like to the more aromatic compositions found in the most primitive CO/OC meteorites (Alexander et al., 2014; Herd et al., 2011). These ranges almost

certainly reflect varying temperatures during alteration and, interestingly, the modifications of the IOM were apparently achieved with little loss of C. However, the isotopic story of the IOM is more difficult to unravel. The IOM in CIs and all but one CM have much less isotopically anomalous compositions than the CR IOM. It is possible that all chondrites started with IOM like that in the CRs and that under certain conditions the IOM exchanged with isotopically more normal fluids during aqueous alteration. Clear evidence for modification of both the elemental and isotopic compositions of IOM during alteration is found in Tagish Lake, where the IOM from the various lithologies exhibit a clear linear correlation between H/C and δD . Hydrothermal experiments conducted for 1-3 days at 270-330°C showed partial to complete H isotope exchange (Oba and Naraoka, 2006; Yabuta et al., 2007) that roughly parallels what is seen in Tagish Lake. These are higher temperature conditions than estimated for the CIs and CMs, and they do not show such a simple relationship between H/C and δD . However, we do not understand how the kinetics of IOM-water exchange and IOM transformation may have varied with conditions.

The IOM in Bells is more isotopically anomalous than any CR as described above, despite its elemental composition and NMR spectra being indistinguishable from other CMs (Alexander et al., 2007; Cody et al., 2008b). Bells experienced rather different conditions during its parent body processing than other CMs – it was much more brecciated and oxidized (Brearley, 1995). It remains to be seen whether these conditions somehow helped Bells preserve a more primitive isotopic composition or, perhaps, generated the isotope anomalies. The latter possibility is only entertained because in the OCs, the IOM D/H ratio (but not $^{15}\text{N}/^{14}\text{N}$) increases dramatically (from 2300‰ to ~12,000‰) with increasing metamorphism. Either there is a very D-rich component of the IOM that is more stable than others under OC metamorphic conditions, or there is a mechanism(s) for making very large isotopic anomalies in parent bodies.

The chemical species of sulfur in IOM could be an indicator of oxidative conditions on the meteorite parent bodies. Variations in sulfur K-edge x-ray absorption near edge structure (XANES) spectra of IOM from CI, CM, CR and Tagish Lake meteorites are reported (Orthous-Daunay et al., 2010). High abundances of heterocyclic sulfur were identified from highly altered CM2 Cold Bokkeveld and CI chondrites Orgueil, Alais, and Ivuna, while aliphatic sulfide (disulfides, thiols, and thioether) and inorganic sulfide were main species in the other CM, CR, and Tagish Lake IOM. Oxidized organic sulfur was also identified from CI IOM. These variations in oxidation states of S-2 – S+6 indicate that Cold Bokkeveld and CI chondrites experienced mile-temperature oxidation on their parent body (Orthous-Daunay et al., 2010). Bose et al. observed the formation of thiophenes and thiol compounds after hydrothermal treatment of CM Murray IOM (Bose et al., 2017), suggesting that hydrothermal alteration in an asteroid may generate heterocyclic S in chondritic IOM.

It is thought that free radical concentrations (diradicaloids), which are never observed in terrestrial organic solids, may record the irradiation histories of IOM (Binet et al., 2004). The free radical concentrations decreased in the order of Tagish Lake ($20 \times 10^{18} \text{ spin g}^{-1}$) > Orgueil ($7 \times 10^{18} \text{ spin g}^{-1}$) > Paris ($5.5 \times 10^{18} \text{ spin g}^{-1}$) > Murchison ($1.8 \times 10^{18} \text{ spin g}^{-1}$) (Binet et al., 2004; Binet et al., 2002; Vinogradoff et al., 2015). It is discussed that lower radical content of Murchison than that of Paris may be due to partial removal of free radical moieties by hydrothermal alteration, while higher radical contents of more altered Tagish Lake and Orgueil implies that the parent bodies of these four chondrites have initially accreted OM with different organic radical content resulting from different irradiation/thermal conditions of the disk (Vinogradoff et al., 2015).

Thermal metamorphism. Thermal metamorphism on meteorite parent bodies also diversifies the molecular features of IOM and may decrease its abundance. For example, the IOM abundances in the most primitive COs and CVs are somewhat lower than in other carbonaceous chondrites (Alexander et al., 2007). Despite their relatively high degree of metamorphism and uncertainties in their original matrix abundances, the ECs have remarkably similar matrix-normalized C abundances (Alexander et al., 2007). Presumably this is due to their highly-reduced nature. Thermal metamorphism features of chondritic organics have been measured using several techniques, including micro-Raman, XANES, and Fourier transform infrared spectroscopy.

Micro-Raman spectroscopic analyses of the bulk powders of OC (Quirico et al., 2003), CV (Bonal et al., 2006), CO (Bonal et al., 2007) chondrites showed the correlations between petrologic types 3.0-3.7 and Raman parameters (D-band width (Γ_D) and band intensity ratio of D-band to G-band (I_D/I_G)), respectively, indicating the development of aromatic structure condensation with the progress of parent body thermal metamorphism. Busemann et al. extended and applied this spectroscopic approach to the IOM from 51 unequilibrated chondrites and showed systematic correlations between the Raman features (in particular, Γ_D , Γ_G , and I_D/I_G), meteorite classification, and IOM chemical compositions, which identified parent body thermal metamorphism, terrestrial weathering, and amorphization due to irradiation in space (Busemann et al., 2007).

X-ray absorption near edge structure (XANES) spectroscopic analyses of IOM from 25 chondrites showed that the peak intensity at 291.63 eV (Frenkel type $1s-\sigma^*$ exciton), which is derived from highly conjugated sp^2 carbon such as graphene, increased with petrologic-sub types (Cody et al., 2008b) (Fig. 6). Moreover, in that study, flash heating of IOM from Murchison CM2 chondrite was conducted (600, 1000, and 1400°C for 10s), development of the peak intensity of $1s-\sigma^*$ exciton of IOM with temperature was observed, and the XANES spectrum of IOM heated at 1400°C became similar to that of Vigarano CV3.1 IOM. Based on a well-resolved time-temperature relationship for the development of the exciton, assuming a duration of 10^7 years of parent body heating and 700 °C for temperature of CO3.7 Isna chondrite, peak temperatures of the individual meteorite parent bodies were estimated. The values are comparable to the mineralogically estimated temperature ranges (Huss et al., 2006a).

Fourier transform infrared spectroscopy (FTIR) study of IOM from 22 carbonaceous and ordinary chondrites was able to classify into a group where the carbonyl stretching is assigned to cyclic unsaturated lactones (e.g., CV3.0 Kaba, CV3.3 Vigarano, CV3.2 Mokoia, LL3.15 Bishunpur, and CV3.2 Allende), and another group where carbonyl exists predominantly in the form of unsaturated ketone moieties (e.g., CV3.0 Leoville, CO3.2 Kainsaz, H/L3.6 Tieschitz, and LL3.4 Chainpur), which relate to the activity of water and oxygen at different stages of thermal metamorphism, in addition to the other two groups of types 1 and 2 chondrites, and the least metamorphosed type 3 chondrites and Tagish Lake (Kebukawa et al., 2011).

Impact-induced dehydration. Although aqueous alteration generally occurred at low temperatures, a group of meteorites, the heated CM chondrites, are regarded as impact-dehydrated material of hydrous parent bodies (Nakamura, 2006; Nakato et al., 2008; Rubin, 1995). Solid-state ^{13}C NMR study showed H/C ratios and aliphatic/aromatic ratios of IOM from heated CM chondrites (Yamato 793321, Asuka 881280, Asuka 881334, Belgica 7904) were lower than those of IOM from CM chondrites (Murchison, Yamato 791198) (Yabuta et al., 2005). This result was consistent with the observation that H/C ratios of IOM from CM chondrites decreased and became similar values to that of Belgica 7904 after heating experiment up to 800°C at 10°C/min (Naraoka et al., 2004). Aliphatic carbon of IOM could have been aromatized and/or lost during dehydration.

Depletion of aliphatic carbon of heated CM would also be consistent with very small amounts of soluble organics (Shimoyama and Harada, 1984; Shimoyama et al., 1989a) and the labile fraction of IOM by pyrolysis (Komiya et al., 1993; Yabuta et al., 2010) from the same chondrites.

Short-term thermal evolution changes the molecular and isotopic compositions of chondritic IOM from more ordered to more heterogenous. Elemental and molecular features of IOM from heated CM were diverse and were not correlated with those of other meteorite groups (Alexander et al., 2007). Heated CM, PCA 91008 and Yamato 86720, which experienced 500°C and 700°C, respectively (Wang and Lipschutz, 1998), exhibit very weak 1s- σ^* exciton intensities in their XANES spectra, indicating that their IOM structures are not ordered even at such a high temperature range. In contrast, the CV 3.1 Vigarano meteorite that experienced a lower temperature of ~300-400°C (Huss et al., 2006a) than those meteorites, showed a highly-developed peak of 1s- σ^* exciton in the XANES spectrum (Cody et al., 2008b; Yabuta et al., 2010), indicating the formation of graphene. Therefore, heated CM IOM that experienced short-term heating shows different behaviors from thermal metamorphosed type3+ IOM that experienced long-term heating due to radiogenic decay.

Ungrouped C2 WIS 91600 is an intriguing meteorite, in terms of the spectroscopic and oxygen isotopic similarities to D-type asteroid and Tagish Lake (Clayton, 2003) and evidence of mild heating (Moriarty et al., 2009; Tonui et al., 2001). Solid-state ^{13}C NMR study revealed that the peak intensity of aromatic carbon in WIS 91600 IOM is greater than that in Tagish Lake, while the peak intensity of CH_xO and carbonyls in WIS 91600 IOM is lower than that in Tagish Lake (Yabuta et al., 2010). These results support the conclusion that WIS 91600 probably experienced dehydration and dehydrogenation superimposed on oxidative alteration. Comparing a growth and a decay of NMR signal intensity with different contact time for IOM in various meteorites, the magnetization of WIS 91600 IOM was as quick as those from Murchison and Tagish Lake, but its full magnetization stayed till 5.5 ms unlike the other two meteorites, and its relaxation pathway was rather similar to that of PCA 91008 (Yabuta et al., 2010). Contact time is an important NMR parameter which carbon nuclei acquires for its magnetization transferred from hydrogen nuclei during measurement. It gives us information about the mean distance between C and H within macromolecular structure. Therefore, WIS 91600 IOM appeared to have two distinct domains of carbon with different average degrees of aromatic condensation (non-heated and heated). Such heterogeneity is explained by local impact events. WIS 91600 experienced very moderate, short duration heating (< 500°C) after an episode of aqueous alteration under conditions that were similar to those experienced by Tagish Lake.

4.3.1.4. Origin and formation pathways of IOM

The different degrees of parent body processing modified the IOM precursor but the IOM itself should not have been produced in that environment. Here the authors suggest that IOM were formed either in the diffuse interstellar medium (ISM) or locally in the solar protoplanetary disk

Formation in ISM. Alexander et al. argued that the most straightforward model is for all chondrites, as well as the parent bodies of IDPs (primitive asteroids and comets), accreted a common primordial IOM (Alexander et al., 2007). Subsequent parent body process produced the range of elemental and isotopic compositions found in chondrites and IDPs. This was based on: (1) common structural features, and trends in structure and chemistry that accompany parent body

processes, and (2) similar IOM abundances in primitive chondrite matrices and relative to presolar nanodiamonds. As attractive as this model is, it remains speculative.

The relatively constant IOM/nanodiamonds ratio and the large D and ^{15}N enrichments suggest that the IOM is interstellar in origin, although D enrichments in gas-phase molecules are possible in the outer solar nebula (Aikawa et al., 2002). Further evidence in favor of the IOM's presolar origins is found in the similarity between the 3-4 μm infrared (IR) spectrum of the IOM and the refractory organic matter in the diffuse ISM (Pendleton and Allamandola, 2002). The IOM may also be partly responsible for the ubiquitous 2175 \AA UV absorption feature in the diffuse ISM (Bradley et al., 2005). This would be consistent with the inference of Adamson et al. (1999) that the carriers of the 3-4 μm and 2175 \AA features share many of the same characteristics. However, the chondritic IOM is composed of small PAHs ($< \text{C}_{20}$) with highly branched aliphatic chains (Cody et al., 2002). Of the models for refractory organics in the diffuse ISM, this most closely resembles that of Pendleton & Allamandola (2002), although their PAHs are larger (C_{20-200}) and more abundant ($\sim 80\%$). Alexander et al. suggested that when in the dense protosolar molecular cloud the refractory grains are trapped in ice at very low temperatures and irradiated by cosmic rays (Alexander et al., 2008). The cosmic rays damage the large PAHs and surrounding ice. When the grains are warmed up during formation of the Solar System, the damaged PAHs reacted with radicals etc. (e.g., H, O, OH, NH_3) in the damaged ice creating highly branched aliphatic material bonded to the surviving aromatic rings. Having formed at very cold temperatures the ice is expected to be very D- and ^{15}N -rich.

Formation in the solar protoplanetary disk. Gourier et al. find an inverse correlation between the D/H ratio of functional groups in the IOM and the C-H bond energy in those groups (Gourier et al., 2008). This inverse correlation they suggest is due to exchange with highly deuterated H_3^+ near the surface of the solar protoplanetary disk. Cleaves et al. have questioned whether H_3^+ would have been deuterated enough or in high enough concentration to explain the IOM compositions, or whether it would interact with IOM grains (Cleaves et al., 2014; Cleaves et al., 2016). Nevertheless, given the growing recognition that photochemistry at the surfaces of disks may be of huge importance to disk chemistry and evolution, this and other disk models for the origin of the IOM need to be pursued vigorously. Whatever its ultimate origin, IOM would have been delivered to the surface of the early Earth in meteorites and IDPs. The IOM is a complex aromatic molecule which is not related to the "present" bio-related molecules, but may have played a role as the first functional material, using an advantage of macromolecule. It has been shown that the macromolecular material in Murchison will break down by hydrous pyrolysis into PAHs (Sephton et al., 1998; Yabuta et al., 2007). N-, O-, and S-bearing aromatic heterocycles and water soluble molecules, such as benzimidazoles, hydroxyquinolines, morpholine, and dicarboxylic acids (Yabuta et al., 2007), acetic acid (Oba and Naraoka, 2006), ammonia (Pizzarello et al., 2011), and other reducing volatiles that could have contributed to the organic inventory available for the origin of life on the prebiotic Earth. These compounds if present in macromolecular material found in IDPs, could have been released by further chemical reactions in the early Earth atmosphere and ocean.

4.3.2. Soluble Organic Matter (SOM)

Ultrahigh resolution molecular analyses of the soluble organic component of the CM2 Murchison meteorite have revealed tens of thousands of unique molecular compositions and likely millions of distinct chemical structures (Schmitt-Kopplin et al., 2010), the vast majority of which

have not yet been identified. The range of concentrations of several soluble organic compound classes found in Murchison and other meteorites and the total number of molecular species that have been uniquely identified in each carbonaceous chondrite group to date are listed in Table 3. Due to the limited availability of sample mass for interplanetary dust particles (IDPs) and micrometeorites, there have been no reports on the composition of any soluble organics in IDPs and only two reports of extraterrestrial amino acids in micrometeorites collected in Antarctica (Brinton et al., 1998; Matrajt et al., 2004). However, new state-of-the-art analytical techniques with increased sensitivities and higher mass resolution will make it possible to extend the range of soluble organic compounds identified in very small meteorites samples, including IDPs (Callahan et al., 2014).

Table 3. Concentrations of soluble organic compounds and current total number of molecular species that have been identified in carbonaceous chondrites and Antarctic micrometeorites (updated from Botta and Bada 2002; Pizzarello et al. 2006). The names of the individual amino acids that have been identified are shown in Table 4. The names of all other molecular species can be found in the cited references.

Compound Class	Total Concentration (ppm)	Molecular Species Identified
Amino Acids		
CM meteorites	<0.1 – 71 ^[1]	92 ^{[2]*}
CI meteorites	0.1 – 6.9 ^[3]	23 ^[4]
CR meteorites	~2 – 320 ^[5]	23 ^[4]
CH meteorites	13 – 16 ^[6]	23 ^[6]
CB meteorites	0.3 – 2.3 ^[6]	23 ^[6]
CV meteorites	0.7 – 6.1 ^[7]	18 ^[7]
CO meteorites	0.3 – 2.4 ^[7]	16 ^[7]
CK meteorites	<0.1 – 0.6 ^[8]	15 ^[8]
C2 ung. Tagish Lake	<0.1 – 5.4 ^[9]	23 ^{[9]*}
Antarctic micrometeorites	< 0.001 – 0.2 ^{[10]**}	7 ^[10]
Antarctic micrometeorites	< 0.1 – 280 ^{[11]**}	7 ^[11]
Diamino Acids	~0.4 ^[12]	7 ^[12]
Imino Acids	n.d.	10 ^[13]
Aromatic Hydrocarbons	15 – 28 ^[14]	87 ^[14]
Aliphatic Hydrocarbons	>35 ^[15]	140 ^[15]
Monocarboxylic Acids		
CM meteorites	~100 – 700 ^[16]	50 ^{[16]*}
CR meteorites	26 – 90 ^[17]	22 ^[17]
Hydroxycarboxylic Acids		
CM meteorites	15 ^[18]	7 ^{[18]*}
CR meteorites	76 ^[19]	20 ^[19]
Dicarboxylic Acids		
CM meteorites	13 – 26 ^[20]	17 ^[20]
CR meteorites	121 ^[19]	19 ^[19]
Hydroxy Acids	15 ^[21]	50 ^{[21]*}
N-Heterocycles	7 ^[15]	31 ^[15]
Purines	0.01 – 0.5 ^[22]	7 ^[22]

Aliphatic Amines		
CM meteorites	4 – 20 ^[23]	24 ^[23]
CR meteorites	70 – 117 ^[24]	25 ^[24]
Amides	n.d.	27 ^{[25]*}
Alcohols	11 ^[26]	4 ^[26]
Aldehydes and Ketones	14 – 189 ^[27]	28 ^[27]
Sulfonic Acids	68 ^[28]	4 ^[28]
Phosphonic Acids	2 ^[28]	4 ^[28]
Polyols	30 ^[29]	19 ^[29]

*Compound class contains many more molecular species than were identified; individual enantiomers are not included in the total number of compounds. **Range of total abundances of α -aminoisobutyric acid (AIB) only.

References:

- ¹(Burton et al., 2014a; Glavin et al., 2010; Shimoyama and Ogasawara, 2002)
- ²(Burton et al., 2012d; Koga and Naraoka, 2017)
- ³(Burton et al., 2014b; Ehrenfreund et al., 2001a)
- ⁴(Glavin et al., 2010)
- ⁵(Glavin et al., 2010; Martins et al., 2007)
- ⁶(Burton et al., 2013)
- ⁷(Burton et al., 2012a)
- ⁸(Burton et al., 2015)
- ⁹(Glavin et al., 2012)
- ¹⁰(Matrajt et al., 2004)
- ¹¹(Brinton et al., 1998)
- ¹²(Meierhenrich et al., 2004a)
- ¹³(Lerner and Cooper, 2005)
- ¹⁴(Pering and Ponnampereuma, 1971)
- ¹⁵(Cronin et al., 1988) and references therein
- ¹⁶(Huang et al., 2005b; Yuen and Kvenvolden, 1973)
- ¹⁷(Pizzarello et al., 2008; Pizzarello et al., 2012)
- ¹⁸(Peltzer and Bada, 1978a)
- ¹⁹(Pizzarello et al., 2008)
- ²⁰(Lawless et al., 1974; Martins et al., 2006)
- ²¹(Cronin et al., 1993a)
- ²²(Callahan et al., 2011b)
- ²³(Aponte et al., 2014a; Pizzarello and Holmes, 2009)
- ²⁴(Aponte et al., 2016)
- ²⁵(Cooper and Cronin, 1995)
- ²⁶(Jungclaus et al., 1976b)
- ²⁷(Jungclaus et al., 1976b; Krishnamurthy et al., 1992b; Monroe and Pizzarello, 2011; Pizzarello and Holmes, 2009)
- ²⁸(Cooper et al., 1992)
- ²⁹(Cooper et al., 2001b; Cooper and Rios, 2016)

4.3.2.1. Amino Acids, Formation Pathways, and Enantiomeric Excesses

Amino acids are the building blocks of proteins and enzymes that are essential for biology as we know it on Earth. These compounds can be synthesized under a variety of prebiotic conditions (Ferris et al., 1978; Miller, 1953; Miller, 1955) and have been detected in carbonaceous chondrites. Soluble organic compounds, and in particular amino acids have been most extensively characterized in the CM2s Murchison and Murray. The large sample mass of the Murchison (~100 kg) and Murray (~ 12.6 kg) falls and their relatively high soluble organic abundances have enabled their analysis by many researchers over the last five decades. However, in recent years, the analysis of amino acids and other organic classes in meteorites has expanded to include a variety of other

carbonaceous chondrite groups and types (Elsila et al., 2016), enabled in part by the recovery of additional meteorites from Antarctica (Richter et al. 2014).

Kvenvolden and co-workers first identified five common protein amino acids in Murchison and twelve non-proteinogenic amino acids including α -aminoisobutyric acid (AIB) and isovaline that are both rare on Earth (Kvenvolden et al., 1970a; Kvenvolden et al., 1971b). They concluded that all of amino acids were extraterrestrial in origin given their high relative abundances (several parts per million) compared to known terrestrial sources and nearly equal abundances of left (L) and right handed (D) enantiomers of the chiral amino acids that argued strongly against contamination, since terrestrial amino acids are predominately L. Moreover, isotopic measurements of amino acids in Murchison show that these molecules are enriched in deuterium, ^{13}C , and ^{15}N compared to terrestrial organic matter, providing further evidence that these compounds are extraterrestrial in origin (Engel and Macko, 1997; Engel et al., 1990; Epstein et al., 1987; Pizzarello et al., 1994b; Pizzarello et al., 1991). Since the original amino acid work on Murchison published by Kvenvolden, over 90 different amino acids have now been named in the Murchison meteorite and many more have yet to be identified (Table 4). The Murchison meteorite contains 11 of the 20 most common protein amino acids, however the vast majority of amino acids found in this meteorite are rare or nonexistent in the terrestrial biosphere (Burton et al., 2012b; Cronin and Chang, 1993). This finding is important since these unusual non-protein amino acids are much less affected by contamination and provides additional evidence that the amino acids in Murchison are extraterrestrial in origin. Among those amino acids recently identified in Murchison is a new family of compounds that include nine hydroxy amino acids (Koga and Naraoka, 2017). Seven di-amino acids have also been detected in the Murchison meteorite and they are racemic indicating an extraterrestrial origin (Meierhenrich et al., 2004b). Amino acids in Murchison range from two- to ten-carbons in length and exhibit nearly complete structural diversity (all isomeric forms present) with an exponential decrease in abundance with increasing carbon number within a homologous series (Cronin and Pizzarello, 1986; Glavin et al., 2010). Based on the total number of possible enantiomers and isomers (*e.g.*, 8 possible enantiomers and isomers of four-carbon amino acids, 23 possible five-carbon amino acids, >100 possible six-carbon amino acids, etc.) for amino acids with carbon numbers up to C_{10} , it is likely that there are thousands of individual amino acids in Murchison. Most of these amino acids have not yet been identified due to insufficient analytical sensitivity, poor chromatographic resolution and a lack of standards for amino acids with six or more carbons (Glavin et al., 2010).

The amino acids in Murchison are present at part per million levels and are predominately α -amino isomers, although other structural isomers are present at lower abundances (Table 4). This α -amino acid isomer dominated distribution is also seen in other moderately aqueously altered CM2 chondrites and the CR2 and CR3 chondrites. However, meteorites that experienced a greater degree of aqueous alteration without significant heating such as the CI1s Orgueil and Ivuna, CM1s MET 01070 and SCO 06043, and the CR1 GRO 95577 have much lower total abundances of amino acids and higher relative abundances of γ - and δ -amino acid isomers compared to Murchison (Glavin et al., 2010). The high relative abundances of γ - and δ -amino acids in Type 1 chondrites may be related to their increased stability relative to α - and β -amino acids (Glavin et al., 2010; Li and Brill, 2003). Carbonaceous chondrites exposed to extensive aqueous alteration as well as elevated temperatures up to 400-600°C (*e.g.* the CI1 chondrites Y-980115 and Y-86029 and the CM2 Sutter's Mill) contain much lower amino acid abundances than the CI1 Orgueil and CM2 Murchison meteorites and are dominated by the more thermally stable γ -amino acids (Burton et al., 2014a; Burton et al., 2014b). Meteorites that exposed to more parent body heating such as the

moderately heated CO3 and CV3 chondrites and the extensively heated CK4-6 chondrites also have much lower amino acid abundances than the CM2 and CR2/3 chondrites and are dominated by straight-chain *n*- ω -amino acids including δ -amino acids consistent with their formation at elevated temperatures (Burton et al., 2012a; Burton et al., 2015). The formation pathways and processing histories of amino acids in different carbonaceous chondrites groups will be discussed in more detail in the next section.

Table 4. The names of the amino acids that have been identified in carbonaceous chondrites including ten new amino acids recently discovered in Murchison (Glavin et al., 2010; Koga and Naraoka, 2017; Pizzarello et al., 2006a; Pizzarello and Holmes, 2009; Pizzarello and Shock, 2010). Amino acids also found in protein are *italicized*.

Two carbons	Five carbons	4-Amino-3-methylpentanoic acid
<i>Glycine</i>	<i>Valine</i>	4-Amino-4-methylpentanoic acid
Three carbons	<i>Glutamic acid</i>	6-Aminohexanoic acid
<i>Alanine</i>	Norvaline	α -Aminoadipic acid
<i>Serine</i>	3-Aminopentanoic acid	β -Aminoadipic acid
β -Alanine	3-Amino-2-methylbutanoic acid	2-Methylglutamic acid
Isoserine*	<i>allo</i> -3-Amino-2-methylbutanoic acid	Other isomers detected, but not identified
Sarcosine	3-Amino-2,2-dimethylpropanoic acid	Seven carbons
Four carbons	3-Amino-3-methylbutanoic acid	2-Amino-2,3,3-trimethylbutanoic acid
<i>Aspartic acid</i>	3-Amino-2-ethylpropanoic acid	2-Amino-2-ethyl-3-methylbutanoic acid
<i>Threonine</i>	4-Aminopentanoic acid	2-Amino-2-ethylpentanoic acid
Isothreonine*	4-Amino-2-methylbutanoic acid	2-Amino-3-ethylpentanoic acid
<i>allo</i> -Threonine	4-Amino-3-methylbutanoic acid	2-Amino-2,3-dimethylpentanoic acid
<i>allo</i> -Isothreonine*	5-Aminopentanoic acid	2-Amino-2,4-dimethylpentanoic acid
Homoserine*	2-Methylaspartic acid	2-Amino-3,3-dimethylpentanoic acid
β -Homoserine*	3-Methylaspartic acid	2-Amino-3,4-dimethylpentanoic acid
α -Methylserine*	<i>allo</i> -3-Methylaspartic acid	2-Amino-4,4-dimethylpentanoic acid
α -Aminobutyric acid	<i>N</i> -Methylaspartic acid	<i>allo</i> -2-Amino-2,3-dimethylpentanoic acid
β -Aminobutyric acid	4,4'-Diaminoisopentanoic acid	<i>allo</i> -2-Amino-3,4-dimethylpentanoic acid
α -Aminoisobutyric acid	β -(Aminomethyl)-succinic acid*	2-Amino-2-methylhexanoic acid
β -Aminoisobutyric acid	Six carbons	2-Amino-3-methylhexanoic acid
<i>N</i> -Ethylglycine	<i>Leucine</i>	<i>allo</i> -2-Amino-3-methylhexanoic acid
<i>N,N</i> -Dimethylglycine	<i>Isoleucine</i>	2-Amino-4-methylhexanoic acid
<i>N</i> -Methylalanine	<i>allo</i> -Isoleucine	<i>allo</i> -2-Amino-4-methylhexanoic acid
<i>N</i> -Methyl- β -alanine	Norleucine	2-Amino-5-methylhexanoic acid
3-Amino-2-(hydroxymethyl)-propanoic acid*	Pseudoleucine	2-Aminoheptanoic acid
2,3-Diaminobutanoic acid	Cycloleucine	α -Aminopimelic acid
2,4-Diaminobutanoic acid	2-Methylnorvaline	1-Aminocyclohexanecarboxylic acid
3,3'-Diaminoisobutanoic acid	Pipecolic acid	Other isomers detected, but not identified
4-Amino-2-hydroxy-butanoic acid*	2-Amino-2-ethylbutanoic acid	Eight carbons
4-Amino-3-hydroxy-butanoic acid*	2-Amino-2,3-dimethylbutanoic acid	Isomers detected, but not identified
	3-Amino-2-ethylbutanoic acid	Nine carbons
	3-Amino-2,3-dimethylbutanoic acid	<i>Phenylalanine</i>
	3-(Methylamino)pentanoic acid	<i>Tyrosine</i>
	4-Aminohexanoic acid	Other isomers detected, but not identified
	4-Amino-3,3-dimethylbutanoic acid	Ten carbons
	4-Amino-2-methylpentanoic acid	Isomers detected, but not identified

*New amino acids identified in the Murchison meteorite (Koga and Naraoka, 2017)

Formation Pathways and Processing Histories. Multiple formation pathways and synthetic routes for amino acids in meteorites have been proposed based on the distributions, relative

abundances of various isomers, and carbon, nitrogen and hydrogen isotopic compositions (Fig. 7). The most likely synthetic routes of formation for amino acids found in meteorites are as follows: (1) α -amino acids can be formed by the Strecker-cyanohydrin pathway and HCN polymerization inside the meteorite parent body during aqueous alteration (Lerner et al., 1993; Matthews and Minard, 2008; Peltzer et al., 1984b) or by mineral surface catalyzed reactions of H_2 , CO , and NH_3 at elevated temperatures (Hayatsu et al., 1971). α -Amino acids can also be formed outside the parent body on ice grain surfaces exposed to radiation (de Marcellus et al., 2011; Elsila et al., 2007), for example by carboxylation of amines with CO_2 under proton irradiation (Hudson et al., 2007); (2) β -amino acids are believed to form by Michael addition of ammonia to α,β -unsaturated nitriles during parent body aqueous alteration (Ehrenfreund et al., 2001a); (3) γ - and δ -amino acids can be formed by decarboxylation of α -amino dicarboxylic acids or the hydrolysis of lactams during parent body aqueous alteration (Cooper and Cronin, 1995). In addition, γ - and δ -amino acids could be produced during parent body alteration at elevated temperatures and pressures leading to predominately straight-chain, amino-terminal acids (Islam et al., 2003).

The discovery of high relative abundances of α -amino acids and the analogous α -hydroxy acids and iminodicarboxylic acids found in Murchison (Lerner and Cooper, 2005; Peltzer et al., 1984b) that are predicted to form from these chemical precursors during Strecker-cyanohydrin synthesis (see Fig. 7) suggests that amino acid Strecker synthesis occurred within the Murchison parent body during an aqueous alteration phase. The CR2/3 carbonaceous chondrites EET 92042, QUE 99177 and GRA 95229 are the most amino acid-rich chondrites ever analyzed with high concentrations up to 320 ppm, approximately ten times higher than Murchison (Glavin et al., 2010; Martins et al., 2007). These primitive CR chondrites also have much higher abundances of the corresponding α -amino and α -hydroxy acids compared to Murchison providing additional support that the Strecker mechanism was active on the parent body of the CR meteorites. However, the Strecker pathway itself cannot produce the large D, ^{13}C , and ^{15}N isotope enrichments observed in the amino acids found in these carbonaceous chondrites (Kung et al. 1979; Chang et al. 1983; Elsila et al. 2012). In particular, the large D enrichments of amino acids ($\delta D \sim +300$ to $+3000$ ‰), in Murchison and other CM2 carbonaceous chondrites (Elsila et al., 2012a) is consistent with the large D/H values measured in hot cores of the interstellar medium (ISM), and may indicate that these compounds formed from precursor molecules (e.g. HCN, NH_3 , aldehydes, and ketones) synthesized in the ISM and later incorporated into the Murchison parent body during accretion. Laboratory experiments have also shown that a variety of amino acids can be formed by irradiation of interstellar ice analogues (Bernstein et al., 2002; Caro et al., 2002; Elsila et al., 2007). Therefore, it is possible that the amino acids themselves were formed directly on icy grains in the ISM and later incorporated into the meteorite parent body.

The formation of α -amino acids by polymerization of HCN during an aqueous alteration phase on the meteorite parent body has also been suggested (Lerner et al., 1993; Peltzer et al., 1984a). However, only two compounds (glycine and alanine) are produced at significant levels from HCN by this mechanism (Levy et al. 2000), therefore a wide variety of aldehydes and ketones must have been present in the meteorite parent body at the time of amino acid formation in order to obtain the diversity of amino acids observed in Murchison and other carbonaceous meteorites. Alternatively, it has been suggested based on laboratory experiments that α -amino acids in meteorites could be formed by mineral surface-catalyzed reactions of H_2 , CO , and NH_3 at elevated temperatures known as Fischer-Tropsch Type (FTT) synthesis (Hayatsu et al., 1971). However, FTT reactions alone cannot reproduce the diversity of amino acids observed in Murchison, which also include β -, γ , and δ -amino acid isomers.

The broad diversity of amino acids observed in meteorites (Table 4) suggest multiple formation mechanisms (Fig. 7). For example, more than one mechanism may be necessary to form β -amino acids, which in contrast to α -amino acids, cannot be directly produced by Strecker synthesis. β -amino acids are believed to form under aqueous conditions by Michael addition of ammonia to pre-existing α -, β -unsaturated nitriles such as cyanoacetylene and acrylonitrile followed by reduction/ hydrolysis steps. Because liquid water is required, Michael addition has been suggested as a plausible explanation for the elevated levels of β -alanine and β -amino-*n*-butyric acid relative to their respective α -amino acid isomers that have been identified in the aqueously altered CI1 meteorites Orgueil and Ivuna (Ehrenfreund et al., 2001a; Glavin et al., 2010). The origins of the γ - and δ -amino acids detected in meteorites are not as well understood. It is possible that these compounds are decomposition products that result from the thermal decarboxylation or deamination of α -amino dicarboxylic acids or diamino acids during parent body alteration (Burton et al., 2012b). It has also been proposed that some γ - and δ -amino acids found in Murchison could have been produced from the hydrolysis of lactams that have also been identified in this meteorite (Cooper and Cronin, 1995). Lactam formation has been shown to protect some γ - and δ -amino acids such as γ -amino-*n*-butyric acid and δ -amino-*n*-valeric acid from decarboxylation under hydrothermal conditions (Islam et al., 2003). The enhanced thermal stability of these amino acids under hydrothermal conditions relative to less stable α - and β -amino acids may explain why γ - and δ -amino acids are observed in much higher relative proportions in the more altered type 1 CI, CM and CR chondrites and the CO3, CV3, and CK4-6 chondrites compared to less altered CM2 and CR2/3 chondrites (Elsila et al., 2016).

The dominant distribution of the linear straight-chained *n*- ω -amino acids including β -alanine, γ -amino-*n*-butyric acid and δ -amino-*n*-valeric acid found in thermally altered CO3 and CV3 chondrites may also be the result of FTT and Haber-Bosch (HB) catalytic reactions that occurred between trapped CO, H₂, and N₂ gases and metals inside the meteorites as they cooled on their respective parent bodies (Burton et al., 2012a). Moreover, carbon isotope measurements of γ -amino-*n*-butyric acid in the CV3 LAP 02206 showed that it was isotopically light ($\delta^{13}\text{C} = -27\text{‰}$, (Burton et al., 2012a)) relative to amino acids in less thermally altered meteorites, which is consistent with the ¹³C depletions observed previously in hydrocarbons produced by FTT reactions (Hu et al., 1998; Lancet and Anders, 1970). The metal rich CB3 and CH3 chondrites which contain 60-80 wt.% and 20 wt.% metal by volume, respectively also have high relative abundances β -, γ -, and δ -amino acids compared to their corresponding α -amino acid isomers providing evidence that multiple amino acid formation mechanisms were important in these carbonaceous chondrites as well (Burton et al., 2013).

The large range of total amino acid abundances observed across the carbonaceous chondrite groups shown in Figure 8 can be attributed to differences in parent body alteration conditions and/or differences in the initial concentration of amino acid precursors in the source regions of the parent bodies. Although the total abundance and relative distribution of amino acids cannot be used to predict the relative degree of aqueous alteration between carbonaceous chondrite groups, current observations do suggest that the most primitive, least aqueously altered CM and CR type 2 and type 3 chondrites have the highest amino acid abundances while the more aqueously altered type 1 chondrites and meteorites that have experienced higher degrees of thermal alteration have much lower abundances. Even without significant heating, extensive parent body aqueous alteration will lead to amino acid decomposition as observed for the CM1 and CR1 chondrites (Botta et al., 2007; Glavin et al., 2010) Given that amino acids start to decompose at temperatures

above 150°C in the solid state (Rodante, 1992), it is also not surprising that the lowest amino acids levels are found in the more thermally altered CO, CV, and CK chondrites that were heated to temperatures up to 600°C (Burton et al., 2012a; Burton et al., 2014b; Burton et al., 2015). For the chondrites that experienced the highest temperatures, it is highly likely that any amino acids and amino acid precursors originally incorporated into the parent body were destroyed, while the trace levels of predominately *n*- ω -amino acids currently present in these thermally altered meteorites were formed by FTT/HB reactions as the parent bodies cooled to lower temperatures.

Amino Acid Enantiomeric Excesses and the Origin of Homochirality. The homochirality observed in biological molecules on Earth, the “left handed” or L-amino acids and “right handed” or D-sugars is a property that is crucial for molecular recognition, enzymatic function, information storage and structure and is thought to be a prerequisite for all life. However, the origin of homochirality in terrestrial life is a major unresolved problem in origin of life research and remains an area of considerable debate. Despite the fact that equal abundances of left and right handed forms (L=D) of many protein amino acids and sugars common to life on Earth were likely available on the prebiotic Earth by local abiotic synthetic mechanisms and extraterrestrial input, only L-amino acids and D-sugars constitute the basic building blocks of all living systems on Earth today. In fact, there appear to be no biochemical reasons why left-handed amino acids should be favored over right-handed amino acids in enzymes (Milton et al., 1992), and therefore some have argued that the selection of left-handed amino acid homochirality by life on Earth was a random process (Bada, 1995). Moreover, since aqueous solutions of amino acids and sugars will racemize (conversion of one enantiomer to the other until a racemic mixture is reached) over relatively short periods on geological time scales (Bada, 1972; Fedoronko and Königstein, 1969), it becomes even more difficult to explain how the evolution to homochirality occurred on the early Earth.

Although the first amino acid analyses of the Murchison meteorite shortly after its fall found that the chiral α -hydrogen protein amino were racemic (Kvenvolden et al., 1971a), more recent analyses of amino acids in Murchison have shown that there are slight L-enantiomeric excesses (L_{ee}) ranging from 0 to 15.2% for several α -dialkyl non-protein amino acids including isovaline, α -methylnorleucine, α -methylvaline, α -methylnorvaline, α -methylisoleucine, and 2-amino-2,3-dimethylpentanoic acid (Pizzarello and Cronin, 2000; Pizzarello et al., 2003a). Two different environments have been considered for the origin of L-enantiomeric excesses in carbonaceous chondrites – asteroidal parent bodies and interstellar/circumstellar environments.

In a chondritic parent body, the large L-enantiomeric excesses are difficult to explain since abiotic formation of α -dialkyl amino acids in this environment (*e.g.* Strecker-cyanohydrin synthesis) should produce racemic mixtures. It has been suggested that for some amino acid diastereomers like isoleucine and *allo*-isoleucine, the observed enantiomeric excesses could have been inherited from their asymmetric chiral aldehyde precursors (Pizzarello et al., 2008), however this was likely not the case for isovaline whose most plausible ketone precursor (2-butanone) is achiral. In contrast to the α -hydrogen amino acids, α -dialkyl amino acids are not prone to rapid racemization under aqueous or radiogenic conditions on geological timescales (Bonner et al., 1979; Pollock et al., 1975); therefore, small enantiomeric excesses should be preserved for these amino acids since the time of their formation. Since isovaline is not common in biology (Brückner and Toniolo, 2009), the L-isovaline excess is unlikely to be attributed to terrestrial contamination. However the most powerful evidence for a non-terrestrial origin of the L-isovaline excess in Murchison is from isotopic measurements showing the same $^{13}\text{C}/^{12}\text{C}$ ratio in the individual D- and L-isovaline enantiomers detected in Murchison (Pizzarello et al., 2003b). If terrestrial

contamination was the source of the L-isovaline excess in the meteorite, the L-enantiomer should have had a lower $^{13}\text{C}/^{12}\text{C}$ ratio compared to the D-enantiomer (Elsila et al., 2010), however this was not observed.

L-Isovaline excesses of up to 21% have now been reported across a wide range of carbonaceous chondrites (Table 5) and may be related to the degree of aqueous alteration of the meteorites as inferred from their mineralogy (Elsila et al., 2016; Glavin and Dworkin, 2009). In situ aqueous alteration was an important process on the CM meteorite parent body with liquid water timescale estimates ranging from 10^2 to 10^4 years (Zolensky and McSween, 1988) and may have been the driving force for amplification of amino acid ee in Murchison and other CM chondrites. Further support for this hypothesis was found by Glavin and Dworkin (2009) and Glavin et al. (2010) who identified L-isovaline enrichments in the type 1 CI, CM and CR chondrites that also experienced extensive aqueous alteration. In contrast, very little enrichment of L-isovaline found in the much less altered type 2/3 CR chondrites (Glavin and Dworkin, 2009; Pizzarello et al., 2008). The metal-rich CH and CB chondrites also have large L-isovaline excesses (Burton et al., 2013) and since these meteorites contain a mix of heavily hydrated and anhydrous materials (Greshake et al., 2002), it is possible that an aqueous alteration phase that produced the hydrated minerals also led to the amplification of L-isovaline excesses.

Analysis of multiple fragments of the C2 ungrouped Tagish Lake meteorite that experienced varying degrees of aqueous alteration on the parent body showed even larger enantiomeric excesses with L_{ee} of ~99, 80, 55, and 44%, respectively, measured for the protein amino acids threonine, serine, aspartic and glutamic acids. In contrast, alanine, another biologically common protein amino acid was found to be nearly racemic in the same fragments, suggesting minimal terrestrial biological contamination of the meteorite (Glavin et al., 2012). Enriched ^{13}C contents of both D- and L-enantiomers of alanine and aspartic acid confirmed a non-biologic, extraterrestrial origin of these compounds. These unusual Tagish Lake L_{ee} findings can be explained by differences in the solid-solution behavior of aspartic and glutamic acids which form conglomerate enantiopure (all D or all L) solids during crystallization, and alanine, which can only form racemic (D = L) crystals. Amplification of a small initial L_{ee} during periods of aqueous alteration on the Tagish Lake parent body could have led to the large L-enrichments observed for aspartic acid and other conglomerate amino acids, but would not lead to significant L-enrichments for amino acids such as alanine that form racemic crystals (Klussmann et al., 2006). A schematic illustration of the behavior of conglomerate and racemic amino acid crystals during parent body aqueous alteration is shown in Fig. 9. Asymmetric autocatalysis experiments have also shown that small initial imbalances can be amplified under aqueous conditions to produce enantiomeric excesses of up to 90% (Blackmond, 2004; Soai et al., 1995). The correlation between asymmetry-carrying isovaline and hydrous silicate abundances in some Murchison meteorite fragments (Pizzarello et al., 2003b), provides additional evidence that the formation of meteoritic amino acid L-excesses may have been a secondary process due to aqueous interaction with the lithic environment. Although water may have played an important role in amplification of amino acid enantiomeric excesses inside the parent body, another mechanism is required to break chiral symmetry and provide an initial L_{ee} .

The most common explanation for the origin of the L_{ee} found in Murchison and other aqueously altered carbonaceous chondrites is enantioselective photolytic decomposition of amino acids or their precursors by ultraviolet circularly polarized light (UV CPL), possibly from a nearby neutron star (Bonner and Rubenstein, 1987). Laboratory experiments have shown that chiral amino acid symmetry breaking and enantiomeric enrichment of up to a few percent can be produced by

exposure to UV CPL (Flores et al., 1977; Takano et al., 2007), however polarized light cannot be the sole source of the large enantiomeric excesses observed in some carbonaceous chondrites since L_{ee} exceeding 15% would require photodestruction of more than 99.5% of the amino acid requiring extremely high initial concentrations (Flores et al., 1977). The molecular distributions and stable isotope ratios of the α -amino acids in Murchison and other CM2 meteorites (Elsila et al., 2012a; Peltzer and Bada, 1978b) indicate that these compounds were mostly produced during aqueous alteration inside their parent bodies where they would have been shielded from circularly polarized radiation. Therefore, the initial amino acid chiral symmetry breaking by polarized radiation must have occurred prior to incorporation of amino acids and their chemical precursors inside the parent body.

Regardless of how the enantiomeric excesses observed in meteorites were created, the detection of nonracemic amino acids in several different carbonaceous chondrites suggests that meteoritic delivery to planetary surfaces could have contributed to the origin of homochirality in life on Earth. The observation that only L-excesses have been found in amino acids containing a single asymmetric carbon (one amino acid with two chiral carbons, *allo*-isoleucine has been reported to have a D-excess (Pizzarello and Groy, 2011) although these results have been challenged (Elsila et al., 2012b), could indicate that the origin of life on Earth, and possibly elsewhere in our Solar System, was biased toward L-amino acid homochirality from the beginning, prior to the stratification of the solar nebula.

Table 5. L-Isovaline enantiomeric excesses measured in carbonaceous chondrites.

Meteorite	Classification	Isovaline % $L_{ee} = (L - D) / (L + D) \times 100$
ALH 85085	CH3	20.5 ± 7.1^a
Murchison	CM2	18.5 ± 2.6^b
Murchison	CM2	17.2 ± 7.1^c
Murchison	CM2	$0-15.2^d, 8.4^e$
SCO 06043	CM1	16.5 ± 7.5^c
Orgueil	CI1	15.2 ± 7.5^b
MIL 07411	CB3	14 ± 4^a
PCA 91467	CH3	13 ± 3^a
GRO 95577	CR1	11.0 ± 7.2^c
MIL 05082	CB3	9.7 ± 3.0^a
Tagish Lake 5b	C2 ung.	7.0 ± 1.9^f
Tagish Lake 11h	C2 ung.	0.0 ± 2.8^f
Murray	CM2	6.0^g
PAT 91546	CH3	5 ± 2^a
LEW 90500	CM2	3.3 ± 1.8^b
LON 94102	CM2	2.4 ± 4.1^b
QUE 99177	CR3	0.3 ± 2.1^b
EET 92042	CR2	-1.0 ± 4.3^b

References: ^aBurton et al. (2013); ^bGlavin and Dworkin (2009); ^cGlavin et al. (2010); ^dPizzarello et al. (2003); ^eCronin and Pizzarello (1997); ^fGlavin et al. (2012); ^gPizzarello and Cronin (2000).

4.3.2.2. Aliphatic Amines and Amides

Amines. Acyclic aliphatic monoamines (hereafter called “amines”) are ubiquitous organic compounds that share analogous structural backbones with amino acids. The primordial origins of meteoritic amines were initially proposed from the decarboxylation of amino acids through parent body processes (Pizzarello et al., 1994a). Later results from CR2 chondrites, however, suggested that inherent parent body differences and precursor molecule content could affect their synthesis (Aponte et al., 2016; Pizzarello and Holmes, 2009). Nevertheless, the carbon compound-specific isotopic amine data is consistent with an interstellar origin of amines and their potential precursor molecules.

Amines were first reported qualitatively by (Hayatsu et al., 1975b) from the acid hydrolyzed extract of the Murchison meteorite using a combination of paper chromatography, infrared and ultraviolet spectroscopy, and mass spectrometry. A year later, (Jungclaus et al., 1976a) reported a suite of ten free and derivatized amines from the aqueous and acid-hydrolyzed extract of the Murchison meteorite using ion exchange chromatography and mass spectrometry. Meteoritic amines remained uninvestigated for the next eighteen years when Pizzarello et al. (1994) reported the molecular distribution and abundance of twenty amines and the bulk isotopic composition of basic organic compounds from water extracts of two Murchison meteorite pieces. Isotopic analyses of meteoritic aqueous extracts containing the bulk of basic compounds (including ammonia) in the Murchison meteorite showed stable isotopic enrichments ($D = +1221\%$, $^{13}C = +22\%$, and $^{15}N = +93$; Pizzarello et al., 1994).

Subsequent amine analyses expanded the search of these compounds to CR1, CR2 and CR3 Antarctic carbonaceous chondrites, the identification and quantification of amines was obtained by chemical derivatization using pentafluoropropionic anhydride (PFPA) followed by gas chromatography mass spectrometry (GC-MS); however, the isotopic ratios and enantiomeric compositions of amines were not determined (Pizzarello et al., 2008, 2012; Pizzarello and Holmes, 2009). Aponte et al. (2014a) reported the first simultaneous CSI analysis and enantiomeric quantification of 25 amines from hydrolyzed and unhydrolyzed aqueous extracts of the Murchison meteorite using (*S*)-(-)-*N*-(trifluoroacetyl)pyrrolidine-2-carbonyl chloride (*S*-TPC) as derivatization agent and a hybrid GC-MS isotope ratio mass spectrometer (GC-MS/IRMS). Using that same methodology, similar analyses were completed in Orgueil (CI1), and five CM and CR Antarctic carbonaceous chondrites (Aponte et al. 2015, 2016). Pizzarello and Yarnes (2016) also reported carbon compound specific isotope data from aqueous extracts of the CR2 chondrites GRA 95229 and LAP 02342, and enantiomeric quantification of chiral amines in six CR Antarctic carbonaceous chondrites after derivatization with *N*-trifluoroacetic anhydride (TFAA), and analysis using GC-MS and GC-IRMS. To date, only ^{13}C -CSI of amines have been reported showing isotopic enrichments that range from -20 to $+59\%$ in Orgueil (CI1), $+2$ to $+129\%$ in CM1/2 and CM2 chondrites, and -15 to $+65\%$ in CR2 chondrites (Aponte et al., 2014a; Aponte et al., 2015; Aponte et al., 2016; Pizzarello and Yarnes, 2016).

From all these collective data, some variability in the amine concentration is apparent across samples from the same petrologic type; however, a clear overall lower amine concentration in CI1, CM1/2, and CM2, relative to that of CR2 chondrites is observed. All C₁-C₅ amines found in CM2 and CR2 show a complete suite of structural isomers, and follow a trend of decreasing in concentration with increasing molecular weight (Pizzarello et al., 1994; Pizzarello et al., 2008, 2012; Pizzarello and Holmes, 2009; Aponte et al., 2014a, 2016). In the aqueous extracts of CI1, CM2 and CM1/2 chondrites methylamine was the most abundant amine, however, in CR2

chondrites isopropylamine was the most abundant amine. With a few exceptions, in CM2 and CR2 chondrites, a tendency of amines having the amino group ($-NH_2$) on a secondary carbon being more abundant than those having the $-NH_2$ in a primary or tertiary carbon is observed among amines. Isopropylamine is more abundant than *n*-propylamine, C_4 primary amines having the $-NH_2$ on a secondary carbon are found in higher abundances than their isomeric compounds having the $-NH_2$ on the primary carbon or the tertiary carbon; similarly, C_5 primary amines with the $-NH_2$ over their secondary carbon were more abundant than their primary and tertiary carbon isomers. The concentration of amines is lower than that of amino acids in CI1, CM2, and CM1/2 chondrites, however, the opposite is true in CR2 chondrites (Aponte et al., 2014a; Aponte et al., 2015; Aponte et al., 2016).

The observations of the enantiomeric composition of chiral amines are divergent. Two different derivatization methods suitable for GC-MS analysis have been used to analyze chiral amines including (*S*)-*sec*-butylamine, (*S*)-*sec*-pentylamine, and (*S*)-3-methyl-2-butylamine. Pizzarello and Yarnes (2016) reported enantiomeric excesses of (*S*)-*sec*-butylamine and (*S*)-*sec*-pentylamine ranging from 0 to 66% in the CR chondrites LAP 02342, GRA 95229, MIL 07525, PCA 91082, and EET 92042. These large enantiomeric enrichments reported were attributed to the break in symmetry and synthesis of amines from achiral ketone precursors through their absorption on mineral phases inside an ammonia-rich environment. However, the authors provided inconclusive evidence that the methodology used for meteoritic amine extraction and derivatization did not result in sample contamination, deracemization, and the enantiomeric report lacked the necessary compound specific stable isotopic composition evaluation of both, (*R*)- and (*S*)-enantiomers leading to insufficient evidence for claiming a non-terrestrial origin of the enantiomeric enrichment of amines. Contrary, Aponte et al. (2014a, 2015, 2016) reported racemic compositions of these chiral amines supported with compound specific isotope data of (*R*)- and (*S*)-*sec*-butylamine in different fragments of the CR2 chondrites LAP 02342, GRA 95229; and in CM2 chondrites Murchison, LON 94101, and LEW 90500, CM1/2 chondrite ALH 83100, and CI1 chondrite Orgueil. The racemic nature of amines is supported by anisotropy studies suggesting that ultra-violet circularly polarized light (UVCPL) may induce enantiomeric excess aliphatic amino acids, but not in amines and monocarboxylic acids (Meinert et al., 2012; Meinert et al., 2016a; Myrgorodska et al., 2017).

Alkyl Amides. Twenty seven different alkyl amide compounds have been identified in water extracts of the Murchison meteorite (Cooper and Cronin, 1995). These include monocarboxylic and dicarboxylic acid amides, cyclic imides, carboxy lactams, lactams, amino acid hydantoins, N-acetyl amines acids and hydroxy acid amines. There are likely many more alkyl amides present in Murchison with isomers and homologs up to eight carbons. It is possible that some amides formed by partial hydrolysis of interstellar nitriles such as acetonitrile and propionitrile or from a reaction involving the addition of another known interstellar molecule (cyanate) to amino acids or their derivatives (Cooper and Cronin, 1995). Although the abundance of the alkyl amides in Murchison have not been reported, the carboxy lactams, lactams, hydantoins, and N-acetyl amino acids are all converted to amino acids by hydrolysis as acid-labile amino acid precursors and may account for the roughly two fold increase in total amino acids after acid hydrolysis of hot-water extracts (Glavin et al., 2010).

4.3.2.3. Aliphatic and Aromatic Hydrocarbons

Aliphatic Hydrocarbons. The history of detections of aliphatic hydrocarbons in carbonaceous chondrites has been reviewed extensively (Pizzarello et al., 2006b; e.g., Sephton, 2002). The first reports of meteoritic hydrocarbons came in 1868 from studies of the Orgueil meteorite (Berthelot, 1868). Renewed interest in the analysis of carbonaceous chondrites in the 1960s and 1970s led to further investigations of these compounds. These studies led to many reports of aliphatic hydrocarbons in meteorites, as well as to debate over the origin (terrestrial or extraterrestrial) of these compounds. Aliphatic hydrocarbons were reported from the Orgueil meteorite and were controversially claimed to be potential evidence of biological activity (Meinschein, 1963a; Nagy et al., 1961); similar claims were made for alkanes detected in other carbonaceous chondrites, including Alais, Ivuna, and Murray (Meinschein, 1963a; Meinschein, 1963b; Meinschein et al., 1963). Kvenvolden et al. (1970b) reported a complex mixture of alkanes, including cycloalkanes, in the Murchison meteorite. Studier and co-workers (1972) detected a suite of aliphatic and aromatic hydrocarbons in Murchison, dominated by *n*-alkanes, mono- and dimethylalkanes, alkenes, alkylbenzenes, and alkylnaphthalenes above C₈, and aromatics and branched alkanes below C₈; although some terrestrial contaminants were detected (see below), many of these compounds were believed to be indigenous. More recently, the Tagish Lake meteorite, considered by some to be pristine due to its rapid collection after fall, was shown to contain saturated and cyclic and/or unsaturated aliphatic hydrocarbons, while the recently analyzed Paris meteorite contains a series of *n*-alkanes (C₁₆ to C₂₅) (Pizzarello, 2001); a lack of other common terrestrial hydrocarbon signatures such as pristane and phytane was used to argue for the indigenous nature of the Paris alkanes (Martins et al., 2015).

Isotopic analyses of combined aliphatic fractions from Murchison meteorite revealed average values of $\delta D = +211\%$ and $\delta^{13}C = +9\%$, suggesting an extraterrestrial origin (Krishnamurthy et al., 1992b). A series of low molecular weight (C₁ to C₆) hydrocarbons identified in Murchison showed ¹³C enrichments, with $\delta^{13}C$ values between +2.4 to +9.2 ‰ for *n*-alkanes, also suggesting an indigenous component (Yuen et al., 1984). The observed trend of decreasing ¹³C enrichment with increasing molecular weight was used to suggest a kinetically controlled synthesis of higher homologs from lower ones through a chain elongation mechanism (Yuen et al., 1984). The Tagish Lake meteorite, considered by some to be pristine due to its rapid collection after fall, contains saturated and cyclic and/or unsaturated aliphatic hydrocarbons, including a dominant series of *n*-alkanes that are ¹³C-depleted ($\delta^{13}C = -18$ to -29%) compared to extraterrestrial compounds in other meteorites, but similar to the isotopic values of other Tagish Lake materials that are considered indigenous (Pizzarello, 2001).

Although these isotopic analyses supported the idea that some meteoritic aliphatic hydrocarbons are extraterrestrial in nature, analyses of Murchison and other meteorites showed that the *n*-alkane abundances were concentrated at the surface of the meteorites, decreasing towards the interior (Cronin and Pizzarello, 1990). In addition, the presence of isoprenoidal hydrocarbons (Cronin and Pizzarello, 1990; Studier et al., 1972) and similarities in alkane content between multiple meteorites origin (Nooner and Oro, 1967), suggested that the detected compounds were the results of terrestrial contamination rather than extraterrestrial. In recent years, examinations of meteorites have continued to show evidence of terrestrial hydrocarbon contamination combined with evidence of indigenous compounds. Studies of Tagish Lake suggested that the *n*-alkanes present in that meteorite are likely terrestrial based on variabilities in different samples and association with other compounds suspected to be terrestrial contamination (Hilts et al., 2014). Similarly,

examinations of the C2 ungrouped Bells and CI1 Ivuna carbonaceous chondrites (Monroe and Pizzarello, 2011) and the Chelyabinsk LL5 chondrite (Richter et al., 2015) also suggest terrestrial contamination, identified both by the presence of compounds such as isoprenoids and by the structural composition and heterogeneous distribution of the aliphatic hydrocarbons.

It was argued that the structural selectivity and distribution of aliphatic hydrocarbons observed in Murchison supported the idea of hydrocarbon formation by Fischer-Tropsch-Type (FTT) reactions (Studier et al., 1968, 1972). Further studies, however, suggested that most of the *n*-alkanes previously identified in Murchison were terrestrial contamination and that the indigenous compounds, primarily a suite of structurally diverse C₁₅ to C₃₀ branched alkyl-substituted mono-, di-, and tricyclic alkanes, did not support FTT reactions as a primary synthetic mechanism (Cronin and Pizzarello, 1990). In addition, the isotopic ratio of carbon monoxide in Murchison was found to be depleted in ¹³C ($\delta^{13}\text{C} = -29.1\%$); the comparison of this value with those of the *n*-alkanes was not consistent with an FTT synthetic origin (Yuen et al., 1984).

After over fifty years of analyses of aliphatic hydrocarbons in meteorites, it is clear that meteorites are susceptible to terrestrial aliphatic hydrocarbon contamination and that analyses of these compounds must include careful attention to context in order to understand the source of the detected molecules. However, some of these compounds may be indigenous to the meteorites. The formation mechanism responsible for these compounds has not been identified.

Aromatic Hydrocarbons. As with aliphatic hydrocarbons, meteoritic analyses of aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) have been previously reviewed (Pizzarello et al., 2006b; Sephton, 2002). Aromatics have been detected via a variety of techniques, including solvent extraction and gas-chromatography mass spectrometry (Basile et al., 1984; Huang et al., 2015; Krishnamurthy et al., 1992b; Martins et al., 2015; Naraoka et al., 2000; Olson et al., 1967; Oró et al., 1971; Pering and Ponnampereuma, 1971; Studier et al., 1972) as well as two-step laser-desorption, laser-ionization mass spectrometry (Botta et al., 2008; Hahn et al., 1988; Plows et al., 2003; Zenobi et al., 1989). Various solvent extraction methods have been utilized, with correlations observed between the molecular weight of aromatic compounds detected and the extraction method, as volatile aromatics may be prone to loss (Sephton, 2002 and references therein). Although many studies have identified extracted PAHs, far fewer studies have focused on quantitative analysis of individually identified PAHs from meteorites.

The Murchison meteorite has been the most extensively studied chondrite for aromatic content, but PAH studies have been performed on CI, CM, CR, CV, CO, and CK chondrites, as well as ungrouped C2 chondrites and LL and H ordinary chondrites (Basile et al., 1984; Botta et al., 2008; Hahn et al., 1988; Huang et al., 2015; Krishnamurthy et al., 1992b; Martins et al., 2015; Naraoka et al., 2000; Olson et al., 1967; Oró et al., 1971; Pering and Ponnampereuma, 1971; Plows et al., 2003; Studier et al., 1972; Zenobi et al., 1989). The suite of compounds identified in these chondrites includes benzene, toluene, alkyl benzenes, and PAHs such as naphthalene, phenanthrene, pyrene, and alkylated derivatives, up to 5- and 6-ring compounds (Basile et al., 1984; Sephton et al., 1998; Studier et al., 1972). The four most abundant aromatics in many carbonaceous chondrites are pyrene, fluoranthene, phenanthrene and acenaphthene, which can account for greater than 50% of a total aromatic extract (Basile et al., 1984; Naraoka et al., 2000; Shimoyama et al., 1989b).

The suite of aromatic hydrocarbons in meteorites has been subject to terrestrial contamination, much the same as the aliphatic hydrocarbons (Monroe and Pizzarello, 2011). Even meteorites collected quickly after fall and considered “pristine,” such as Tagish Lake, show signs of some

hydrocarbon contamination (Hilts et al., 2014), although they also contain PAHs considered to be indigenous (Pizzarello, 2001). Analyses of Antarctic meteorites compared to Antarctic ice showed that the meteoritic PAHs were distinct from those found in snowmobile exhaust, suggesting that the PAHs are indigenous to the meteorites (Botta et al., 2008). In addition, isotopic measurements of PAHs in carbonaceous chondrites point to an extraterrestrial origin for most of these compounds.

Carbon isotopes have been measured for aromatic bulk fractions and individual aromatic compounds in the CM2 chondrites Murchison, A-881458, and LON 94101 (Huang et al., 2015; Krishnamurthy et al., 1992b; Naraoka et al., 2000). Values from Murchison for bulk fractions were -5.5‰ (Krishnamurthy et al., 1992b), while individual compounds range from -5 to -23 ‰ (Huang et al., 2015). Carbon isotope analysis of PAHs extracted from Murchison and A-881458 revealed distinct patterns of $\delta^{13}\text{C}$ expression that relate to ring number as well as ring condensation (Fig. 10), with a 10‰ difference in $\delta^{13}\text{C}$ between the fully aromatic species (pyrene family) and partially aromatic species (fluoranthene family) (Naraoka et al., 2002). The relationship between H/C ratio and $\delta^{13}\text{C}$ suggests distinct cyclization pathways by which larger rings are formed from smaller, less ^{13}C -enriched rings (Gilmour and Pillinger, 1994), perhaps with a kinetic barrier prior to the synthesis of phenanthrene that created the two separate cyclization series (Naraoka et al., 2000). Larger PAHs tend to have less ^{13}C enrichment than smaller PAHs, suggesting the possibility of formation under kinetically controlled conditions (Huang et al., 2015). However, this trend was reversed for lower molecular weight compounds obtained using supercritical fluid extraction, an observation used to suggest the formation of small aromatics by cracking of larger molecules (Sephton et al., 1998). The overall low $\delta^{13}\text{C}$ values for the most volatile aromatics may be an indicator of some terrestrial contamination (Naraoka et al., 2000).

Bulk deuterium measurements of aromatic hydrocarbons show an enrichment consistent with extraterrestrial origin (Krishnamurthy et al., 1992b). There have been only two studies reporting the D/H composition of individual meteoritic PAHs (Huang et al., 2015; Naraoka et al., 2002), with vastly different results; one measured deuterium enriched PAHs with δD values in the +120 to +900 ‰ range (Huang et al., 2015), while the other reported values in the -400 to -600‰ range (Naraoka et al., 2002). In the more recent study, a general trend of decreasing δD value with increasing molecular weight was observed (Huang et al., 2015).

4.3.2.4. Alcohols, Aldehydes and Ketones

Alcohols were identified in only a few studies of CM2 carbonaceous chondrites. Mass spectrometric evidence of alcohols in the Murray meteorite was first reported in 1965 (Studier et al., 1965), but no individual compounds were identified. A later study detected C_1 to C_4 alcohols, including both straight-chain and branched isomers) in the Murchison and Murray meteorites (Jungclaus et al., 1976b). These compounds were present at low abundances, with individual compound concentrations in the 1-5 ppm range in Murchison, and lower in Murray. No further investigations of alcohols in carbonaceous chondrites have been published; studies of these compounds may be hampered by their high volatility.

Carbonyl compounds, particularly formaldehyde, have been of interest in understanding prebiotic chemistry. It has been suggested that formose reactions may have played an important role in organic synthesis of meteoritic sugars, sugar alcohols, and insoluble organic matter (Cody et al., 2011; Cooper et al., 2001b; Meinert et al., 2016c). There have been relatively few investigations of carbonyl compounds such as aldehydes and ketones in carbonaceous chondrites

belonging to the CM2, CR2, C2 ungrouped, and CI1 groups. One study observed that aliphatic aldehydes and ketones are not readily extracted in hot (80-100°C water); this is notable both because of its potential effect on meteoritic analyses and because it suggests that these compounds may be shielded from solution in meteorites, perhaps by chemisorption on clays or reversible bonds with other organics (Pizzarello and Holmes, 2009).

Aliphatic aldehydes and ketones have been reported in five carbonaceous chondrites: Murchison (CM2), Bells (C2 ungrouped), GRA 95229 (CR2), LAP 02342 (CR2), Tagish Lake (C2 ungrouped), and Ivuna (CI1) (Jungclaus et al., 1976b; Monroe and Pizzarello, 2011; Pizzarello and Holmes, 2009; Simkus et al., submitted; (Simkus et al., 2016). These studies were carried out with colorimetric analysis, gas chromatography, and gas chromatography-mass spectrometry. These studies showed similar compound diversities, with C₁ to C₆ aldehydes and C₃ to C₆ ketones detected in all the meteorites; ketones with up to 10 carbons were reported in Ivuna (Monroe and Pizzarello, 2011). Aromatic ketones, alkyl aryl ketones, and benzaldehyde are also present in carbonaceous chondrites, with a variety of individual aromatic ketones identified in Murchison (Basile et al., 1984; Krishnamurthy et al., 1992b).

Reported total abundances of carbonyl compounds range from ~200 nmol/g in the CM2 Murchison to >3000 nmol/g in the CR2 GRA 95229. High levels of formaldehyde and acetone detected in the CI1 Ivuna may have had a terrestrial component (Monroe and Pizzarello, 2011), but deuterium isotopic measurements showed enrichment of six carbonyl compounds in Bells ($\delta D = +37$ to $+324$ ‰), suggesting that at least a portion of these compounds were indigenous to the meteorite (Monroe and Pizzarello, 2011). Compound-specific carbon isotopic measurements for carbonyl compounds in Murchison showed values of $\delta^{13}C = +1.3$ to $+29.1$ ‰; these values are similar to those observed for other prebiotic organic compounds in Murchison, but significantly less enriched than the highly ¹³C-enriched carbonyl compound of the interstellar medium (Simkus et al., submitted).

4.3.2.5. Aliphatic Carboxylic and Hydroxy Acids

Carboxylic Acids. These compounds are aliphatic chains that comprise fatty acids and lipids that are important components of the bi-layer cell membrane structure in life on Earth. Lipid-like membrane structures that form closed vesicles in aqueous solution have been identified in the Murchison meteorite (Deamer, 1997) and have also been synthesized in laboratory irradiation experiments of interstellar ice analogs (Dworkin et al., 2001). The two simplest carboxylic acids, formic acid and acetic acid, have been identified in the interstellar medium (Irvine, 1998). Aliphatic mono- and di-carboxylic acids up to 12 carbons in length and with total abundances 10 to 100 times the amount of amino acids have also been identified in Murchison, Orgueil, Tagish Lake and Antarctic C2, CM, CR, and CV carbonaceous meteorites (Aponte et al., 2011; Aponte et al., 2014b; Cronin et al., 1993a; Herd et al., 2011; Huang et al., 2005b; Krishnamurthy et al., 1992b; Lawless and Yuen, 1979; Lawless et al., 1974; Martins et al., 2008b; Martins et al., 2006; Peltzer and Bada, 1978a; Pizzarello et al., 2008; Pizzarello et al., 2001; Pizzarello and Huang, 2002; Pizzarello et al., 2012; Pizzarello et al., 2010; Shimoyama et al., 1989a; Yuen et al., 1984; Yuen and Kvenvolden, 1973). Isotopic enrichments in hydrogen ($\delta D = +319$ to $+2024$ ‰) and carbon ($\delta^{13}C = -57$ to $+33$ ‰) in mono- and di-carboxylic acids in Murchison are consistent with an interstellar origin or formation from interstellar precursors on the parent body.

Huang et al. (2005a) identified 50 monocarboxylic acids in the Murchison meteorite and noted that the branched acids were enriched in the heavier isotopes D and ^{13}C compared to the straight-chained acids, suggesting different synthetic pathways or formation environments for the branched and straight-chained structures. The complex mixture and large distribution of randomly substituted branched monocarboxylic acids is consistent with an origin through random gas phase radical reactions that can proceed at low temperatures (10 to 100 K, see Herbst, 1995) and may indicate that monocarboxylic acids may be mostly of interstellar origin (Cronin and Chang, 1993). An alternative explanation is that the straight-chained monocarboxylic acids were derived from hydrolysis and reduction of alkyl nitriles (e.g., methyl and ethyl cyanide) during an aqueous alteration phase on the meteorite parent body. Alkyl nitriles have been detected in the interstellar medium (Irvine, 1998). However, interstellar cyanonitriles are dominated by those containing an odd number of carbon atoms (e.g., HC_3N , HC_5N , HC_7N , etc.) which would result in a predominance of odd over even carbon numbered monocarboxylic acids in meteorites, which is not observed in Murchison (Huang et al., 2005a). Cronin and Chang (1993) suggested that to obtain the complete structural diversity of branched molecules detected in meteorites, the major route of synthesis would have been free radical reactions such as cyano, amino, hydroxyl, and alkyl groups that combine on dust grains in either an interstellar or parent body environment. Racemic composition of 2-methylbutanoic, 2,3-dimethylbutanoic, and 2-methylpentanoic acids have been reported from CM2 carbonaceous chondrites Murchison, LON 94101, and EET 87770 (Aponte et al. 2014b). Like with aliphatic amines, UVCPL may not induce break in symmetry of monocarboxylic acids given their low small anisotropy values (Meinert et al., 2016b).

Hydroxy Acids. A variety of α -hydroxycarboxylic acids (hydroxy acids) were first identified in the Murchison meteorite by Pelzer and Bada (1978c). Subsequent investigations revealed a suite of over 50 different hydroxy acids (Cronin et al., 1993b) with carbon chain lengths up to C_9 and with a distribution of α -, β - and γ -isomers similar to that of the amino acids, supporting the theory that these compounds were formed as a result of Strecker-cyanohydrin synthesis on the Murchison meteorite parent body (Peltzer et al., 1984a). C and H isotopic measurements of hydroxy acid extracts of Murchison show non-terrestrial values ($\delta^{13}\text{C} = -6 \text{ ‰}$ and $\delta\text{D} = +573 \text{ ‰}$) that are consistent with an interstellar source (Cronin et al., 1993b). In contrast to Pelzer and Bada (1978) who found that the α -hydroxy acids in Murchison were racemic, Pizzarello et al. (2010) reported L-excesses ranging from 3-12% for the three-carbon hydroxy acid lactic acid in Murchison and the CR2 carbonaceous chondrites GRA 95229 and LAP 02342. However, between 70-80% of glycolic acid and lactic acid were reported to be lost during meteorite extraction and workup in this study (Pizzarello et al., 2010). Such significant hydroxy acid losses during processing could lead to enantiomeric ratio changes and isotopic fractionation that could complicate interpretation of the measured data.

4.3.2.6. Nitrogen Heterocycles

Purines and pyrimidines, such as the nucleobases adenine, guanine, cytosine, thymine and uracil, are small nitrogen-containing aromatic ring structures (N-heterocycles) and are central to terrestrial biology. In biochemistry, nucleobases serve as the informational monomers of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) without the sugar and phosphate groups and are ubiquitous and ancient as evidenced by their prominent role in co-enzymes and biochemical pathways (Bloch, 1996). Adenine and guanine are found in RNA and DNA in terrestrial life, while thymine is only found in DNA and uracil only in RNA. The availability of

nucleobases as feedstock for prebiotic chemistry leading to the first self-replicating systems of the early earth depends on their endogenous synthesis and their delivery via exogenous sources. To determine if exogenous material was an important source of purines and pyrimidines on the prebiotic Earth, the composition of nucleobases in carbonaceous chondrites has been investigated.

The origin of nucleobases in chondrites has been debated since the early 1960's when the first reports of purine and pyrimidine bases in extracts of carbonaceous meteorites were published (e.g., Briggs, 1961). Several groups later detected the presence of purines and pyrimidines in carbonaceous chondrites (Folsome et al., 1971; Hayatsu, 1964; Hayatsu et al., 1975a; Stoks and Schwartz, 1979, 1981; Van der Velden and Schwartz, 1977b). However, some of the analytical techniques used were later shown to have contaminated the samples or caused artifacts, particularly the false detection of *s*-triazines and 4-hydroxypyrimidine (Stoks and Schwartz, 1981; Van der Velden and Schwartz, 1977b). Subsequent studies of formic acid extracts have identified several purines including adenine, guanine, hypoxanthine, xanthine, and the pyrimidine uracil in the CM2 meteorites Murchison and Murray, and the CI1 Orgueil (Stoks and Schwartz, 1981; Van der Velden and Schwartz, 1977b) with total abundances around 1 part-per-million. Hypoxanthine and xanthine are not present in DNA or RNA, but are important intermediates in the synthesis and degradation of purine nucleotides. Other N-heterocycles detected in Murchison include 2,4,6-trimethylpyridine, quinolines, and isoquinolines (Krishnamurthy et al., 1992a; Stoks and Schwartz, 1982). Shimoyama et al. also detected guanine, and possibly xanthine and hypoxanthine in the Antarctic CM meteorites Yamato (Y-) 74662 and Y-791198 (Shimoyama et al., 1990). No nucleobases were found in the CV3 Allende meteorite (Stoks and Schwartz, 1981).

Because many N-heterocycles are found on Earth and the nucleobases detected in meteorites are common in biology, a terrestrial origin could not be ruled out (Van Der Velden and Schwartz, 1974). Unlike amino acids, nucleobases do not exhibit molecular chirality, which makes it difficult to distinguish between abiotic and biotic origins of these compounds. Nevertheless, Van der Velden and Schwartz noted that the large amounts of xanthine and the apparent lack of the pyrimidines cytosine and thymine in the Murchison meteorite were inconsistent with the distribution of nucleobases found in terrestrial sediments, supporting an extraterrestrial origin for at least some of these compounds (Van der Velden and Schwartz, 1977a). Isotope measurements found that uracil ($\delta^{13}\text{C} = +44.5\%$) and xanthine ($\delta^{13}\text{C} = +37.7\%$) in the Murchison meteorite showed an enrichment of the ^{13}C isotope compared to uracil extracted from soil at the site of the Murchison fall ($\delta^{13}\text{C} = -10.6\%$), suggesting that the uracil and xanthine in Murchison are extraterrestrial in origin (Martins et al., 2008a). However, these analyses did not have baseline separation from background impurities and the presence of co-eluting ^{13}C enriched carboxylic acids in Murchison could have contributed to the $\delta^{13}\text{C}$ values measured for uracil and xanthine, so these values are not unambiguous (Burton et al., 2012c). Additional measurements would ultimately be necessary to firmly establish an extraterrestrial origin for these and other N-heterocycles detected in carbonaceous meteorites.

An extensive campaign to search for and determine the abundance and distribution of purines and pyrimidines in formic acid extracts of eleven different CI, CM and CR carbonaceous chondrites was taken by Callahan et al. (2011a). They employed a new single use solid phase extraction technique after formic acid extraction of the meteorites to improve the N-heterocycle recovery yield and greatly reduce the presence of interfering carboxylic acids and contamination from the multi-step purification processes used in previous studies (Callahan et al., 2011b). Recent advances in mass spectrometry and analytical techniques have made unambiguous identification and quantification of nucleobases in complex mixtures possible. Callahan et al. used a combination of liquid chromatography coupled to a triple quadrupole mass spectrometer to

identify nucleobases on the basis of parent-to-daughter ion transitions specific to each compound along with chromatographic retention times. In addition, very clean ultrahigh resolution mass spectra were obtained using a Fourier Transform Orbitrap mass spectrometer allowing unambiguous assignment of the elemental formula for each compound. Using these two analytical techniques, they found that the Murchison meteorite and two Antarctic CM2 meteorites LON 94102 and LEW 90500 contained a highly diverse suite of nucleobases, including adenine, guanine, hypoxanthine, and xanthine and three unusual and terrestrially rare nucleobase analogs: purine, 6,8-diaminopurine and 2,6-diaminopurine (Callahan et al., 2011b). The consistent purine distributions found in several different CM2 chondrites that were distinct from terrestrial biology provided the most compelling evidence of the presence of extraterrestrial purines in carbonaceous chondrites to date. The CM2 meteorites analyzed in the Callahan et al. study had the most abundant and diverse suite of purines of the carbonaceous chondrites investigated (with concentrations ranging from ~1 to 244 ppb (Table 6). The more aqueously altered type 1 CI, CM, and CR chondrites showed a decrease in overall abundance and diversity of nucleobases. Laboratory experiments in the same study showed that an identical set of nucleobases and nucleobase analogs were produced in aqueous reactions of ammonium cyanide providing a plausible mechanism for their formation in asteroid parent bodies (Callahan et al., 2011b).

Table 6. The concentration of purines (ppb) in carbonaceous chondrites*. Modified from Callahan et al. (2011a).

Meteorite	Type	G	HX	X	A	Pu	2,6-DAPu	6,8-DAPu
Orgueil	CI1	20	5	< 10	7	5	< 2	-
SCO 06043	CM1	2	4	< 10	4	< 1	< 2	-
MET 01070	CM1	29	< 3	< 10	5	< 1	< 2	-
GRO 95577	CR1	< 2	< 3	< 10	< 0.5	< 1	< 2	-
ALH 83100	CM1/2	21	4	4	1	< 0.1	< 0.2	+
Murchison	CM2	56	26	60	5	3	+	+
LEW 90500	CM2	167	23	22	10	1	< 0.2	+
LON 94102	CM2	244	94	77	30	6	5	+
GRA 95229	CR2	4	4	< 10	21	9	< 2	+
EET 92042	CR2	< 2	< 3	< 10	5	4	< 2	+
QUE 99177	CR3	< 2	< 3	< 10	11	7	< 2	+

*Abbreviations: G (guanine), HX (hypoxanthine), A (adenine), Pu (purine), 2,6-DAPu (2,6-diaminopurine), 6,8-DAPu (6,8-diaminopurine). Concentrations were determined from the multiple reaction monitoring triple quadrupole mass spectrometer chromatogram and represent the sum of all solid phase extraction fractions. Purines that were not detected are reported as upper limits or with a negative sign. The + sign indicates a positive detection for the compound without quantitation. 6,8-diaminopurine was not quantified due to the lack of a pure standard.

It is generally accepted that extraterrestrial nucleobases could have been formed by abiotic reaction mechanisms in a variety of cosmic environments. However, a low formation rate combined with a low stability against UV radiation makes the detection of nucleobases in the

interstellar and circumstellar medium extremely difficult (Peeters et al., 2003). In fact, only upper limits of this class of compounds were detected in the interstellar medium (Kuan et al., 2003). Instead, synthetic processes on the meteorite parent body during aqueous alteration are more likely to be responsible for the presence of meteoritic nucleobases. A number of abiotic synthetic routes have been investigated in laboratory simulations. These include: (1) the polymerization of hydrogen cyanide (Ferris et al., 1978; Levy et al., 1999; Minard et al., 1998; Miyakawa et al., 2002; Oro, 1960, 1961; Oro and Kimball, 1961; Sanchez et al., 1967; Voet and Schwartz, 1983); (2) synthesis by quenching a CO–N₂–H₂O high-temperature plasma (Miyakawa et al., 2000), (3) the reaction of cyanoacetylene with cyanate in relative dilute solution at pH 8 and room temperature (Ferris et al., 1968), and (4) the reaction of cyanoacetaldehyde with urea in eutectic solution (Nelson et al., 2001) or at higher temperature (Robertson and Miller, 1995). Other pathways are also possible (Ferris and Hagan, 1984; Orgel, 2004), and a number of them might have occurred on the Murchison meteorite parent body. Degradation of nucleobases in a hydrated parent body environment during an aqueous alteration phase must also be considered. For example, cytosine degrades to uracil with a half-life of 17,000 years and guanine decomposes to xanthine with a half-life of 1.3 Ma at 0°C and pH 7 (Levy and Miller, 1998). Consequently, the observed meteoritic nucleobase distributions are the result of both synthetic and subsequent degradation reactions.

Also of interest of the origin of life, the monocarboxylic heterocycles nicotinic acid, picolinic acid, and isonicotinic acid have been identified in the Tagish Lake C2 ungrouped carbonaceous chondrite and in nine different CM2 carbonaceous chondrites Murchison, LEW 85311, LAP 02336, LAP 02333, EET 96016, ALH 85013, DOM 08003, DOM 03183, and WIS 91600 (Alexandre et al., 2004; Huang et al., 2005b; Pizzarello et al., 2001; Pizzarello and Huang, 2002; Smith et al., 2014b) with compound-specific isotope ratio values for nicotinic acid in the extraterrestrial range ($\delta D = +129\%$ and $\delta^{13}C = +20\%$) in the Murchison meteorite (Huang et al., 2004; Pizzarello et al., 2004). A joint laboratory cosmochemical syntheses of these pyridine monocarboxylic acids from the proton irradiation of pyridine/CO₂ 20K ice showed the same ratio of these three species as was observed in the CM2 meteorites (Smith et al., 2014a) and that though the relative proportions of these three species was similar, their abundance was inversely proportional with aqueous alteration history. Other functionalized nitrogen heterocycles have also been observed. Recently a suite of alkylated pyridines has been detected by ultrahigh resolution mass spectrometry in the Murchison meteorite (Yamashita and Naraoka, 2014). A few other nitrogen heterocycles, such as condensed phthalic and homophthalic acids, quinolones, and other methylated monocarboxylic pyridines have been detected in Murchison (Pizzarello et al., 2006b).

4.3.2.7. Alkyl Sulfonic and Phosphonic Acids

Phosphates play an important role in terrestrial biochemistry, along with sugars since they form the backbone component of DNA and RNA in biochemistry. Alkyl sulfonates and alkyl phosphonates have been identified in Murchison with total abundances of 2 to 68 parts-per-million (Table 3), respectively (Cooper et al., 1992). The latter class represents the first organophosphorous compounds detected in meteorites. For these sulfonic compounds, a trend of decreasing concentration and $\delta^{13}C$ (Cooper et al., 1997) with increasing carbon number is observed, and a predominance of branched over straight-chain isomers, suggesting a synthetic pathway that includes the addition of single-carbon units to the lengthening compounds. The sulfonic organic acids show $\Delta^{33}S$ values between $-0.40 \pm 0.05 \%$ and $+2.00 \pm 0.05 \%$ (Cooper et al., 1997).

Little work has been done on soluble organo-phosphorous and alkyl sulfonic acids in carbonaceous chondrites. However, this study has spurred research into the sources and implications of these species. There have been a few studies of the reactions of the meteoritic mineral schreibersite, (Fe,Ni)₃P, in aqueous organic fluids to form a variety of organo-phosphorous compounds (Pasek, 2008). Likewise, the presence of these compounds has inspired research into their astrobiological implications (Albertsen et al., 2014; Bryant et al., 2010).

4.3.2.8. Polyols and Sugar Acid Enantiomeric Excesses

Polyhydroxylated compounds (polyols) such as sugars, sugar alcohols, and sugar acids are also vital to life as components of nucleic acids and cell membranes, and as sources of energy. Analysis of carbonaceous chondrite extracts showed a variety of two to six carbon sugar acids and sugar alcohols (Cooper et al., 2001a). The abundances of the sugar acids in the CM2 Murchison and the CR2 GRA 95529 range from 4 to ~8,500 ppb and are shown in Table 7. Some of the C₄ to C₆ sugar acids in the CM2 chondrites Murchison, ALH 83102, LAP 02333 and the CR2 chondrites GRA 95229 and GRA 06100 exhibit significant D-enantiomeric excesses, up to enantiopure in some five- and six-carbon acids (Cooper and Rios, 2016). However, none of the sugars with D-enantiomeric excesses have compelling isotopic data. Furthermore, no D-enrichment was found in the chiral sugar alcohols threitol and arabinitol that were identified in these meteorites. Carbon isotopic measurements show ¹³C enriched values for some sugar acids (Table 7) and the sugar alcohol glycerol ($\delta^{13}\text{C} = 5 \text{ ‰}$) that fall well outside of the terrestrial range indicating an extraterrestrial origin (Cooper and Rios, 2016). The authors indicate that their report of $\delta^{13}\text{C} = +10 \text{ ‰}$ for the sugar acids D-threonic and D+L-erythronic acids in Murchison is unsatisfactory due to the need for higher abundances and improved chromatography. Though unconfirmed by isotopes, a comparison of Murchison meteorite sugar acid distribution is inconsistent with that of a typical soil and of microbial activity, which strengthens the conclusion that these large D-excesses are non-terrestrial in origin (Cooper and Rios, 2016).

There is no obvious correlation between the large D-enantioenrichments of the sugar acids in the tested CM2 and CR2 meteorites, but not the sugar alcohols (Cooper and Rios, 2016), the large L-enantioenrichment of some amino acids (e.g. L-isovaline) in CM2 meteorites but not in CR2 meteorites (Glavin and Dworkin, 2009), and the reported enrichment of L-isoleucine in CR2 and CM2 meteorites (Pizzarello et al., 2012). The mechanism for the formation of the large D-sugar acid enrichment found in the CM2 and CR2 chondrites is currently unknown (Cooper and Rios, 2016). However, it has been shown experimentally that non-racemic mixtures of isovaline and alanine can catalytically transfer their initial asymmetry to the opposite enantiomeric excess of the 4C sugars threose and erythrose during synthesis from glycoaldehyde in water (Pizzarello and Weber, 2004). Therefore, non-racemic meteoritic amino acids themselves could have provided the symmetry breaking and amplification of D- over L-enantiomers by acting as asymmetric catalysts during aqueous synthesis of sugar acids on the meteorite parent body.

Table 7. Enantiomer ratios, abundances, carbon isotope $\delta^{13}\text{C}$ values, and biological occurrence of sugar acids in CM2 and CR2 carbonaceous chondrites*. Modified from (Cooper and Rios, 2016).

Sugar Acids	Meteorite (type)	Percent D _{ee} = (D-L)/(D+L)	Abundance (ppb)	$\delta^{13}\text{C}$ (‰)	Biological Occurrence
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		x 100			
Three carbon acid					
Glyceric	Murchison (CM2)	0	~8,500	+60 (D+L)	D, common
Four carbon acids					
Erythro-2,3-DHB	Murchison (CM2)	0	120	+18	Rare
Threo-2,3-DHB	Murchison (CM2)	0	44	nd	Rare
2,4-DHB	Murchison (CM2)	0	18	nd	Rare
2-Methylglyceric	Murchison (CM2)	0	120	+82	Rare
Threonic	Murchison (CM2) GRA 95529 (CR2)	33, 47, 55 43	480 4	+10 (D) nd	Common
Erythronic	Murchison (CM2)	54	480	+10 (D+L)	D, common
HMG	GRA 95529 (CR2)	—	14	nd	Rare
Five carbon acids					
Lyxonic	Murchison (CM2)	61, 100	83	nd	Rare
Ribonic	Murchison (CM2)	57	98	nd	D, common
Xylonic	Murchison (CM2)	82, 100	148	nd	D, common
Arabinonic	Murchison (CM2)	47, 60	160	nd	L, common
Six carbon acids					
Allonic	Murchison (CM2)	100	trace	nd	Rare
Idonic	GRA 06100 (CR2)	100	trace	nd	Rare
Gulonic	Murchison (CM2)	nd	trace	nd	Rare
Talonic	Murchison (CM2)	100	6	nd	Rare
Galactonic	Murchison (CM2)	100	18	nd	D, common
Gluconic	Murchison (CM2)	100	54	nd	D, common
Mannonic	Murchison (CM2)	nd	146	nd	D, common

*Abbreviations: DHB, dihydroxybutyric acid; HMG, 2-hydroxymethylgluceric acid (achiral compound); nd = not determined.

4.4. Chemical and Spectroscopic Links between Meteorites and Parent Bodies

In general, most meteorites are believed to originate from objects in the asteroid belt, although there is no direct experimental evidence for the actual place of origin of carbonaceous meteorites. Theoretical work has shown that resonance mechanisms are sufficient to solve the dynamical problem of delivering meteorites from the asteroid belt into Earth crossing orbits around the Sun (Wetherill, 1985). A comparison of visible and near-infrared reflectance spectra of C, G, B, and F asteroid types with laboratory measurements of meteorite samples has been used to help link the mineralogical composition of asteroids with carbonaceous chondrites. For example, the reflectance spectrum of the recent Tagish Lake meteorite has a close match to D-type asteroids (Hiroi et al., 2001), while a sample of the Murchison meteorite shows strong similarities in its reflectance spectrum to C- and G-type asteroids, which point to an asteroidal origin for these meteorites (Hiroi et al., 1993).

Primitive meteorites have also been associated with comets. Developments in the identification of comet-asteroid transition objects (Yeomans, 2000), as well as new information on the composition of cometary solids and on the collisional history of Jupiter-family comets provide further evidence for the possibility that comets yield meteorites. It is also possible that after the active phase and loss of primordial ice, extinct comet nuclei could have evolved into near-Earth asteroids (Weissman et al. 2002), fragmenting into smaller meteorites during collisions in the asteroid belt. Based on mineralogical and chemical evidence of CI type carbonaceous meteorites,

including the high deuterium/hydrogen ratio of the CI carbonaceous meteorites Orgueil and Ivuna, it has been suggested that the CI meteorites Orgueil and Ivuna could be fragments of comets or extinct cometary nuclei (Campins and Swindle, 1998; Lodders and Osborne, 1999).

The distribution of amino acids in carbonaceous meteorites has also been used to help constrain the nature of their parent bodies (Ehrenfreund et al., 2001b). While the CM meteorites Murchison and Murray contain a complex distribution of amino acids thought to have formed by Strecker synthesis on an asteroidal parent body rich in aldehydes and ketones, the CI meteorites Orgueil and Ivuna were found to have a much simpler distribution of amino acids consisting of predominantly glycine and β -alanine. The predominance of β -amino acids over α -amino acids in the CIs indicates that the Strecker synthetic pathway was not active on the parent body of these CI meteorites. However, HCN polymerization and Michael addition of NH_3 to cyanoacetylene to form glycine and β -alanine could have occurred if the CI parent body was heated to elevated temperatures. Observations of Hyakutake and Hale-Bopp over the entire electromagnetic spectrum have established an inventory of cometary volatiles, including ammonia, HCN, formaldehyde, and cyanoacetylene (Crovisier and Bockelée-Morvan, 1999). The amino acid distribution found in Orgueil and Ivuna is consistent with the volatiles detected in comets Hyakutake and Hale-Bopp suggesting that the parent body of these CI meteorites could be cometary in origin. However, recent analysis of comet 67P/C-G by Rosetta shows that the nucleus preserves primordial H_2O in a frozen, unreactive state with NIR spectra of the surface indicating that hydrous minerals are rare or absent (Filacchione et al., 2016). Therefore, in stark contrast to asteroids, it remains unclear if aqueous alteration ever took place inside a comet nucleus. Ultimately, a sample return of pristine material from a comet nucleus may be the only way to determine if CI1 or other primitive carbonaceous chondrites have cometary origins.

4.5. Sample Return Missions

Sample return to Earth from carbon-rich targets such as comets and primitive asteroids have and will continue to contribute to our knowledge of the origin and evolution of organic material in our Solar System, and in particular, a deeper understanding of the organic chemistry that preceded life on Earth. These missions can dramatically reduce the terrestrial organic contamination of a sample by controlling and careful documentation of the sample exposure history to contaminants in a way that is impossible with meteorites that are exposed to varying degrees of terrestrial contamination after their fall to Earth. In addition, sample return missions enable scientists to use state-of-the-art ground based analytical instruments to analyze the returned samples without the constraints (mass, power, volume, data rate, limited sample processing, etc.) inherent to *in situ* analyses. Ground-based measurements give scientists an enormous amount of flexibility to make changes to analytical procedures or instrument parameters to fine-tune the measurements over decades which is not possible in spaceflight. Although in rare cases, a meteorite sample can be traced directly to its parent body (e.g. lunar and martian meteorites, HED meteorites from Asteroid 4 Vesta, and the Almahata Sitta meteorites from asteroid 2008 TC₃), this is not the case for vast majority of carbonaceous chondrites whose parent bodies are unknown. Sample return missions from comets such as Stardust and from asteroids, such as JAXA's Hayabusa2 and NASA's OSIRIS-REx missions and that will return material from the surface of the carbon-rich asteroids Ryugu and Bennu to Earth in 2020 and 2023, respectively will provide unique opportunities to analyze extraterrestrial material collected in context. Furthermore, these missions will enable a

direct comparison of the detailed chemistry and mineralogy of the samples to *in situ* measurements of the surface of the asteroids including spectroscopic measurements, and to the hundreds of different carbonaceous chondrites available to study on Earth. Laboratory analyses of both meteorites and sample return materials will continue for decades and will greatly advance our understanding of the origin and evolution of the Solar System and quite possibly the origin of life itself.

4.5.1. Stardust

On January 2, 2004, the Stardust spacecraft flew past the comet 81P/Wild 2 at a relative speed of 6.1 km s^{-1} (Brownlee et al., 2006), over 9 times faster than a speeding bullet. During the fly by, it deployed a dust collector comprised of two elements: low density silica aerogel for capture of dust particles and volatiles, and aluminum foil along the collector tray ribs for capture of particle residues at the bottom of impact craters. Overall, it is estimated that more than 1200 cometary dust grains larger than $1 \text{ }\mu\text{m}$ were captured in the aerogel and returned to Earth (Burchell et al., 2008). The largest dust impactor was estimated to be $\sim 2 \text{ mm}$ in diameter.

Organic matter seems to be relatively rare in the Stardust grains analyzed so far compared to CP-IDPs and chondrite matrices (Matrajt et al., 2008). The material that is seen generally has only modest, if any, D and ^{15}N enrichments (Matrajt et al., 2008; McKeegan et al., 2006), which is very different from the large enrichments found in organics in the most primitive chondrites and IDPs (Section 4.3.1). However some areas with large ^{15}N enrichments have been found (Matrajt et al., 2008), and one of these resembles the organic globules found in primitive chondrites. The elemental compositions and XANES spectra of the organic matter in the Stardust samples are highly varied (Cody et al., 2008a; Matrajt et al., 2008; Sandford et al., 2006b). Raman data suggests that the cometary particles contain material similar to meteoritic IOM (Sandford et al., 2006b), but all particles have O/C and N/C ratios that are higher than bulk IOM from any chondrite. Estimates of the bulk ratios for IOM in one IDP are also higher than the IOM in primitive meteorites and similar to some of the Stardust particles, but it is not known how typical this is of IDPs.

The amino acid glycine was detected at enhanced levels in both cometary exposed aerogel and foil samples; subsequent compound-specific carbon isotopic measurements of cometary exposed foils determined that the glycine was extraterrestrial in origin (Elsila et al., 2009). It is not clear if the detected glycine was in the free form in the cometary coma or if it was liberated from bound precursors during laboratory analysis. It should also be noted that significant thermal modification of the organic material in the particles likely occurred during aerogel and foil impact, therefore the organic signatures detected in these samples may not be representative of the original “pristine” organic material in Wild 2. The organic amine compounds methylamine and ethylamine were detected at high concentrations (part-per-million levels) in aerogel exposed to comet Wild 2, but were found at only trace levels and with very different relative abundances in an aerogel sample not directly exposed to Wild 2 that was located behind the Stardust Whipple shield (Glavin et al., 2008; Sandford et al., 2006b). Since these amines were also detected in aerogel that did not contain visible particle tracks, it is believed that they were delivered by sub-micron icy grains or cometary gas that impacted the collector. Several polycyclic aromatic hydrocarbons (PAHs) were detected in cometary dust particles, as was complex aromatic organic matter (Sandford et al., 2006; Clemett et al., 2010), although it was noted that some of the low molecular weight PAHs observed could have been synthesized from native carbon in the aerogel material itself during impact. The amino

acid, amines, and PAHs detected in Wild 2 have also been detected in chondrites, as discussed in previous sections.

Whilst only a relatively small amount of Stardust material has been examined in detail, and biases introduced by the capture in aerogel and cratering in the Al foil are still not fully understood, it is clear that the silicates from comet 81P/Wild 2 are not as primitive as was originally expected for comets (Brownlee et al., 2012). The majority of the silicates found in the Stardust collection were formed in high temperature environments (Brownlee et al., 2012). It is generally assumed that these high temperatures require an origin in the inner Solar System, although production in high velocity impacts between outer Solar System objects cannot be completely ruled out at this stage. The considerable range of compositions and microstructures in the silicates points to their formation under a wide range of conditions. A similar range of compositions is seen in CP-IDPs and in chondrites, particularly their matrices, although none of them have identical distributions to the Stardust samples (Ishii et al., 2008; Zolensky et al., 2008). In terms of their organic content and isotopic composition, the Stardust material appears to be less primitive than chondrite matrix and IDPs (Sandford et al., 2006a). However, the varied elemental compositions and XANES spectra of the organics, if not the products of capture and/or contamination, point to the organics being more primitive (Cody et al., 2008a; De Gregorio et al., 2011). How this apparent contradiction with other indicators of primitiveness can be reconciled remains to be seen.

The diversity of mineral compositions shows comet 81P/Wild 2 never experienced significant thermal metamorphism but, unlike almost all unmetamorphosed chondrites, it did not experience much aqueous alteration either. At present, it is still not clear whether 81P/Wild 2 dust has a closer affinity to CP-IDPs or chondrites (Zolensky et al., 2008), although Ishii et al. (2008) have argued for the latter. It is also not clear if comet 81P/Wild 2 formed in the vicinity of the asteroid belt and then migrated to the Kuiper belt, or whether it formed in the outer Solar System from inner Solar System material that had been transported outwards. However, if the latter case is true and more primitive material is presumed to have dominated the outer Solar System, why was not more primitive material mixed in with the high temperature inner Solar System material?

4.5.2. Hayabusa and Hayabusa2

Hayabusa is the first asteroid sample return mission developed by the Japan Aerospace Exploration Agency (JAXA) as an engineering test mission. The target of the mission was the near-Earth asteroid Itokawa. Since its launch on May 2003, the spacecraft has experienced several engineering troubles during its navigation and touchdown on the asteroid. Nevertheless, it overcame those difficulties, and returned the sample canister to Earth on June 2010. After the return, the 1-year preliminary examination of 1534 particles of the asteroid Itokawa collected by Hayabusa has been implemented. Mineralogy (Nakamura et al., 2011; Noguchi et al., 2011) petrology (Tsuchiyama et al., 2011), chemistry (Ebihara et al., 2011), and noble gas (Nagao et al., 2011) and oxygen-isotopic investigations (Nakamura et al., 2012; Yurimoto et al., 2011) of the samples have first established the direct link between an S-type asteroid and ordinary LL5-6 chondritic meteorites. They suggested that Itokawa was a rubble pile asteroid derived from a thermally metamorphosed (600-800°C) parent body (> 20 km) (Nakamura et al., 2011) and its surface materials are continuously peeled into space at a rate of tens of centimeters per million years due to space weathering (Nagao et al., 2011; Noguchi et al., 2011).

In the preliminary carbon/organics examinations of Hayabusa, micro-Raman and IR spectroscopic analyses for the Itokawa particles, ToF-SIMS and two-dimensional HPLC analyses

for solvent extracts of the 5 particles were conducted (Naraoka et al., 2012). However, the amounts of carbon in the particles were so low that they were below the detection limits of those analytical techniques. Aside from the Itokawa particles, which were classified into categories 1 and 2, 58 unknown carbonaceous particles were collected from a sample catcher and classified as category 3 (Yada et al., 2014). In order to determine whether they are terrestrial or extraterrestrial, the coordinated analytical investigations for several category 3 particles by nanoSIMS (Ito et al., 2014), STXM/XANES (Yabuta et al., 2014), TEM (Uesugi et al., 2014), micro-FTIR and Raman (Kitajima et al., 2015), and ToF-SIMS (Naraoka et al., 2015) have been carried out. At present, category 3 carbonaceous particles are lack of any robust evidence of extraterrestrial origin and are very likely terrestrial contamination derived from the degradation products of polymer materials used in the spacecraft and/or biological origin. As a result, indigenous organic compounds from Itokawa have not been identified.

Based on those lessons learned from Hayabusa, Hayabusa2 mission will explore the C-type near-Earth asteroid 162173 Ryugu (1999 JU3), collect and return the surface materials of the asteroid. The main scientific goals of Hayabusa2 are to understand (1) the origin and evolution of the solar system and (2) the formation process and structure of the asteroid. These scientific goals are subdivided into (i) Thermal evolution from planetesimal to near-Earth asteroid, (ii) Destruction and accumulation of a rubble pile, (iii) Coevolution of organics, minerals and water on a planetesimal, and (iv) Chemical heterogeneity in the early solar system (Tachibana et al., 2014).

According to the ground-based observation of the surface of the asteroid Ryugu, there is the only one report that a 0.7 μ m absorption feature in a reflectance spectrum, which is derived from iron-bearing phyllosilicates (e.g., serpentine), was detected (Vilas, 2008). On the other hand, the other ground-based observations did not detect a clear feature 0.7 μ m (Lazzaro et al., 2013; Moskovitz et al., 2013). Thus, hydrous minerals may be distributed locally and/or during a limited time period (Kameda et al., 2015). Their reflectance spectra can be also explained by combination of the heated Murchison meteorite at different temperatures (Hiroi et al., 1993), and thus the surface of the asteroid Ryugu may have experienced heterogeneous heating, e.g., impact, space weathering, and solar radiation heating.

The Hayabusa2 spacecraft was launched on December 3, 2014, and will arrive at the asteroid Ryugu on July 2018. During its 18-month stay, observations will be carried out by the on-board remote-sensing instruments and the hopping lander (see Chapter 9), three landing sites will be decided, and samples will be collected from the different locations. It is planned that one of the three locations to collect samples will be around the artificial crater created by the small carry-on impactor (SCI) (Saiki et al. 2016), a new component of the Hayabusa2, which enables collection of internal materials (i.e., impact ejecta) of Ryugu.

The sample catcher and container of Hayabusa2 basically followed those used in Hayabusa; a 5-g Ta projectile will be shot at 300 m/s upon touchdown, and the ejecta will be transferred into a sample catcher through an extendable sampler horn under microgravity (Tachibana et al., 2014). Several improvements have been added for collecting volatiles and organics, such as aluminum metal-seal system and gas-sampling interface (Okazaki et al. 2016). The collected samples, which is estimated at a level of hundreds milligram, will be returned to the Earth in December 2020. After sample description at Institute of Space and Astronautical Science (ISAS) curation facility, initial analyses by international analysis teams will be conducted for 12 months.

4.5.3. OSIRIS-REx

Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx) is the third mission in NASA's New Frontiers program (Lauretta, 2016). OSIRIS-REx launched September 8, 2016 and will return pristine samples of carbonaceous material from the surface of a primitive asteroid in 2023. The target, (101955) Bennu, is ~500m diameter, roughly spherical Apollo near-Earth asteroid (Nolan et al., 2013). It is expected to be carbonaceous, similar to CI or CM carbonaceous chondrites (Clark et al., 2011). This organic-rich remnant from the early Solar System is also among the most potentially hazardous asteroid known cumulative probability of impact of $\sim 10^{-3}$ in the few decades after 2160 (Chesley et al., 2014). OSIRIS-REx will measure the Yarkovsky effect to better constrain future orbit and impact potential of this and other asteroids (McMahon and Scheeres, 2017). OSIRIS-REx will map Bennu via the OCAMS camera suite (Rizk et al. 2017) and OLA lidar (Daly et al., 2017) and characterize the sampling site to sub-centimeter resolution. OSIRIS-REx will spectrally characterize Bennu from 0.4-50 μ m with the OVIRS (Reuter et al., 2017) and OTES instruments (Christensen et al., 2017). There is also a student experiment to map Bennu's elemental distribution via x-ray fluorescence (Masterson et al., 2017). OSIRIS-REx will collect and return >60 g (and up to 2 kg) of regolith, which will be available for study by the global astrochemistry/astrobiology community.

The collection uses a toroidal jet of N₂ to fluidize and collect the top few cm of regolith as well as stainless steel loops to collect surface grains by contact (Bierhaus et al., 2017). Significant effort is carefully placed on both minimizing (contamination control) and characterizing (contamination knowledge) the organic and inorganic contribution to the sample from the spacecraft and spacecraft processing. This combination of contamination control and knowledge will maximize the science produced by analysis of the OSIRIS-REx sample. Unlike meteorites, the sample will come from a known, well-characterized source and will be collected and transported to Earth to keep it pristine from terrestrial contamination (Dworkin et al., 2017).

Upon return, 75% of the sample will be archived for future analysis and the remaining 25% will be studied by the world-wide science team. The analysis of samples of Bennu will help answer questions about extraterrestrial organics often obscured in meteorites by terrestrial contamination and missing geological context. It will also open new science questions to ask of meteorites.

4.6. Conclusions

Research on complex organics in carbonaceous chondrites has entered a new era with both an increase in number and availability of new groups and classes of meteorites available for study and highly sensitive and selective laboratory instruments capable of characterizing the molecular distribution and isotopic composition of organic compounds at lower abundances. Most of the organic matter in carbonaceous chondrites (>50% of total organic carbon) is in the form of a solvent insoluble macromolecular material (IOM) that is very challenging to characterize. Chemical degradation and pyrolysis studies and a variety of other non-destructive techniques point to the IOM being composed of small PAHs that are highly substituted and cross linked by short, highly branched aliphatics, and esters. However, yields from both chemical degradation and pyrolysis studies are very low, so it is not clear how representative of the bulk material their results are. The bulk elemental and isotopic composition of the IOM in the most primitive CR chondrites is very similar to that observed in IDPs that may be from comets. The IOM from all other chondrite groups have lower H/C ratios that roughly reflect the intensity of the parent body processing that they experienced. Currently, there is no consensus about where and how the large amounts of IOM in carbonaceous chondrites formed.

Although much less abundant than the IOM, the soluble organic matter in meteorites has been more broadly studied, in part due to the ease of extraction and analysis and also the presence of a wide range of organic compounds including amino acids, aliphatic amines and amides, aliphatic and aromatic hydrocarbons, alcohols, aldehydes, ketones, aliphatic carboxylic and hydroxy acids, nitrogen heterocycles and nucleobases, alkyl sulfonic and phosphonic acids, and polyols, that are all of interest to astrobiology. Delivery of these prebiotic organic compounds to the early Earth through meteoritic bombardment may have contributed to the origin of life. Furthermore, the analysis of organics in carbonaceous chondrites provides a unique opportunity to explore prebiotic chemistry that occurred in a natural system prior to life, a chemical record that cannot be probed directly on the early Earth due to recycling and thermal modification of the most ancient rocks by plate tectonics. The abundances and structural distributions of organic compounds vary both within and between carbonaceous chondrite groups, reflecting differences in parent body chemistry and alteration histories. Stable isotopic compositions of a variety of individual organic molecules in meteorites reveal different sources and formation pathways. Several meteoritic amino and sugar acids display large enrichments in the L- and D-enantiomers, respectively, which is an astounding observation because life on Earth uses L-amino acids and D-sugars almost exclusively. Future work combining the analysis of meteorites with laboratory analog experiments, as well as the detailed investigation of samples returned to Earth from small bodies, will aid in substantial increases to our understanding of the formation and alteration of meteoritic organics and their potential contributions to the origin of life on Earth or elsewhere.

4.7. References

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FIGURES

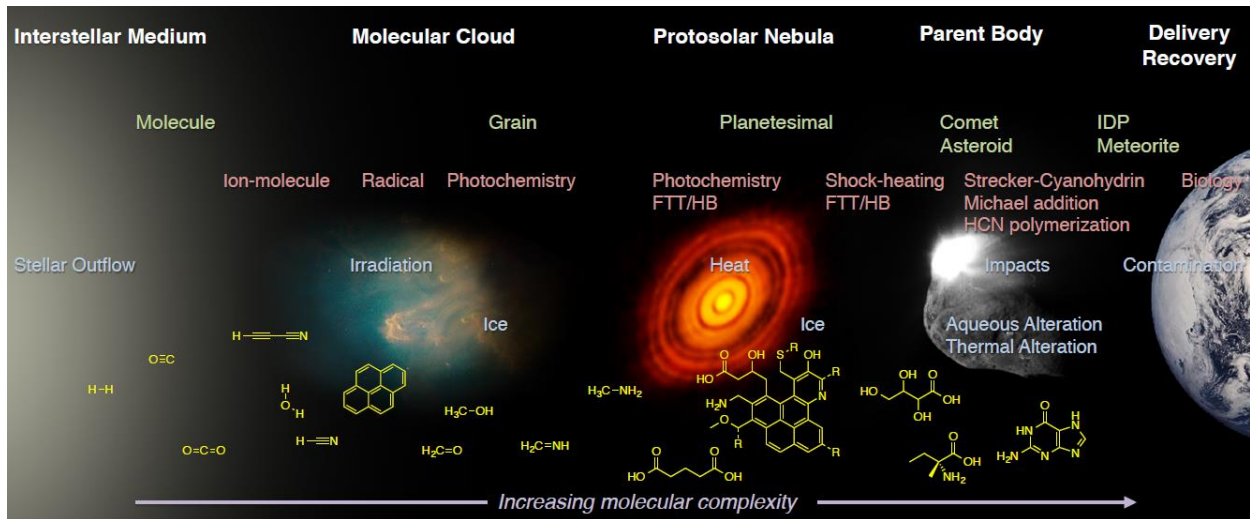


Figure 1. The formation and evolution of simple molecules to more complex organic compounds from the interstellar medium to small bodies and planets in solar systems.

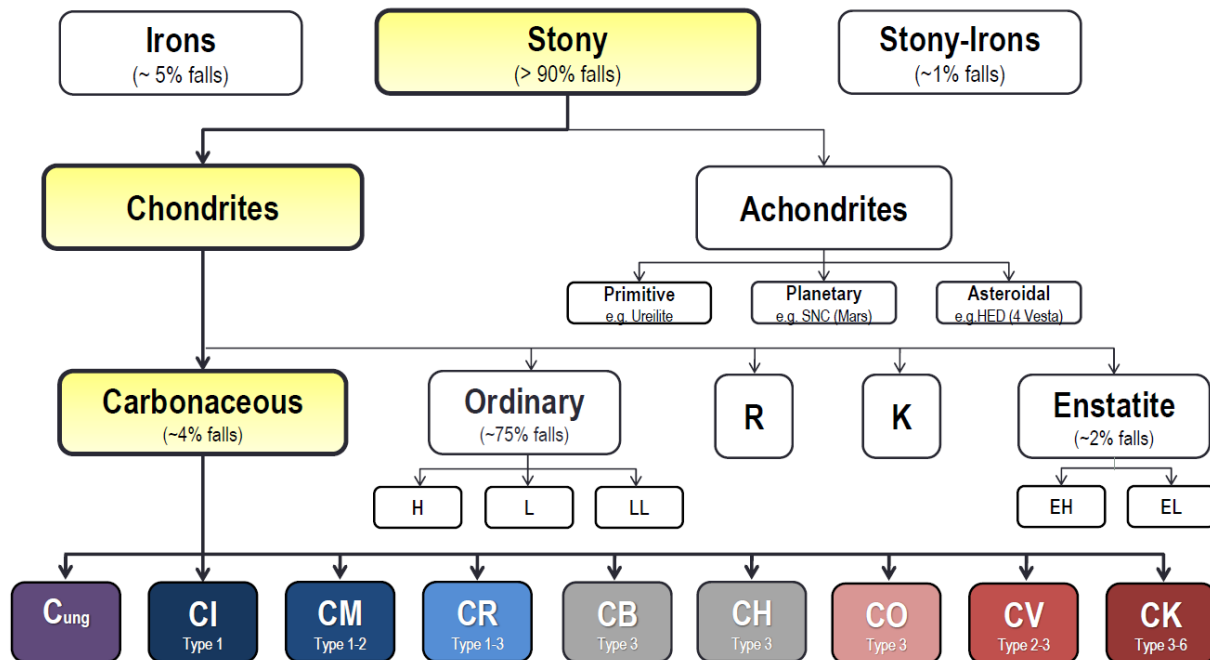


Figure 2. The meteorite classification scheme divides them into groups based on their mineralogy and elemental and isotopic compositions. Petrographic types (1-6) are also assigned based on their parent body alteration history (modified from Elsilá et al. 2016).

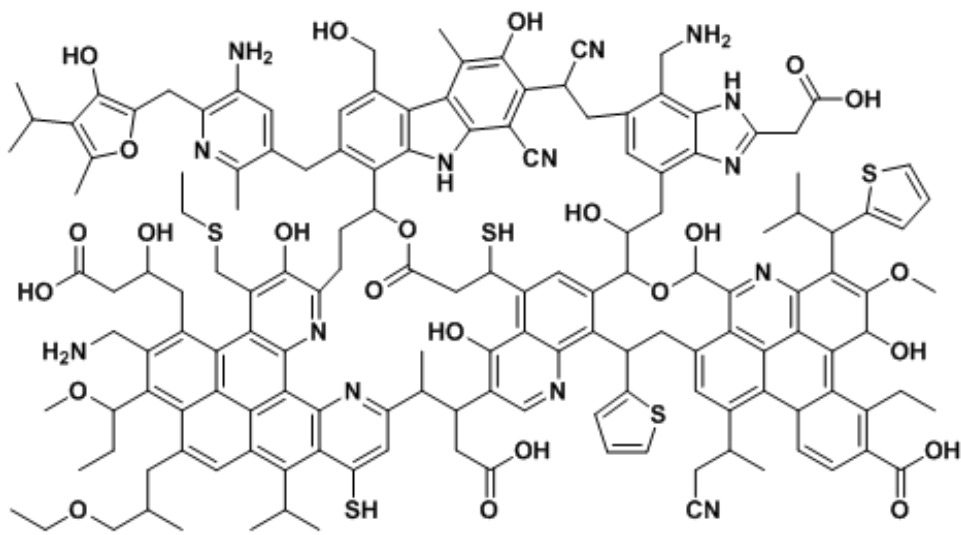


Figure 3. A model of the molecular structure of IOM in the Murchison meteorite based on data from Derenne and Robert (2010) for illustrative purposes only. **Structure to be updated by H. Yabuta before final publication.**

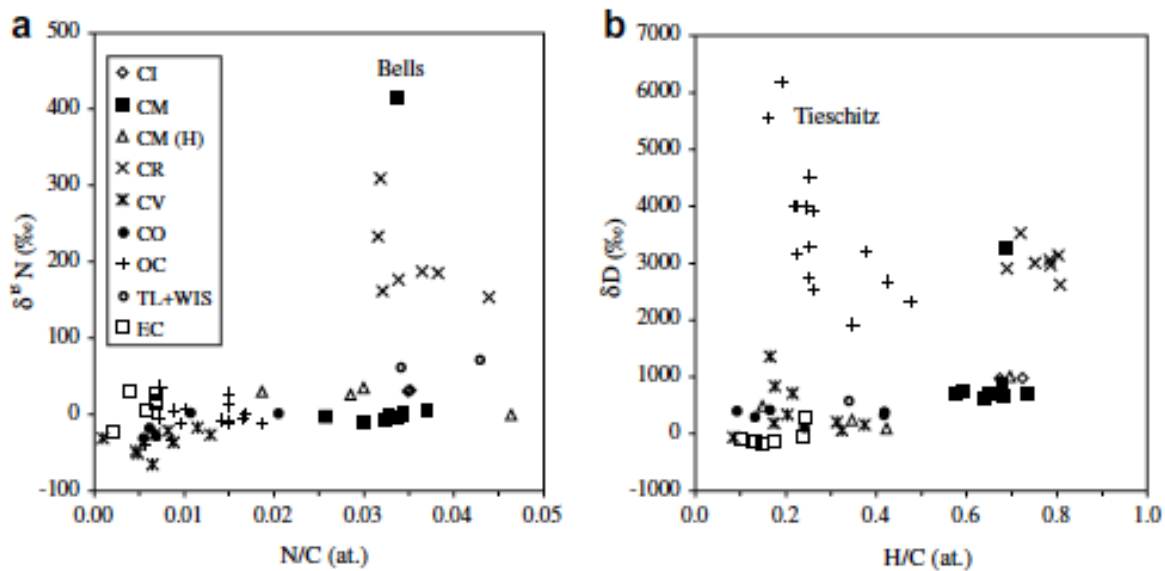


Figure 4. (a) $\delta^{15}\text{N}$ vs N/C (b) δD vs H/C of IOM from carbonaceous chondrites (Alexander et al. 2007)

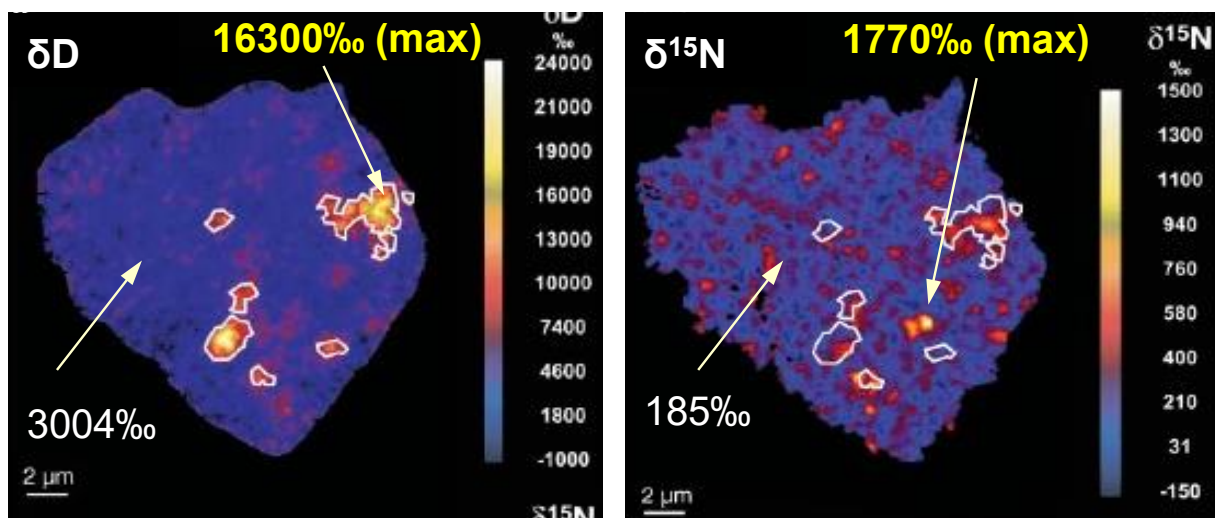


Figure 5. δD and $\delta^{15}N$ maps of IOM from the CR2 EET 92042 chondrite (Busemann et al. 2006).

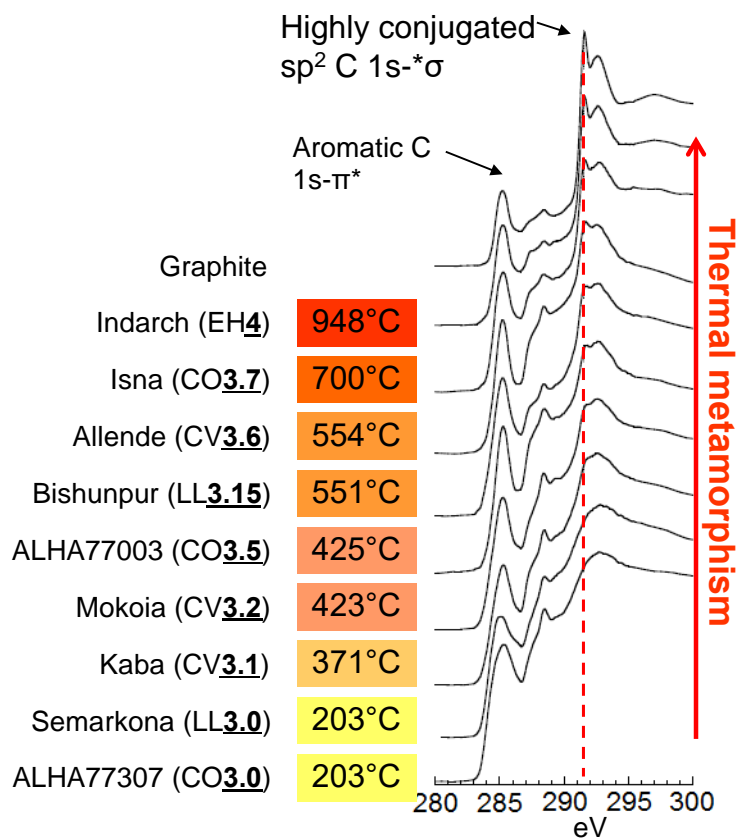


Figure 6. C-XANES spectra of IOM from carbonaceous chondrites in different petrologic types. The peak temperatures evaluated based on the peak intensities of $1s-\sigma^*$ exciton at 291.7 eV are shown (Cody et al. 2008).

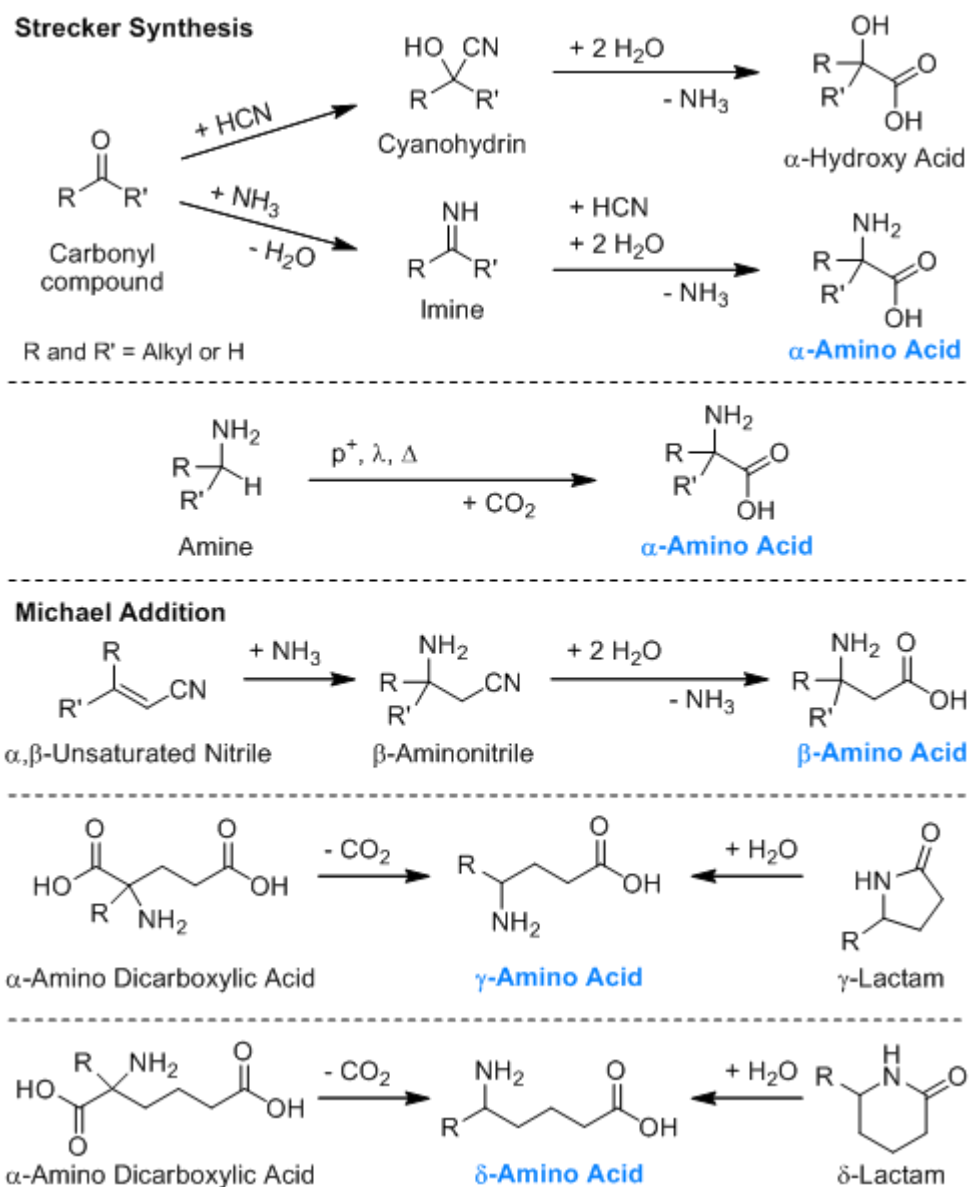


Figure 7. Plausible chemical formation pathways for amino acids found in meteorites. **α -Amino acids:** formed by HCN polymerization or the Strecker-cyanohydrin pathway which yields both α -amino and α -hydroxy acids from carbonyl compounds, hydrogen cyanide, and ammonia precursors inside aqueously altered meteorites. Amines can also be carboxylated to α -amino acids when subjected to radiation in CO_2 -water ice grains. **β -Amino acids:** Formed by Michael addition of ammonia to α, β -unsaturated nitriles forming a β -aminonitrile that can undergo hydrolysis/reduction steps to form β -amino acids. **γ - and δ -Amino acids:** Can form by decarboxylation of α -amino dicarboxylic acids or by the hydrolysis of lactams that are found in meteorites.

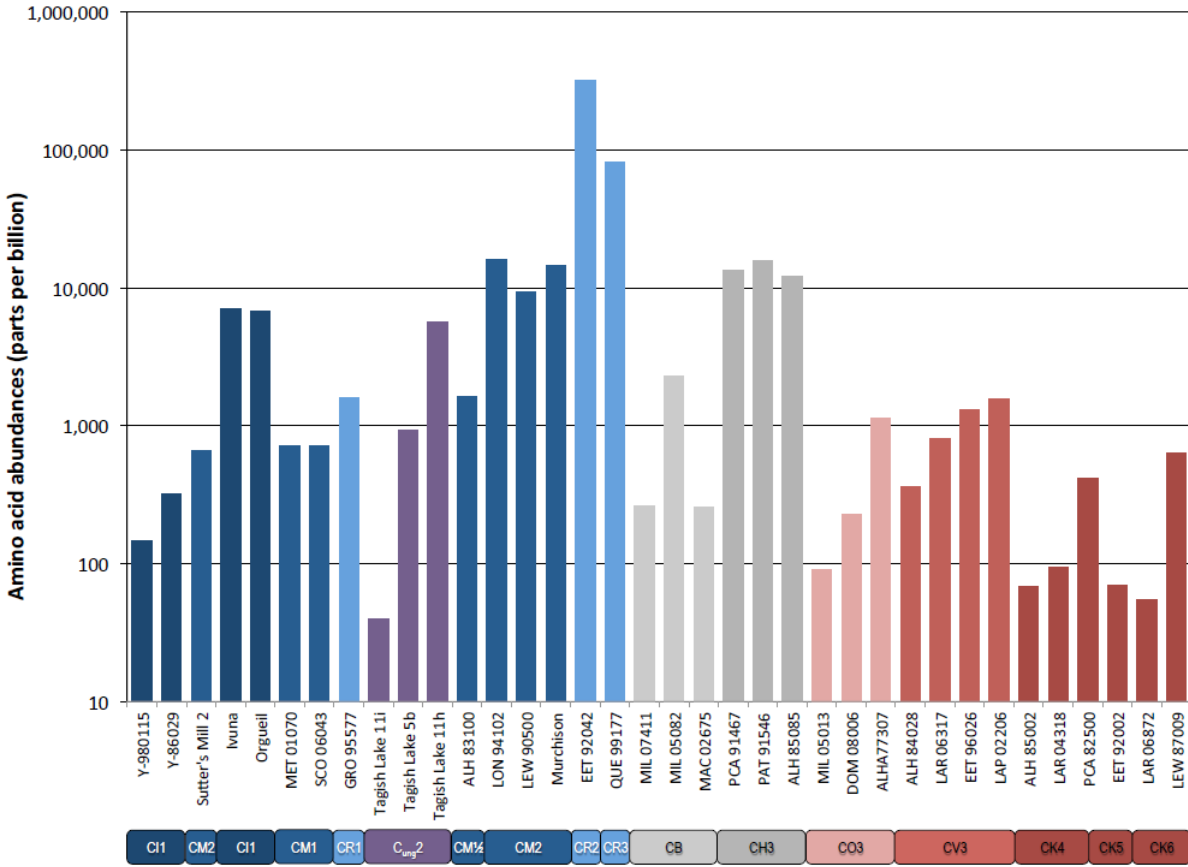


Figure 8. Total amino acid abundances measured in selected CI, CM, CR, CB, CH, CO, CV, and CK carbonaceous chondrites show considerable variation both within and across groups and petrographic type. The highest amino acid concentrations are observed in the least altered type 2 and 3 CR carbonaceous chondrites while the lowest abundances are found in the most aqueously altered type 1 and thermally altered meteorites. Data from: (Burton et al., 2012a; Burton et al., 2013; Burton et al., 2014a; Burton et al., 2014b; Burton et al., 2015; Glavin et al., 2010; Glavin et al., 2006; Glavin et al., 2012).

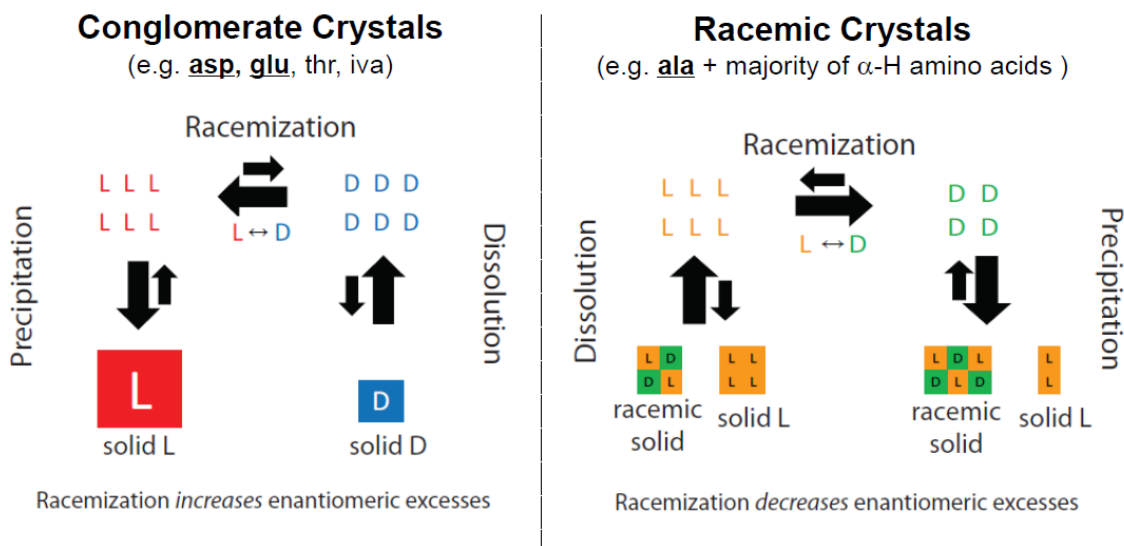


Figure 9. Illustration of the solid-liquid phase behavior of amino acids that form conglomerate (left) and racemic (right) solid crystals. Amplification of a small initial excess (in this case, the L-enantiomer) for conglomerate amino acids like aspartic and glutamic acid) will occur through racemization and precipitation. Abbreviations: asp, aspartic acid; glu, glutamic acid; thr, threonine; ala, alanine; and iva, isovaline. Modified from (Glavin et al., 2012).

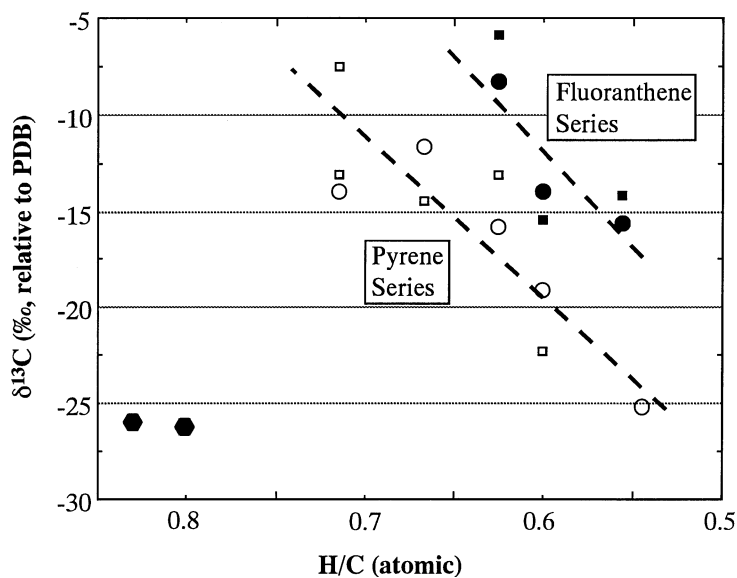


Figure 10. A $\delta^{13}\text{C}$ -H/C diagram for PAHs from carbonaceous chondrites from Naraoka et al. (2000). Open and filled squares represent the data of Asuka-(A)-881458 and Murchison, respectively. Filled hexagons indicate PAHs containing 2-rings (naphthalene and biphenyl). Filled and open circles indicate a 'fluoranthene series' and a 'pyrene series', respectively, suggesting two pathways of the PAH formation. Dashed lines are best fitting of the data including

A-881458 and Murchison for each pathway. There are positive correlations between $\delta^{13}\text{C}$ values and H/C ratios ($r^2 = 0.73$ for pyrene series and $r^2 = 0.59$ for fluoranthene series).