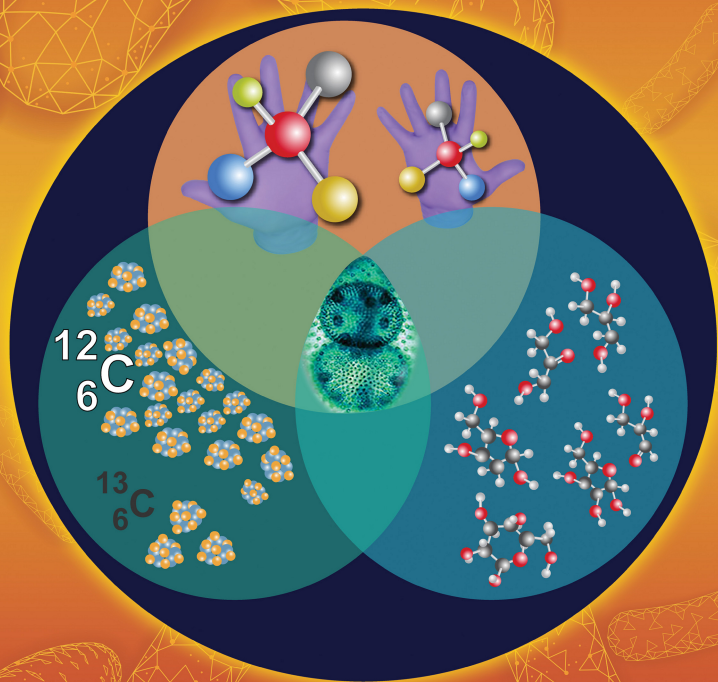


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The Search for Chiral Asymmetry as a Potential Biosignature in our Solar System

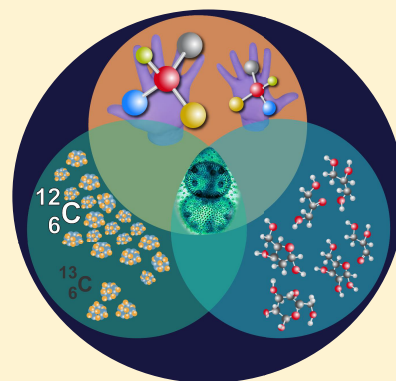
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ABSTRACT: The search for evidence of extraterrestrial life in our Solar System is currently guided by our understanding of terrestrial biology and its associated biosignatures. The observed homochirality in all life on Earth, that is, the predominance of “left-handed” or L-amino acids and “right-handed” or D-sugars, is a unique property of life that is crucial for molecular recognition, enzymatic function, information storage and structure and is thought to be a prerequisite for the origin or early evolution of life. Therefore, the detection of L- or D-enantiomeric excesses (*ee*) of chiral amino acids and sugars could be a powerful indicator for extant or extinct life on another world. However, studies of primitive meteorites have revealed they contain extraterrestrial amino acids and sugar acids (aldonic acids) with large enantiomeric excesses of the same chirality as terrestrial biology resulting from nonbiological processes, complicating the use of chiral asymmetry by itself as a definitive biosignature. Here we review our current knowledge of the distributions and enantiomeric and isotopic compositions of amino acids and polyols found in meteorites compared to terrestrial biology and propose a set of criteria for future life detection missions that can be used to help establish the origin of chiral asymmetry.



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1. INTRODUCTION

The search for convincing evidence of extinct or extant signs of life in our Solar System will require a suite of measurements that focus on identifying characteristic features of life (i.e., potential biosignatures), establishing the environmental context for those measurements, a rigorous understanding of potential terrestrial contamination, and knowledge of the processes that led to the origin of the biosignatures such that all plausible abiotic formation mechanisms can be ruled out. Any life detection investigation should be focused on the key molecular classes and properties at the core of terrestrial biology, including a search for homochirality.^{1–3} Although its origin remains a mystery, biological homochirality (the incorporation of L-amino acids in the production of genetically

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coded proteins and D-ribose and D-deoxyribose in nucleic acids, coenzymes, and metabolic feedstock) is thought to be a prerequisite for, or early product of, life. In terrestrial proteins, enzymatic function is dependent on the folding of the amino acid chain into a highly ordered structure, which is not possible if the amino acids are racemic (equal amounts of both D- and L-enantiomers).

The majority of life on Earth uses L-amino acids and D-sugars (Figure 1, Tables 1 and 2), although there are some rare

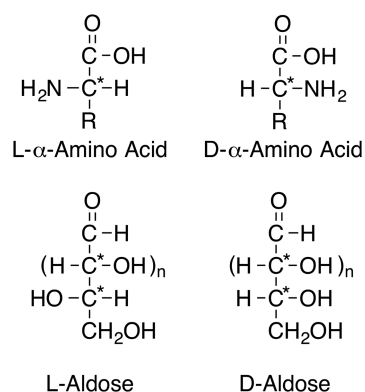


Figure 1. Fischer projections denoting the chirality of a generic α -amino acid and aldose (chiral carbons denoted with asterisks), where L-denotes left and D-denotes right. Based on naming convention for amino acids, the assignment of D or L is based on the chirality of the carbon closest to the carboxylic acid (by analogy to glyceraldehyde), whereas for sugars, D or L is assigned based on the chiral center farthest from the most oxidized carbon (in this figure, the aldehyde group).

exceptions that add molecules of the opposite chirality for specialized purposes.^{4,5} Since the individual L- and D-enantiomers of these chiral molecules have identical physical and chemical properties, there appear to be no biochemical reasons why one enantiomer would be favored over the other.⁶ Although most proteins based on L-amino acids that interact with sugar-containing substrates in biology evolved to recognize D-sugars, experimental studies have shown that some naturally occurring proteins can also catabolize L-sugars,^{7,8} so incorporation of amino acids and sugars of the opposite handedness in proteins and nucleic acids may not be a strict requirement for life.⁹ Thus, it has been inferred that the selection of L-amino acids and D-sugars by life on Earth was a random process and that life elsewhere could be based on either enantiomer.¹⁰ The detection of D-amino acid or L-sugar enantiomeric excesses (*ee*) with the opposite handedness as life on Earth would be a very strong indicator of extraterrestrial biology that evolved from an independent origin, since a terrestrial origin could be ruled out and, as of yet, there are no known abiotic sources of D-amino acid (single asymmetric carbon) or L-sugar excesses within our Solar System (Section 2.3).

In stark contrast to terrestrial biology, laboratory chemistry experiments conducted under a range of plausible prebiotic conditions^{11–15} have shown that chiral species formed by abiotic processes in the absence of a chiral driving force are present in equal (racemic) mixtures of D- and L-enantiomers. (Even when absolute (*R*)- and (*S*)-notations are more chemically appropriate, the amino acid literature uses D- and L-notations based on analogy with glyceraldehyde; thus, for consistency with the nomenclature used in previous meteoritic

and origins of life amino acid studies, here we also use D and L.) Miller spark discharge experiments simulating primordial Earth conditions containing H₂O, CH₄, NH₃, and H₂S have produced 34 different two- to six-carbon protein and nonprotein amino acids^{15–17} (Table 1) with relative abundances similar to those found in carbonaceous meteorites.¹⁷ Amino acid analyses of the Murchison CM2 type meteorite shortly after its fall and recovery in Southeastern Australia in 1969 also found that the chiral α -hydrogen protein amino acids were racemic, suggesting an extraterrestrial, abiotic origin.^{18,19} More recent amino acid analyses of Murchison and a variety of other carbonaceous meteorites have found L-enantiomeric excesses of several nonprotein α -dialkyl amino acids that are rare on Earth,^{20,21} including isovaline with measured L-excesses as high as ~20%.^{22–24} Based on these data, it has been proposed in NASA's Ladder of Life Detection criteria that L- or D-enantiomeric excesses of >20% in multiple amino acids in an extraterrestrial sample would have a high likelihood of being a biosignature provided that systematic errors and other instrument measurement artifacts and terrestrial contamination could be ruled out.²⁵ However, enantiomeric enrichments that exceed 20% have been reported for some extraterrestrial chiral compounds; for example, nonterrestrial L-aspartic acid and L-glutamic acid enantiomeric excesses of up to 60% in the ungrouped C2 Tagish Lake meteorite,²⁶ similarly large L-isoleucine and D-*allo*-isoleucine excesses in two different CR2 carbonaceous chondrites,²⁷ and several nonterrestrial enantiopure (100% *ee*) D-sugar acids (hereafter, D-aldonic acids) were discovered in the Murchison meteorite,²⁸ evidencing that abiotic mechanisms can also produce large enantiomeric enrichments for some chiral compounds. Therefore, the proposed *ee* criteria for using chirality as a chemical biosignature need to be revisited.

The growing body of evidence for large *ee* of amino acids and aldonic acids in carbonaceous meteorites combined with plausible prebiotic mechanisms for the production of chiral asymmetry in interstellar environments²⁹ and subsequent enantioenrichment of both amino acids and sugars under aqueous conditions^{22,30–33} complicates the use of chiral asymmetry alone as a unique feature of life. This review does not provide a detailed overview of the numerous characteristics of “life as we know it” that have been described in detail as part of the “Ladder of Life Detection” framework.²⁵ The primary goal of this paper is to provide a new framework for establishing the origin of enantiomeric excesses in amino acids and sugars that includes several important caveats based on our current understanding of prebiotic chemistry from both meteorites and laboratory experiments. We begin by giving an overview of extraterrestrial amino acids and polyols (aldoses, aldonic acids, alditols, etc.) that have been identified in meteorites and compare their distributions, enantiomeric ratios, and isotopic compositions to those found in terrestrial biology and synthesized under simulated prebiotic conditions. We then draw from these comparisons to propose new guidelines for using chiral asymmetry as a biosignature in future life detection missions. Finally, we discuss how these measurement criteria can best be applied to future life detection missions and describe the limitations of current *in situ* spaceflight instrumentation.

Table 1. List of Amino Acids by Number of Carbon Atoms That Have Been Identified by Name in the Murchison CM2 Meteorite,^{49,87–92} in Various Miller Spark Discharge Experiments^{11,15–17,93} and Ice Experiments^{62,94,95} (as Simple Proxies for Abiotic Syntheses), and/or Found in “Central” Metabolism in Terrestrial Biology, As Well As the Reported L-Enantiomeric Excesses Detected in Carbonaceous Meteorites^a

Name	Meteorite %L _{ee} ^b	Occurrence
2 Carbons		
Glycine	achiral	Biology, Spark, Meteorites, Ice
3 Carbons		
Alanine	0, 33 in Murchison ^{96,97} in Murchison (CM2), –3 to 7 in Tagish Lake (C2) ²⁶	Biology (L)(D), Spark, Meteorites, Ice
Serine	43 in Murchison (CM2), ⁹⁷ 56 to 81 in Tagish Lake (C2) ²⁶	Biology (L), Spark, Meteorites, Ice
β-Alanine	achiral	Biology, Spark, Meteorites, Ice
DL-Isoserine	0 in Murchison (CM2) ⁹²	Spark, Meteorites
Sarcosine	achiral	Biology, Spark, Meteorites, Ice
2,3-Diaminopropanoic acid	0 in Murchison (CM2) ⁹¹	Spark, Meteorites, Ice
Cysteine	nd	Biology (L)
Selenocysteine ^c	nd	Biology (L)
Homocysteic acid ^e	nd	Spark
Cysteic acid, Thiocysteine, 3-Sulfinoalanine	nd	Biology (L)
4 Carbons		
Aspartic acid	14 to 42 in Murchison (CM2), ^{97,92} 43 to 59 in Tagish Lake (C2) ²⁶	Biology (L), Spark, Meteorites, Ice
Threonine	16 in Murchison (CM2), ⁹⁷ 89 to 99 in Tagish Lake (C2) ²⁶	Biology (L), Spark, Meteorites
Asparagine	nd	Biology (L)
allo-Threonine	ee nr	Spark, Meteorites
Isothreonine	ee nr	Meteorites
allo-Isothreonine	–8 ^d in Murchison (CM2) ⁹²	Meteorites
Homoserine	2 in Murchison (CM2) ⁹²	Biology (L), Meteorites
β-Homoserine	ee nr	Meteorites
α-Methylserine	ee nr	Meteorites
α-Amino-n-butyric acid	1 in Murchison (CM2) ⁹²	Spark, Meteorites, Ice
β-Amino-n-butyric acid	0 in Murchison (CM2), ^{92,97} 4 to 5 in Tagish Lake (C2) ²⁶	Spark, Meteorites, Ice
γ-Amino-n-butyric acid	achiral	Biology, Spark, Meteorites, Ice
α-Aminoisobutyric acid	achiral	Spark, Meteorites, Ice
β-Aminoisobutyric acid	–7 ^d in Murchison (CM2) ⁹²	Biology (L), Spark, Meteorites, Ice
N-Ethylglycine	achiral	Spark, Meteorites, Ice
N,N-Dimethylglycine	achiral	Biology, Spark, Meteorites
N-Methylalanine	ee nr	Spark, Meteorites
N-Methyl-β-alanine	achiral	Meteorites
3-Amino-2-(hydroxymethyl)propanoic acid	ee nr	Meteorites
2,3-Diaminobutyric acid	ee nr	Meteorites, Ice
2,4-Diaminobutyric acid	0 in Murchison (CM2) ⁹¹	Meteorites
3,3-Diaminoisobutyric acid	achiral	Meteorites, Ice
4-Amino-2-hydroxybutyric acid	ee nr	Meteorites
4-Amino-3-hydroxybutyric acid	ee nr	Meteorites
Aspartic acid semialdehyde, Homocysteine, Homoserine, 2-Amino-acetoacetic acid	ee nr	Biology (L)
5 Carbons		
Valine	0 to 3 in Murchison (CM2) ^{18,98,22}	Biology (L), Spark, Meteorites, Ice
Glutamic acid	38 to 42 in Murchison (CM2), ^{97,92} 51 to 55 in Tagish Lake (C2) ²⁶	Biology (L), Spark, Meteorites
Proline	0, 49 to 81 in Murchison (CM2) ^{18,99}	Biology (L)(D), Spark, Meteorites, Ice
Methionine	nd	Biology (L), Spark
Glutamine	nd	Biology (L)
Methionine sulfone	nd	Spark
Norvaline	0 to 3 in Murchison (CM2), ^{98,22} 2 to 5 in Tagish Lake (C2) ²⁶	Spark, Meteorites, Ice
Isovaline	0 to 18.5 in Murchison (CM2), ^{21,22} 0 to 7 in Tagish Lake(C2), ²⁶ 20.5 in ALH 85085 (CH3) ²³	Spark, Meteorites, Ice
Ornithine	0 in Murchison (CM2) ⁹¹	Biology (L), Meteorites
3-Aminopentanoic acid	ee nr	Meteorites
3-Amino-2-methylbutanoic acid	ee nr	Meteorites

Table 1. continued

Name	Meteorite %L _{ee} ^b	Occurrence
5 Carbons		
<i>allo</i> -3-Amino-2-methylbutanoic acid	ee nr	Meteorites
3-Amino-2,2-dimethylpropanoic acid	achiral	Meteorites
3-Amino-3-methylbutanoic acid	achiral	Meteorites
3-Amino-2-ethylpropanoic acid	achiral	Spark, Meteorites
4-Aminopentanoic acid	ee nr	Meteorites
4-Amino-2-methylbutanoic acid	ee nr	Meteorites
4-Amino-3-methylbutanoic acid	ee nr	Meteorites
5-Aminopentanoic acid	achiral	Biology, Meteorites, Ice
α -Methylaspartic acid	ee nr	Meteorites
<i>threo</i> - β -Methylaspartic acid	ee nr	Biology (L), Meteorites
<i>N</i> -Methylaspartic acid	ee nr	Meteorites
4,4'-Diaminoisopentanoic acid	achiral	Meteorites
β -(Aminomethyl)-succinic acid	0 in Murchison (CM2) ⁹²	Meteorites
Glutamic acid semialdehyde, 4-hydroxyglutamic acid semialdehyde, 4-hydroxyglutamic acid, methionine sulfoxide	nd	Biology (L)
6 Carbons		
Leucine	72 in Murchison (CM2) ⁹⁹	Biology (L), Spark, Meteorites
Isoleucine	14 in GRA 95229 (CR2), ²⁷ 50 in MET 00426 (CR2) ²⁷	Biology (L), Spark, Meteorites
Histidine	nd	Biology (L)
Arginine	nd	Biology (L)
Lysine	nd	Biology (L)
Ethionine	nd	Spark
<i>allo</i> -Isoleucine	−12 in GRA 95229 (CR2), ²⁷ −60 in MET 00426 (CR2) ²⁷	Spark, Meteorites
Norleucine	ee nr	Spark, Meteorites
Pseudoleucine	ee nr	Meteorites
Cycloleucine	ee nr	Meteorites
α -Methylnorvaline	3 in Murchison (CM2) ⁹⁸	Meteorites
α -Methylvaline	3 in Murchison (CM2) ⁹⁸	Meteorites
Pipecolic acid	ee nr	Biology (L), Spark, Meteorites
2-Amino-2-ethylbutanoic acid	achiral	Meteorites
2-Amino-2,3-dimethylbutanoic acid	ee nr	Meteorites
3-Amino-2-ethylbutanoic acid	ee nr	Meteorites
3-Amino-2,3-dimethylbutanoic acid	ee nr	Meteorites
3-(Methylamino)pentanoic acid	ee nr	Meteorites
4-Aminohexanoic acid	ee nr	Meteorites
4-Amino-3,3-dimethylbutanoic acid	ee nr	Meteorites
4-Amino-2-methylpentanoic acid	ee nr	Meteorites
4-Amino-3-methylpentanoic acid	ee nr	Meteorites
4-Amino-4-methylpentanoic acid	ee nr	Meteorites
6-Aminohexanoic acid	achiral	Meteorites
α -Aminoadipic acid	1 ^d in Murchison (CM2) ⁹²	Biology (L), Meteorites
β -Aminoadipic acid	ee nr	Meteorites
2-Methylglutamic acid	ee nr	Meteorites
Glucosaminic acid	nd	Biology (D)
Citrulline, 5-Hydroxylysine, 2-Aminoadipic acid semialdehyde, 2-Amino-3-oxoadipic acid	nd	Biology (L)
7 Carbons		
2-Amino-2,3,3-trimethylbutanoic acid	ee nr	Meteorites
2-Amino-2-ethyl-3-methylbutanoic acid	ee nr	Meteorites
2-Amino-2-ethylpentanoic acid	ee nr	Meteorites
2-Amino-3-ethylpentanoic acid	ee nr	Meteorites
α -Methyl-isoleucine	7 in Murchison (CM2) ²⁰	Meteorites
α -Methyl-alloisoleucine	9 in Murchison (CM2) ²⁰	Meteorites
2-Amino-2,4-dimethylpentanoic acid	ee nr	Meteorites
2-Amino-3,3-dimethylpentanoic acid	ee nr	Meteorites
2-Amino-3,4-dimethylpentanoic acid	ee nr	Meteorites
2-Amino-4,4-dimethylpentanoic acid	ee nr	Meteorites
<i>allo</i> -2-Amino-3,4-dimethylpentanoic acid	ee nr	Meteorites
2-Amino-2-methylhexanoic acid	4 in Murchison (CM2) ⁹⁸	Meteorites

Table 1. continued

Name	Meteorite %L _{ee} ^b	Occurrence
7 Carbons		
2-Amino-3-methylhexanoic acid	ee nr	Meteorites
<i>allo</i> -2-Amino-3-methylhexanoic acid	ee nr	Meteorites
2-Amino-4-methylhexanoic acid	ee nr	Meteorites
<i>allo</i> -2-Amino-4-methylhexanoic acid	ee nr	Meteorites
2-Amino-5-methylhexanoic acid	ee nr	Meteorites
2-Aminoheptanoic acid	ee nr	Meteorites
α -Aminopimelic acid	ee nr	Meteorites
1-Aminocyclohexanecarboxylic acid	ee nr	Meteorites
2,6-diaminopimelic acid	nd	Biology (L,L)(<i>meso</i>)
8 Carbons		
Isomers detected, but not identified	ee nr	Meteorites
9 Carbons		
Phenylalanine	ee nr	Biology (L) , Meteorites
Tyrosine	ee nr	Biology (L) , Meteorites
Dopaquinone, 3,4-Dihydroxyphenylalanine, Iodotyrosenes	nd	Biology (L)
Isomers detected, but not identified	ee nr	Meteorites
10 Carbons		
Kynurenine, 3-Hydroxykynurenine	nd	Biology (L)
Isomers detected, but not identified	ee nr	Meteorites
11 Carbons		
Tryptophan	nd	Biology (L)
5-Hydroxytryptophan	nd	Biology (L)
12 Carbons		
Pyrrolysine ^c	nd	Biology (L)

^aCentral metabolism is not intended to be exhaustive and only chiral primary amine, nonencoded amino acids that are not found in meteorites are shown for simplicity. Those encoded in terrestrial proteins^{72,73} are bold. All chiral amino acids synthesized in the spark discharge experiments are racemic (D = L). Amino acid detections without associated isotope measurements may be terrestrial contamination, particularly if common in biology. ee nr = enantiomeric excesses not reported, although compounds were identified in meteorites. nd = compound not detected in meteorites.

^bAmino acid enantiomeric excesses found in meteorites are given in %L_{ee} = [(L - D)/(L + D)] × 100 (negative values correspond to D-excesses). Isotopic measurements of the amino acid enantiomers are required to firmly establish the origin of any chiral asymmetry. ^cNonstandard proteinogenic amino acids. ^dOverlapping peaks interfered with enantiomeric measurements leading to higher uncertainty in the reported ee value.

^eOxidation product of homocysteine.

2. AMINO ACIDS IN METEORITES AND LIFE

2.1. Abiotic Distributions and Formation Pathways

Asteroids, comets, and their fragments including meteorites, micrometeorites, and interplanetary dust particles (IDPs) preserve records of physical and chemical processes and conditions during the origin and early evolution of the Solar System and serve as delivery vehicles for organic matter to the Earth and other planets.³⁴ At present, $\sim 4 \times 10^7$ kg of extraterrestrial material, ranging in size from micron-sized IDPs to meter-sized meteorites and with organic carbon abundances of up to several weight percent for meteorites and higher for IDPs,^{35,36} rain down on the Earth every year.³⁷ Moreover, the flux of 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.³⁸ Therefore, exogenous delivery may have been an important source of organic carbon on the early Earth and other Solar System bodies, including the delivery of a wide range of complex prebiotic molecules available for the origin of life.

It is presently unknown whether extraterrestrial life in our Solar System would be similar to terrestrial biochemistry; however, given the ubiquity of amino acids and sugars in life on Earth and the potentially significant organic matter input through exogenous delivery, these prebiotic molecules would have been available and could have played a role in the emergence of biochemistry on other planets. Thus, a detailed

understanding of the chemical compositions of prebiotic organic matter found in meteorites and IDPs is critical to the search for evidence of life elsewhere, since these primitive materials contribute both the raw ingredients for life as well as a nonbiological chemical background “noise” that could overprint chemical signatures of extinct or extant biotic chemistry.

Over the past 50 years, a complex and highly diverse suite of soluble organics have been identified in carbonaceous chondrites,^{39,40} a class of meteorites that can contain up to ~ 5 wt % carbon, most of which is derived from organic matter as opposed to inorganic carbonate, graphite, etc.³⁶ The carbonaceous chondrites are subdivided into eight groups (CI, CM, CR, CH, CB, CO, CV, and CK) based on their mineralogy and elemental and isotopic compositions,^{41,42} along with several ungrouped meteorites that are sufficiently different from those eight groups, and other ungrouped meteorites, to preclude specific classification. An additional petrographic classification scheme divides the chondrites into six types: types >3–6 reflect increasing thermal metamorphism, and types <3–1 reflect increasing degrees of parent body aqueous alteration. Shortly after the fall of the Murchison CM type 2 carbonaceous chondrite in 1969, Kvenvolden and co-workers identified five common protein amino acids (glycine, alanine, valine, proline, and glutamic acid) and 12 nonproteinogenic amino acids in the meteorite, including high relative abundances of α -aminoisobutyric acid (α -AIB) and

Table 2. List of Chiral Polyols That Have Been Identified by Name in Meteorites, Their Percent D-Enantiomeric Excesses, Presence in “Central” Metabolism²⁰⁴ (All Species Have at Least Some Minor Presence in Biology), and Example Abiotic Detections^a

Class	Name	Meteorite %D _{ee}	Occurrence
3 Carbons			
Aldose	Glyceraldehyde	ee nr ^f	Biology (D), Formose, Ice, Meteorites
Deoxyaldose	Lactaldehyde	nd	Biology (D), Ice
Aldonic acid	Glyceric acid	ee nr ^b	Biology (D), Ice, Meteorites
Deoxyaldonic acid	Lactic acid	−3 to −12 in Murchison (CM2), ^{d,g} 6 in LAP 02342 (CR2), ^{d,g} −3 in GRA 95229 (CR2) ^{d,g}	Biology (D > L), Meteorites
4 Carbons			
Aldose	Erythrose	nd	Biology (D)
Aldonic acid	Erythro-2,3-dihydroxybutyric acid	0 in Murchison (CM2) ^b	Ice, Meteorites
Aldonic acid	Threo-2,3-dihydroxybutyric acid	0 in Murchison (CM2) ^b	Ice, Meteorites
Aldonic acid	Erythronic acid	54 in Murchison (CM2) ^b	Ice, Meteorites
Aldonic acid	Threonic acid	33 to 55 in Murchison (CM2) ^b 34 in ALH 83102 (CM2) ^b 43 in GRA 95229 (CR2) ^b	Biology (L), Ice, Meteorites
Aldaric acid	Tartaric acid	ee nr ^c	Biology (L), Meteorites
Deoxyaldonic acid	2,4-Dihydroxybutyric acid	0 in Murchison (CM2) ^b	Meteorites
Deoxyaldonic acid	2,3-Dihydroxybutyric acid	ee nr ^b	Meteorites
Deoxyaldonic acid	3,4-Dihydroxybutyric acid	ee nr ^b	Meteorites
Deoxyaldonic acid	2-Methylglyceric acid	0 in Murchison (CM2) ^b	Meteorites
Deoxyaldaric acid	Malic acid	ee nr ^f	Biology (L), Meteorites
Alditol	Threitol	0 in Murchison (CM2) ^b 0 in LAP 02333 (CM2) ^b 0 in ALH 83102 (CM2) ^b 0 in GRA 95229 (CR2) ^b	Formose, Ice, Meteorites
5 Carbons			
Aldose	Ribose	ee nr ^e	Biology (D), Formose, Ice, Meteorites
Aldose	Arabinose	ee nr ^e	Biology (L), Formose, Ice, Meteorites
Aldose	Xylose	ee nr ^e	Biology (D), Formose, Ice, Meteorites
Aldose	Lyxose	ee nr ^e	Formose, Ice, Meteorites
Deoxyaldose	2-Deoxyribose	nd	Biology (D), Formose, Ice
Ketose	Ribulose	nd	Biology (D > L), Formose
Ketose	Xylulose	nd	Biology (D,L), Formose
Aldonic acid	Ribonic acid	57 in Murchison (CM2) ^b	Ice, Meteorites
Aldonic acid	Arabinonic acid	47 to 60 in Murchison (CM2) ^b	Ice, Meteorites
Aldonic acid	Xylonic acid	82 to 100 in Murchison (CM2) ^b	Biology (L), Ice, Meteorites
Aldonic acid	Lyxonic acid	61 to 100 in Murchison (CM2) ^b	Biology (L), Ice, Meteorites
Alditol	Arabinitol	0 in GRA 95229 (CR2) ^b	Biology (L), Formose, Ice, Meteorites
Alditol	Ribitol	ee nr ^b	Biology (D), Formose, Meteorites
6 Carbons			
Aldose	Glucose	nd	Biology (D), Formose
Aldose	Galactose	nd	Biology (D), Formose
Aldose	Mannose	nd	Biology (D), Formose
Deoxyaldose	Fucose	nd	Biology (L)
Deoxyaldose	Rhamnose	nd	Biology (L)
Ketose	Fructose	nd	Biology (D), Formose
Aldonic acid	Allonic acid	100 in Murchison (CM2) ^b	Meteorites
Aldonic acid	Altronic acid	100 in GRA 06100 (CR2) ^b	Meteorites
Aldonic acid	Gluconic acid	100 in Murchison (CM2) ^b , 100 in GRA 06100 (CR2) ^b	Biology (D), Meteorites
Aldonic acid	Mannonic acid	ee nr ^b	Meteorites
Aldonic acid	Gluonic acid	ee nr ^b	Biology (L), Meteorites
Aldonic acid	Idonic acid	100 in GRA 06100 (CR2) ^b	Meteorites
Aldonic acid	Galactonic acid	100 in Murchison (CM2), ^b 100 in GRA 06100 (CR2) ^b	Meteorites
Aldonic acid	Talonic acid	100 in Murchison (CM2), ^b 100 in GRA 06100 (CR2) ^b	Meteorites
Aldaric acid	Glucaric acid	nd	Biology (D)
Alditol	Sorbitol	nd	Biology (D)

Table 2. continued

^aThe more common enantiomers of simple chiral polyols in biology are shown, and all abiotic syntheses produce racemic products. Errors have not generally been reported for individual analyses, but when multiple results are shown in a reference they are listed as ranges. Detections without associated carbon isotope measurements (Table 3) may be terrestrial contamination, particularly if common in biology. The conditions and reactants of both ice^{197,198} and formose^{189,192,205} reactions can be adjusted to change the product distributions. %D_{ee} = (D - L)/(D + L) × 100 (negative values correspond to L-excesses). Isotopic measurements are required to firmly establish the origin of any enantiomeric excesses. ee nr = enantiomeric excess not reported, although compound was identified in meteorites. nd = compound not detected in meteorites. ^bCooper and Rios²⁸ ^cCooper et al.²⁰² ^dPizzarello et al.²⁰⁶ ^eFurukawa et al.²⁰⁷ ^fPizzarello et al.²⁷ (Tables in supplement, not discussed in the text). ^gSubstantial material was lost in the workup, complicating the interpretation.

isovaline (2-amino-2-methylbutanoic acid) that are both rare on Earth.^{18,43} They concluded that all of the amino acids in the meteorite were abiotic and extraterrestrial in origin based on nearly equal abundances of L- and D-enantiomers of the chiral amino acids that argued strongly against terrestrial biological contamination that consists of mostly L-amino acids.

A variety of gas and liquid chromatography mass spectrometry techniques have been used to characterize the soluble organic composition of meteorites over the past five decades.⁴⁴ For amino acids, meteorite powders are first extracted in hot water, followed by acid hydrolysis of a portion of the water extract to liberate “bound” amino acids or generate free molecules from precursors, and then the extracts are subjected to multiple dry-down and purification steps to remove salts and metal ions that can interfere with chemical derivatization and chromatographic separation of the amino acids and their enantiomers.⁴⁴ To date, 96 different amino acids have been named in the Murchison CM2 type carbonaceous chondrite (Table 1), and likely hundreds more have been detected but have yet to be identified.²⁴ Other meteorites have shown similar amino acid diversity, and many have shown less, but no meteorite has shown greater amino acid complexity than Murchison.⁴⁵ The Murchison meteorite contains 12 of the 20 most common protein amino acids found in biology (Table 1); however, the vast majority of amino acids identified in Murchison are rare or absent in the terrestrial biosphere.^{46,47} Amino acids that have been detected in Murchison range from two- to ten-carbons in length and appear to exhibit complete structural diversity of aliphatic amino acids (all possible structural isomers present) with an exponential decrease in abundance with increasing carbon number within a homologous series.^{48,49} Based on the total number of possible enantiomers and isomers for acyclic monoamino alkanolic acids with carbon numbers up to ten (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.), and also including cyclic and diamino alkanolic and alkanedioic acids that have been found in meteorites,^{50–52} it is likely that there are thousands of individual amino acids in the Murchison meteorite. Most of these amino acids have not yet been identified due to insufficient analytical sensitivity, insufficient chromatographic separation of higher molecular weight amino acids, and a lack of commercially available standards to enable unambiguous identification of amino acids with six or more carbons.⁴⁹ Owing to the inherently limited sample masses of IDPs and micrometeorites, there have been no reports on the composition of any soluble organic compounds in IDPs and only two reports of the extraterrestrial amino acid α -AIB in micrometeorites collected in Antarctica.^{53,54} As analytical techniques and sensitivities improve with time,⁵⁵ our knowl-

edge of the soluble organic diversity of IDPs and micrometeorites should greatly expand.

Multiple formation pathways and synthetic routes for amino acids in meteorites (Figure 2) have been proposed based on the observed distributions and relative abundances of various

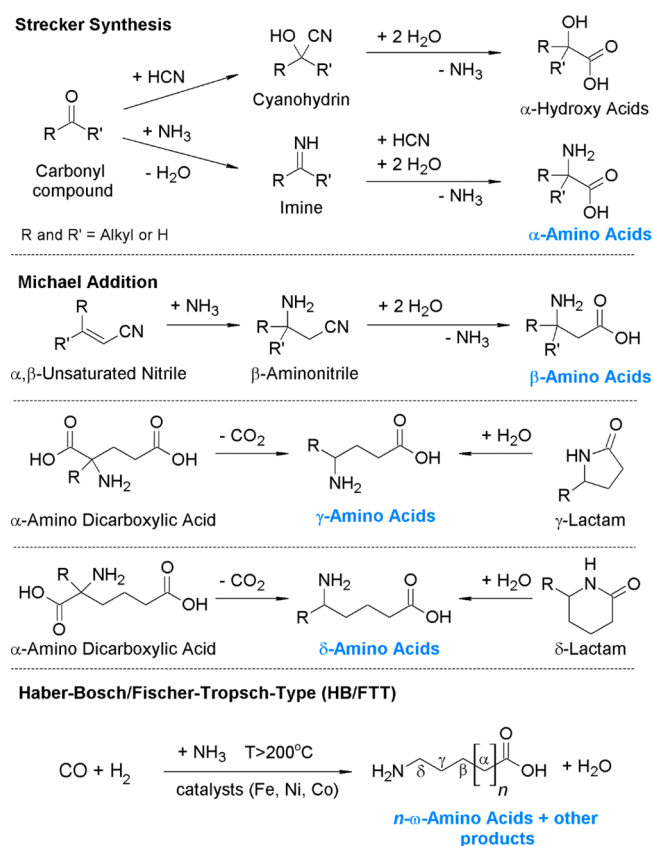


Figure 2. Plausible chemical formation pathways for amino acids found in meteorites. α -Amino acids are produced by HCN polymerization (not shown) or the Strecker-cyanohydrin pathway in the presence of water and ammonia. β -Amino acids are formed by Michael addition of ammonia to α,β -unsaturated nitriles forming a β -aminonitrile that can undergo hydrolysis/reduction steps to form β -amino acids. γ - and δ -Amino acids can be produced by decarboxylation of α -amino dicarboxylic acids or by the hydrolysis of lactams that are found in meteorites. n - ω -Amino acids and many other straight-chain hydrocarbons can be formed by Haber–Bosch/Fischer–Tropsch-Type (HB/FTT) mineral surface-catalyzed reactions of H₂, CO, and NH₃ at elevated temperatures. Modified version of a figure published in *Primitive Meteorites and Asteroids: Physical, Chemical, and Spectroscopic Observations Paving the Way to Exploration*, D. P. Glavin, C. M. O’D. Alexander, J. C. Aponte, J. P. Dworkin, J. E. Elsila, and H. Yabuta, The Origin and Evolution of Organic Matter in Carbonaceous Chondrites and Links to Their Parent Bodies, Page 229, Copyright Elsevier (2018).

isomers. The amino acids in the Murchison CM2 carbonaceous chondrite as well as less altered CR2 type carbonaceous meteorites are dominated by α -amino isomers (Figure 1; amino group is attached to the central carbon immediately adjacent to the carboxylic acid group), although other structural isomers are present in these meteorites at lower abundances.⁴⁹ The presence of high relative abundances of α -amino acids and the analogous α -hydroxy acids and iminodicarboxylic acids found in Murchison^{56–58} suggests that amino acid Strecker-cyanohydrin synthesis occurred within the Murchison meteorite parent body during an aqueous alteration phase. The formation of α -amino acids by polymerization of HCN during aqueous alteration has also been suggested;⁵⁷ however, only two amino acids (glycine and alanine) are produced at significant levels from HCN by this mechanism.⁵⁹ α -Amino acids could also have been formed prior to incorporation into the parent body on ice grain surfaces exposed to radiation,^{60–62} for example, by carboxylation of amines with CO₂ or of nitriles under proton irradiation.^{63,64} The wide diversity of amino acids in Murchison and other aqueously altered CI, CM, and CR meteorites also include β -, γ -, and δ -amino acids that cannot be formed by Strecker synthesis and indicate that multiple amino acid formation mechanisms were active in these meteorite parent bodies.⁴⁵ For example, β -amino acids in carbonaceous meteorites have been hypothesized to form under aqueous conditions by Michael addition of ammonia to α,β -unsaturated nitriles, followed by reduction and hydrolysis.^{49,65} It has also been proposed that some γ - and δ -amino acids found in the Murchison meteorite could have been formed by decarboxylation of α -amino dicarboxylic acids or the hydrolysis of lactams that have also been identified in the meteorite.⁶⁶

In contrast to the aqueously altered CI, CM, and CR carbonaceous chondrites, thermally metamorphosed meteorites that were exposed to additional parent body heating such as the moderately heated CO3 and CV3 chondrites and the extensively heated CK4–6 chondrites have a much more limited distribution of amino acids dominated by achiral straight-chain terminal amine “*n*- ω -amino acids” including glycine, β -alanine, γ -amino-*n*-butyric acid, δ -aminovaleric acid, and ϵ -amino-*n*-caproic acid.^{67,68} The predominance of these linear, straight-chain amino acids and depletion of other branched isomers in these thermally altered meteorites may be the result of Haber–Bosch/Fischer–Tropsch type (HB/FTT) mineral-surface catalyzed reactions that occurred between trapped CO, H₂, and NH₃ gases and metals (e.g., Fe, Co, or Ni) inside the meteorites as they cooled on their parent bodies.^{69,70} Alternatively, laboratory hydrothermal reactions of potassium cyanide, formaldehyde, and ammonium hydrogen carbonate at elevated temperatures and pressures (up to 400 °C at 250 atm) can also yield *n*- ω -amino acids.¹⁴ In summary, a wide range of amino acid compositions have been observed in carbonaceous chondrites, including both simple and highly complex distributions that can be attributed to the availability of their corresponding starting materials in presolar environments and Solar System parent bodies and to the different formation mechanisms as well as physical and/or chemical characteristics and compositions of their respective parent bodies.

2.2. Amino Acids in Terrestrial Biology

Amino acids are the monomers of proteins and enzymes, the molecular machines responsible for catalyzing nearly all

chemical reactions necessary for life on Earth. Protein amino acids account for approximately 55% of the total dry weight of a single prokaryotic cell⁷¹ and are prevalent in the terrestrial biosphere. In contrast to the broad diversity of amino acids found in meteorites and produced in prebiotic experiments (Table 1), all life on Earth uses only 20 standard genetically encoded (proteinogenic) L-amino acids.⁷² There are also 2 additional nonstandard amino acids (L-selenocysteine and L-pyrrolysine) in some organisms that are not coded for directly in the genetic code but can be encoded by special translational mechanisms.^{73,74} The same 20 standard amino acids have been used in proteins in life on Earth since the existence of the Last Universal Common Ancestor (LUCA). With the exception of glycine which is achiral, all proteinogenic amino acids are chiral and terrestrial biology has evolved to use only L-amino acids in the production of genetically encoded proteins.

There are many other noncoded amino acids known to occur in biology; however, they are used as metabolic intermediates in biosynthesis, are post-translationally formed in proteins, or possess a physiological role, such as neurotoxins.⁷³ For example, L-ornithine is a metabolic intermediate that is biosynthetically produced but is not incorporated into proteins. Although all proteinogenic amino acids are α -amino acids, there are some non- α -amino acids that are used in biology (e.g., β -alanine is a component of vitamin B₅ and γ -amino-*n*-butyric acid acts as a major inhibitory neurotransmitter in mammals). β -alanine and γ -amino-*n*-butyric acid are also found in marine sediments,^{75,76} and their presence is generally attributed to bacterially mediated α -decarboxylation of aspartic and glutamic acids, respectively, which takes place during the diagenesis of sedimentary organic matter.⁷⁷ In most bacteria, the only D-amino acids produced in significant quantities are D-alanine and D-glutamic acid, that are incorporated into cell wall peptidoglycan,⁷⁸ and a few other D-amino acids that are produced in some organisms to help modulate cell wall synthesis⁷⁹ and other specialized functions.⁸⁰ Some fungal peptides contain the rare nonprotein α -dialkyl amino acids (usually D-isovaline and α -AIB, which have antibiotic properties.^{81,82}

Prior to the emergence of biosynthetic pathways on Earth, there were at least 10 prebiotic α -amino acids (Ala, Asp, Glu, Gly, Ile, Leu, Pro, Ser, Thr, and Val) available for protein formation,⁸³ and experimental and modeling results suggest that 10 amino acids are at the theoretical minimum limit for a foldable set.^{84–86} It remains unclear why terrestrial biology evolved to use a specific set of only 20 standard α -amino acids since prebiotic environments on the early Earth should have included a wide variety of amino acids, based on laboratory experiments simulating primordial environments and delivery from meteorites.^{11,16,34} This likely reflects an evolutionary compromise between diminishing improvements in protein folding and function from increasing the amino acid alphabet, and decreases in translation fidelity and buffering capacity against mutations that would result from reduced degeneracy in the genetic code.

It is unknown whether or not life elsewhere would evolve independently to use the same set of 20 protein amino acids present in life on Earth. Nevertheless, a search for chiral amino acids with a limited distribution of structural isomers, including protein amino acids such as histidine and tryptophan that are present in terrestrial biology but have not yet been reported in abiotic syntheses under plausible prebiotic conditions (Table 1), should be part of a robust life detection strategy. Two

important caveats to this approach must be considered to avoid false negatives and false positives. Amino acid racemization (conversion of one enantiomer to the other, leading to an equal abundance of both enantiomers) can slowly erase homochiral signatures of extant biology after death, eventually resulting in a racemic mixture that could be mistaken for an abiotic origin (false negative). In addition, racemization (epimerization) can also facilitate the non-biological amplification of one amino acid enantiomer over the other under certain environmental conditions that could lead to a false positive detection of extant life. Both possibilities will be discussed in more detail in the following sections.

2.3. Amino Acid Racemization

The racemization rates of α -hydrogen protein amino acids have been studied in great detail and vary with amino acid species, position of the amino acid within the protein, temperature, pH, water availability, and ionic strength.^{100,101} Amino acids and sugars in the presence of water will undergo racemization (conversion of one enantiomer into the other until a racemic mixture is reached) over relatively short periods on geological time scales.^{100,102,103} For example, total racemization of L-aspartic acid in wet sediments was estimated to occur in $\sim 4 \times 10^3$ years at 300 K and $\sim 2 \times 10^7$ years at 252 K.^{104,105} Under dry conditions over the same temperature range, complete racemization of L-aspartic acid in a desiccated sample would occur in $\sim 3 \times 10^5$ years and $\sim 5 \times 10^9$ years, respectively.¹⁰⁴ Enantiomeric measurements of protein amino acids recovered from extinct ~ 1 million-year-old Pleistocene fossil mollusk shells had D/L aspartic acid, D/L alanine, and D/L valine ratios of 0.88, 0.95, and 0.85, respectively, indicating that significant amino acid racemization had occurred.¹⁰⁶ With knowledge of the past environmental conditions (including burial temperature, humidity, pH, etc.), the measured amino acid D/L ratio (assuming $D/L < 1$) can be used to estimate the age of an extinct organism.^{107,108} However, if complete amino acid racemization has occurred ($D/L = 1$), it would be impossible from the enantiomeric ratio alone to distinguish between an extinct biological origin and abiotic chemistry that could also result in racemic mixtures. In this case, the amino acid abundance, distribution, and knowledge of their stable isotopic compositions would be needed to establish their origin.

Cohen and Chyba calculated the D/L ratios of several α -hydrogen amino acids found in meteorites based on their known racemization half-lives over a variety of asteroid parent body thermal histories and determined that in many cases α -hydrogen amino acids with an original enantiomeric excess would not undergo complete racemization since the time of their formation.¹⁰⁹ In contrast to the α -hydrogen amino acids, α -dialkyl amino acids such as isovaline found in meteorites and fungal peptides are not prone to rapid racemization under aqueous or radiogenic conditions on geologic time scales.^{110,111} In fact, α -dialkyl amino acids with a chiral center decompose much faster than they racemize.¹¹² Therefore, any enantiomeric excesses should be preserved for these non-proteinogenic amino acids since the time of their formation. On Mars or other Solar System bodies where conditions are much colder and drier than Earth, amino acid racemization and hydrolysis would be extremely slow and any chiral signature of past life could be preserved for billions of years.^{104,113}

2.4. Amino Acid Asymmetry and Amplification Mechanisms

One of the key open questions in origins of life research is how and when homochirality began. Reports over the last two decades of large protein amino acid enantiomeric excesses in some meteorites, likely not due to terrestrial contamination, provide evidence that the transition to homochirality could have been initiated by abiotic mechanisms, prior to the start of life. The first such report was by Engel and Macko,¹¹⁴ who reported a 33% L-enantiomeric excess for alanine in the Murchison meteorite (Table 1). They argued against terrestrial alanine contamination based on the L- and D-enantiomers both being significantly enriched in ^{15}N ($\delta^{15}\text{N} = +60$ and $+57\%$, respectively), compared to terrestrial biology, which produces amino acids that are less enriched in ^{15}N (Section 4). It was argued by others, however, that the compound-specific stable N isotope measurements could have been interfered with by coeluting compounds.¹¹⁵ That same year, Cronin and Pizzarello reported L-enantiomeric excesses for four α -methyl amino acids from the Murchison (CM2) meteorite, ranging from 2.8 to 10.4%.¹¹⁶ The authors did not provide isotopic measurements but argued that the enantiomeric excesses were likely not the result of contamination because the amino acids found in excess are not common in terrestrial biology and the α -hydrogen analogs of these amino acids were racemic. Over the next decade, Pizzarello, Cronin, and others observed amino acid enantiomeric excesses up to $\sim 15\%$ in multiple meteorites, including Murchison (CM2), Murray (CM2), and Graves Nunataks (GRA) 95229, a CR2 chondrite.^{21,98,117,118} All of these studies were performed by chemical derivatization of concentrated and purified meteorite water extracts followed by gas chromatography–mass spectrometry (GC-MS) analysis of various *N*-trifluoroacetyl-isopropyl derivatives, which is well-suited for the separation of complex suites of amino acids found in many carbonaceous meteorites.

Glavin and Dworkin and co-workers built on these results by developing analytical methods to analyze meteorite extracts based on *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization and ultrahigh performance liquid chromatography–mass spectrometry (LC-MS), which offers orders of magnitude greater sensitivity than GC-MS for amino acids, enabling the analysis of smaller masses of meteorite samples and less abundant amino acids, albeit with somewhat reduced chromatographic separation efficiency.^{22,49,119} Focusing on amino acids from two- to five-carbons in length, LC-MS based amino acid analyses have now been performed on meteorite samples from each of the eight carbonaceous chondrite groups, including all petrographic subtypes that are available for each group, as well as ungrouped chondrites.^{49,70,120,121} These analyses have revealed L-enantiomeric excesses for the amino acid isovaline of up to $\sim 20\%$ (Table 1), with a general correlation between the extent of aqueous alteration and magnitude of enantiomeric excess, particularly for CI, CM, and CR chondrites. Analyses of multiple samples of the Tagish Lake meteorite, an ungrouped C2 chondrite that has both heavily hydrated and slightly hydrated lithologies, revealed that the least aqueously altered sample had isovaline that was essentially racemic, while the most aqueously altered fragment analyzed had an L-isovaline enantiomeric excess of $\sim 7\%$, further supporting the correlation between extent of aqueous alteration and isovaline enantiomeric excesses.^{26,122} There is an additional trend observed in carbonaceous meteorites, where the magnitude of L-isovaline enantiomeric excess is inversely

correlated with total abundance. Pizzarello and co-workers also noted that there appeared to be a link between the abundance of hydrated minerals (serpentine) and the isovaline enantiomeric excesses measured in the Murchison meteorite.²¹

In addition to the original report by Engel and Macko on L-alanine enantiomeric excesses in Murchison, there have been more recent reports of L-enantiomeric excesses for multiple proteinogenic amino acids that appear to be extraterrestrial in origin. Pizzarello and co-workers have focused on isoleucine, which has two chiral centers, and, therefore four possible stereoisomers: L-isoleucine (*S,S*); D-isoleucine (*R,R*); D-*allo*-isoleucine (*R,S*); and L-*allo*-isoleucine (*S,R*). Enantiomeric excesses of up to 50% for L-isoleucine (relative to D-isoleucine) and up to 60% for D-*allo*-isoleucine (relative to L-*allo*-isoleucine) have been reported in CR2 chondrites.^{118,123} Slight D-enantiomeric excesses of the nonproteinogenic amino acids *allo*-isothreonine ($D_{ee} \sim 8\%$) and β -aminoisobutyric acid ($D_{ee} \sim 7\%$) have also been recently reported in the Murchison meteorite (Table 1); however, the analytical uncertainties in these measurements were $>10\%$,⁹² so it is not clear if these D-amino acid excesses are real. In addition, stable isotope measurements for these amino acids were not made to firmly establish their extraterrestrial origin, and it was argued that there could have been analytical interferences that affected the enantiomeric ratios.^{92,124,125}

Glavin and co-workers reported an excess of L-aspartic acid of up to $\sim 60\%$ in the Tagish Lake meteorite (Table 1), and stable carbon isotope measurements revealed that both enantiomers were significantly enriched in ^{13}C ($\delta^{13}\text{C} = +24\%$ and $+29\%$, respectively), confirming that the large L-aspartic acid excesses in the meteorite were extraterrestrial in origin.²⁶ Interestingly, other proteinogenic amino acids including glutamic acid, serine, and threonine were also present with large L-enantiomeric excess in the Tagish Lake meteorite ($L_{ee} \sim 50$ to 99% , Table 1), whereas alanine, another common protein amino acid, was nearly racemic. Although an extraterrestrial origin for the L-glutamic acid, L-serine, and L-threonine excesses in Tagish Lake could not be confirmed by stable isotope measurements due to low abundances and analytical challenges, it is striking that alanine was found to be racemic in the same sample. Typically, in meteorites that have experienced terrestrial biological contamination, the samples do not have racemic mixtures of any common proteinogenic amino acids.^{126–129} Friedrich and co-workers made a similar observation for multiple samples of the Murchison meteorite, where aspartic acid, glutamic acid, and serine were also all present with large L-enantiomeric excesses up to 43% (Table 1), but alanine was racemic.¹³⁰ Notably, in both Murchison and Tagish Lake, the abundances of aspartic acid and glutamic acid are not significantly lower (within a factor of 2 or less) than the alanine abundances,^{26,97} so these observations cannot be readily explained by biological contamination.

The evidence for amino acid enantiomeric excesses in meteorites at this point is overwhelming, particularly for isovaline and other α -methyl amino acids not commonly used in biology. It is also important to emphasize that all of the amino acids found in enantiomeric excess have been α -amino isomers, and, with the one exception of D-*allo*-isoleucine excesses in two CR2 type carbonaceous chondrites,²⁷ only L-amino acid enantiomeric excesses have been found in meteorites so far, as these are the structural and stereoisomers used universally in biology. It is at least plausible, then, that the

preference for α -L-amino acids was driven by a process that existed very early in the history of our Solar System.

Understanding how and where the amino acids formed and how they have evolved over time during meteorite parent body alteration can provide important clues as to how the initial amino acid asymmetry occurred and how any small enantiomeric imbalances could have been amplified, either outside or inside the meteorite parent bodies. Considering that all of the amino acids present in enantiomeric excess have been α -isomers, we focus here on reactions capable of producing α -amino acids. The Strecker-cyanohydrin synthesis (Section 2.1) is one particularly well-known mechanism, in which an aldehyde or ketone reacts with ammonia and cyanide to form an amino nitrile, which is subsequently hydrolyzed to an amino amide and then an amino acid (Figure 2). The detection of all of the necessary reaction components, including cyanide, ammonia, and a range of aldehydes and ketones, along with the presence of structurally analogous α -hydroxy acids produced as side products of this pathway, provides evidence of its plausibility.^{56,131,132} With respect to chirality, chiral amino acids produced by Strecker chemistry are expected to be racemic in composition for multiple reasons. First, no asteroid-relevant processes have yet been demonstrated that are capable of stereochemically selective addition of cyanide to achiral imines, which are the Strecker precursors for isovaline, aspartic acid, and most of the amino acids found in enantiomeric excess in meteorites. Second, the cyanide addition step is readily reversible at a much faster rate than the effectively irreversible step of nitrile hydrolysis (reaction half-life on the order of a thousand years at $0\text{ }^\circ\text{C}$), which fixes the chirality at the α -carbon.^{133,134} In other words, any parent body-relevant Strecker-type mechanism or catalyst preferentially forming L- or D-amino nitriles would also need to catalyze subsequent nitrile hydrolysis sufficiently rapidly to retain that chirality. Although the Strecker aldehyde precursor for isoleucine (2-methylbutanal) is chiral, and therefore could preferentially favor cyanide addition to one face of the adjacent imine, there would still need to be a viable mechanism for rapid cyanide hydrolysis. Thus, while the Strecker synthesis remains a viable route for the racemic production of amino acids, there is no evidence suggesting it could generate appreciable levels of enantiomeric excesses in those amino acids. An alternative route to α -amino acids compatible with meteorites is reductive amination, where α -keto acids react with ammonia to produce α -imino acids, which are then reduced to α -amino acids. In this case, the reduction step creates the chiral center and is not readily reversible, and α -keto acids have been found in meteorites.¹³⁵ However, α -methyl amino acids cannot be produced by this chemistry, meaning that this route could not explain the isovaline enantiomeric excesses observed in meteorites. Given the present state of knowledge, in the absence of a chiral enantioenriched initiator, there are no routes to generate the observed enantiomeric excesses in the interior of asteroids.

An avenue that has shown great promise is the preferential synthesis or destruction of a single enantiomer by exposure to ultraviolet circularly polarized light (UV-CPL).¹³⁶ Interstellar and circumstellar UV-CPL is considered to be a potential symmetry breaking generator; when an enantiomer of a given chiral molecule has a higher optical response or absorption (i.e., differential extinction coefficient $\Delta\epsilon$ ¹³⁷) toward left- or right-handed CPL, this results in its faster photolytic destruction relative to its enantiomer of opposite handedness,

thus generating an enantiomeric excess (ee) of the less absorbing enantiomer.^{138,139} Conversely, the synthesis of enantioenriched amino acids in cold interstellar ice analogs using UV-CPL will largely depend on various factors including the type of polarization used, the photon energy intensity (eV), and the nature of both the starting materials and intermediates generated during irradiation.¹⁴⁰ Although the degree of circular polarization is negligible for low to medium mass stars including our Sun, strong circular polarization has been detected in light from the Orion star formation region with up to 17% polarization for high mass O- and B-type stars.^{3,141,142} Therefore, it is possible that our Solar System was exposed to CPL of a single sign from one quadrant of a neighboring massive star which would lead to preferential destruction and/or synthesis of a single hand of any chiral molecules such as amino acids present in the young solar nebula. The resulting amino acid chiral asymmetry could then be incorporated inside comets and asteroids and delivered to young planets. Other potential astronomical sources of UV CPL that could have led to chiral molecule symmetry breaking in the solar nebula are described in detail elsewhere.^{143–146}

The synthesis or destruction of a single enantiomer depends on the interaction between a given chiral molecule and UV CPL. The magnitude of the response is dependent on the anisotropy factor $g(\lambda)$, which is defined as the ratio of $\Delta\epsilon$ and the extinction coefficient ϵ . Therefore, anisotropy may be defined as the direct measure of the effectiveness of asymmetric photochemical reactions; meaning that for photochemical reactions, ee is a function of $g(\lambda)$, where higher g values will lead to higher enantioenrichments.^{29,137,147} After calculating the specific g values at varying wavelengths, amino acids such as alanine, leucine, and isovaline were predicted to yield enantiomeric excesses ranging from 2 to 5% in quantitative asymmetric photolytic reactions (99.999% extent of reaction, ξ);^{137,148} those values are in agreement with the L-enantiomeric excesses found for amino acids present in interstellar ice analogs^{61,140,149,150} and those found in carbonaceous chondrites.^{20,23,49} Similarly, the anisotropy values measured for aliphatic chiral monoamines, monoalcohols, and monocarboxylic acids¹⁵¹ suggested that these compounds would yield low (0.1 to 0.5%) enantiomeric excesses after complete asymmetric photolysis, which is in agreement with enantiomeric measurements of meteoritic chiral amines and carboxylic acids.^{152–156} From those same experiments,¹⁵¹ the anisotropy values of a prochiral epoxide (S-glycidol, -3%) and a vicinal diol (2S,3S-butanediol, 0.4%) were significantly larger than that of an isolated diol (S-1,3-butanediol, 0.2%). These results are consistent with the varying levels of ee that have been observed in some meteoritic polyols (Table 2). Although much work remains to identify and measure the enantiomeric composition of these diols and other chiral organic species in meteorites, the anisotropy factor of various chiral molecules determined as a function of specific UV-CPL wavelengths can be a useful tool to predict which organic compounds in meteorites or other extraterrestrial samples would be expected to possess enantiomeric excesses.

In an early study, it was demonstrated that leucine enantiomeric excesses of up to 2.5% could be generated with the destruction of ~75% of the starting leucine by asymmetric photolysis with UV-CPL (212.8 nm).¹⁴⁹ In another study, the synthesis of amino acids by the gas-phase proton irradiation of carbon monoxide, ammonia, and water yielded alanine that was then subsequently enantioenriched up to 0.5% by exposure

to UV-CPL.¹⁵⁷ More recently, there has been a systematic campaign to understand the effects of UV-CPL on amino acids and related compounds, such as amines, sugars, and aldehydes and ketones, both during molecule synthesis and destruction.¹³⁶ These studies demonstrated that the chirality and extent of induced enantiomeric excess are dependent on the helicity, wavelength, and flux of irradiating UV-CPL.^{158,159} In one study, 16 amino acids (24 amino acids counting individual enantiomers) containing two to five carbon atoms were produced by the irradiation of methanol, water, and ammonia ice at 10.2 eV.¹⁵⁹ Of these amino acids, five (alanine, 2,3-diaminopropanoic acid, 2-aminobutanoic acid, valine, and norvaline) were present in sufficient abundance to have their enantiomeric compositions accurately measured. For each of those five amino acids, enantiomeric excesses of 0.2% to 2.5% were induced, and importantly, all of the enantiomeric excesses were in the same direction (all L- or all D-excesses) for a given UV light polarization. Although aspartic acid was produced in these experiments, it was not sufficiently abundant for enantiomeric measurements to be made, and thus it has not yet been experimentally demonstrated that aspartic acid enantiomeric excesses could be generated by UV-CPL, though it seems plausible. Isovaline was also not detected in these experiments, but its behavior under UV-CPL irradiation has been well characterized.^{160,161} Interestingly, in contrast with α -hydrogen amino acids, the direction of enantiomeric excesses induced in isovaline does not vary with irradiation wavelength, but only with light polarization. However, UV-CPL-induced enantiomeric excesses observed thus far tend to be significantly smaller than the observed enantiomeric excesses in meteorites, meaning that if UV-CPL is responsible for breaking chiral symmetry, there must have been a process to amplify these small chiral excesses. Other chiral symmetry breaking mechanisms at the level of elementary particle interactions (e.g., parity violation in the weak interaction) have also been proposed.¹⁶²

A variety of enantioenrichment mechanisms for amino acids and other chiral molecules have been suggested and are discussed in detail elsewhere.^{3,30,163–166} Here we focus on one promising mechanism for amplifying enantiomeric excesses that is based on the behavior of chiral molecules during phase transitions, such as from solid/vapor and solid/solution transitions. For example, Viedma and others have demonstrated that sublimation of amino acids could be used to preferentially separate an enantiomer present in excess away from a racemic solid.^{167–169} Viedma, Blackmond, Breslow, and others have also demonstrated that this phenomenon can be exploited in the solution phase.^{170–174} Serine, which exhibits a very high eutectic enantiomeric excess of >99% in water at 25 °C, provides a virtually enantiopure solution from a nearly racemic sample under solid–liquid equilibrium conditions.³² The physical separation of enantiomers can be applied to most of the 20 proteinogenic amino acid and is based on them forming racemic crystals (D and L) that have lower solubility (or vapor pressures) than enantiopure solids (D or L) of those same compounds.^{32,175} If one enantiomer is present in excess over the other, that will be the predominant molecule chirality in the solution or gas phase above the solid. The enantioenriched gas or liquid phase can then be moved away, leaving behind the racemic solid phase material. Other amino acids preferentially form enantiopure (conglomerate) crystals, meaning that enantioenriched pools of amino acids cannot be formed by this process. However, if one enantiomer

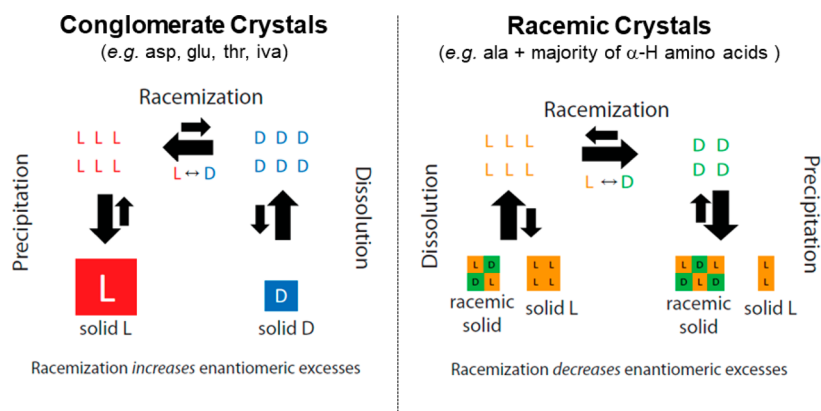


Figure 3. Illustration of the solid–liquid phase behavior of amino acids that form conglomerate (left) and racemic (right) solid crystals. Amplification of a small initial excess (in this case, the L-enantiomer) for conglomerate amino acids such as aspartic acid and glutamic acid will occur through racemization and precipitation. Modified from a figure published in *Primitive Meteorites and Asteroids: Physical, Chemical, and Spectroscopic Observations Paving the Way to Exploration*, D. P. Glavin, C. M. O’D. Alexander, J. C. Aponte, J. P. Dworkin, J. E. Elsila, and H. Yabuta, *The Origin and Evolution of Organic Matter in Carbonaceous Chondrites and Links to Their Parent Bodies*, Page 234, Copyright Elsevier (2018).

is present in excess over the other, it is possible that a different enantioenrichment process can occur. If one enantiomer happens to form larger crystals than the other enantiomer (because there is more of it, for example), the larger crystals will dissolve more slowly than smaller crystals. The solution phase will be racemic, but if there is enough time to epimerize molecules in the solution phase prior to recrystallization, it is possible to convert nearly all of the minor enantiomer to the major enantiomer, which has been experimentally demonstrated, yielding true enantiomeric enrichment.^{171,176–178} An illustration of the solid–liquid phase behavior of amino acids that form conglomerate and racemic solid crystals is shown in Figure 3.

With respect to the amino acids found in enantiomeric excess in meteorites, both aspartic acid and isovaline form enantiopure conglomerate crystals, whereas isoleucine forms racemic crystals. Thus, isoleucine could undergo physical separation to yield both enantioenriched and racemic pools of amino acids. Isovaline and aspartic acid, on the other hand, could have experienced some interconversion of their D-enantiomers into L-enantiomers via racemization within their parent asteroids. A caveat to this is that isovaline, as an α -methyl amino acid, is much more difficult to epimerize than α -hydrogen amino acids. The most plausible mechanism for epimerization of isovaline in the meteorite parent body would have been radioracemization.¹⁷⁹ Nevertheless, conglomerate crystal amplification during parent body alteration remains arguably the most plausible asteroid-relevant mechanism for amplification of UV-CPL-generated enantiomeric excesses. The fact that only L-amino acid excesses with a single asymmetric carbon have been observed in meteorites within analytical uncertainties suggests that the origin of life on Earth or elsewhere in our Solar System could have been biased toward L-amino acid homochirality from the very beginning. It is also likely that similar amino acid amplification mechanisms occurred in ancient sedimentary environments on the early Earth where prebiotic amino acid mixtures could be exposed to multiple wet–dry cycles.¹⁸⁰ It has even been suggested that spontaneous resolution of conglomerates is the most likely terrestrial mechanism for the origin of homochirality on the early Earth.¹⁸¹ Finally, given the preponderance of evidence for prebiotic L-amino acid excesses in primitive meteorites, it could

be expected that if life originated elsewhere in our Solar System from similar starting materials, it would be based on the same handedness as life on Earth.

3. POLYOLS IN METEORITES AND LIFE

3.1. Distributions and Formation Pathways

Terrestrial biology relies on homochirality not only in amino acids but also in sugar compounds (polyols). Sugars make up approximately 2% of the total dry mass of a prokaryotic cell,⁷¹ so their abundances relative to amino acids (55% dry mass of cell⁷¹) are much lower in terrestrial biological samples. Sugars are fundamental components of nucleic acids (D-ribose in RNA and D-2-deoxyribose in DNA), are found in coenzymes as metabolic intermediates, and are the monomers of structural and energy storage polymers. The majority of biological sugars and their derivatives contain higher abundances of the D forms relative to the L forms.

Polyols are aliphatic compounds with three or more hydroxyl groups. A few examples of three-carbon polyols are given in Figure 4. By convention, sugar-related compounds are

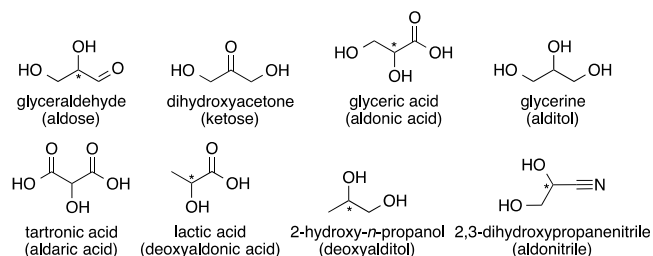


Figure 4. Example structures of 3-carbon polyols and related compounds. Carbons with an asterisk represent chiral centers. All but the deoxy alditol and aldonitrile have been detected in meteorites.

polyols where every carbon is bound to an oxygen, except in the case of so-called deoxy sugars that have one or more alcohols replaced by a methylene. Sugars are polyols with either an aldehyde (aldose) (glycolaldehyde (HO–CH₂–CHO) is categorized as the simplest aldose, though it is not a polyol and is achiral.) or ketone (ketose). These are in equilibrium with the geminal diol or hydrate. Sugar acids

Table 3. Comparison of the Stable Isotopic Values of Amino Acids and Sugars from Terrestrial and Extraterrestrial Sources^a

Isotope ratio	Terrestrial amino acids ^{220–222}	Terrestrial sugars ^{207,230,231}	Murchison (CM2) amino acids ^{223,224,234,235}	GRA 95229 (CR2) amino acids ^{89,152,236}	LAP 02206 (CV3) amino acids ⁷⁰	Murchison polyols ^{207,229}
$\delta^{13}\text{C}$ (‰VPDB)	–70 to +11	–52 to –5	–6 to +52	–18 to +51	~–25 ^f	+5 to +82
$\delta^{15}\text{N}$ (‰AIR)	–20 to +30	n/a	+37 to +184	+77 to +139	nr	n/a
δD (‰VSMOW)	–270 to +66 ^b	nr	+180 to +3419	+868 to +7245	nr	nr

^an/a = not applicable since there is no nitrogen in compound for isotopic measurement. nr = data not reported. ^bValues are for bulk organic hydrogen, not just amino acids, in a variety of materials. ^cOnly achiral *n*-*o*-amino acids were measured.

(aldonic acids) resemble aldoses, except that they have a carboxylic acid instead of an aldehyde, and sugar diacids (aldaric acids) have an additional acid group on the terminal carbon. Sugar alcohols (alditols), a class of polyols without any carbonyls, provide an energy source in terrestrial biology, are found in carbonaceous meteorites, and are commonly produced through the hydrogenation of sugars. Sufficiently large carbonyl-containing sugars frequently cyclize into 5- or 6-membered rings (furanose and pyranose, respectively for sugars) and sugar acids cyclize into lactones under aqueous conditions. Larger polyols can have multiple chiral centers creating numerous diastereomer isomers. Naturally, other more complicated branched structures or those with multiple functional groups are also possible and found in terrestrial biology (e.g., sialic acids, glucuronic acid, sulfoquinovose, glucosamine, ascorbic acid, etc.) as well as dimers and larger polymers.

Butlerow (1861) first demonstrated and many others have investigated the formose reaction^{182–187}—the polymerization of formaldehyde under aqueous basic conditions in the presence of divalent metal ion (typically calcium). It was even proposed as a food source for astronauts¹⁸⁷ and cosmonauts,¹⁸⁸ though the toxicity of the complex and racemic mixture proved to be an obstacle.¹⁸⁷ The formose reaction produces a wide array of racemic sugars,^{185,189} and numerous variations of the reaction have been explored under conditions with varying relevance to meteorite parent body conditions, leading to different product distributions.^{186,190–194} Most studies have focused on the formation of aldoses, especially ribose, with only minor attention on the aldonic acids, aldaric acids, and alditols; the abundances of these products depend on whether the reaction conditions permit Cannizzaro reactions, an aldehyde redox reaction producing the acid and alcohol, which is usually viewed as a dead-end to the desired aldose.¹⁹⁰ Thus, comparisons with the breadth of meteoritic polyols have been limited. Furthermore, the standard formose reaction produces insoluble organic material that is spectrally similar to meteoritic insoluble organic material¹⁹⁵ and could plausibly be related to it.

Polyols have also been synthesized under nonformose reaction conditions, such as simulated interstellar or icy body conditions where water, methanol, and ammonia ices were photolyzed at low temperature to produce a suite of two- to six-carbon aldoses, ketoses, aldonic acids, and alditols^{196,197} or their deoxy variants from photolysis of ices without ammonia.¹⁹⁸ Aldoses in particular are well-known to be unstable in the presence of amines (Mannich reaction) and general bases,¹⁹⁹ and follow a complex decomposition pathway. Even at neutral pH, the half-life of ribose is 73 min at 100 °C and 44 years at 0 °C.¹⁹⁹ Small aldoses efficiently dimerize, oxidize to aldonic acids, and react with cyanide to form aldonitriles (sugar nitriles). These serve as intermediates

in reactions similar to Kiliani–Fischer or Ruff degradation reactions^{200,201} to form a complex network of species. It is thus unsurprising that the detection of free sugars has been difficult in meteorites since these samples have been exposed to varying degrees of hydrothermal alteration on their parent bodies.

The most comprehensive search for various polyols in meteorites has been conducted by Cooper et al.,^{202,203} resulting in the discovery of a suite of aldonic acids and alditols, including several aldonic acids with significant D-enantiomeric enrichments (Table 2). As with amino acids, sugar derivatives in meteorites typically follow a decreasing abundance with increasing number of carbon atoms. The comparison of meteorite petrographic type with polyol abundance and enantiomeric excess has elicited speculation and predictions, but as of yet none have been confirmed.²⁰³ Since aldoses are highly susceptible to oxidation or other degradation, extensive testing of standards must be performed to understand the system.²⁸ The methods currently used to extract and analyze polyols in meteorites are complex²⁸ and not yet readily adaptable for spaceflight. In short, crushed meteorite samples are extracted in ambient temperature water under agitation and inert atmosphere followed by repeated cycles of centrifugation and washes. Combined washes were acidified, concentrated, purified via cation exchange resin, concentrated and made alkaline and then further purified on anion exchange resins and dried. Small compounds were analyzed as their trimethylsilyl derivatives and others as their acyclic isopropyl ester/trifluoroacetyl ester derivatives via gas chromatography.²⁸ Stable carbon isotopic measurements of the sugar derivatives can also be made by gas chromatography isotope ratio mass spectrometry.²⁸ The derivatization protocols used require stepwise reactions and carefully controlled drying steps. The level of operator care, the number of transfers, and number of steps required to analyze polyols makes their analysis by robotic spacecraft instrumentation impractical with current technologies (discussed further in Section 6).

The extraction and identification of aldoses such as ribose, xylose, arabinose, and lyxose in carbonaceous meteorites by gas chromatography mass spectrometry have proven to be a challenge,²⁰⁷ and even these analyses lack enantiomeric separation due to the complexity of the samples and relatively low sugar abundances. In all cases of meteoritic polyol detection, further work is needed to understand how their distribution and enantiomeric compositions vary between meteorite lithologies and across meteorite petrologic types. A more complete characterization of polyols in carbonaceous meteorites as has been done for amino acids will be required to understand the abundances of the terrestrially rare, branched, or other chemically related (nitrile-, thio-, amino-sugars, etc.) species to further elucidate the chemistry leading to their syntheses and associated enantiomeric excesses and isotopic

compositions needed to distinguish abiotic from biotic carbohydrates.

3.2. Aldonic Acid Enantiomeric Excesses in Meteorites

Aldoses, ketoses, aldonic acids, and alditols often exhibit at least one chiral center, and many are diastereomers. Surprisingly, D-excesses in aldonic acids in the CM2 Murchison meteorite range from 0% (racemic) in glyceric acid and all alditols up to 100% (enantiopure) for six-carbon acids and are believed to be nonterrestrial in origin based on some heavy carbon isotopic measurements and comparisons to sugars found in terrestrial soils. Like amino acids, no “unnatural” (in this case L) aldonic acid enrichments in meteorites have been observed, with the exception of a report of lactic acid (%L_{ee} = 3 to 12; Table 3) where 70%–80% of lactic acid was lost during meteorite extraction and workup.²⁰⁶ Such large analyte losses could lead to fractionation and even enantiomeric ratio changes that could complicate data interpretation. However, lactic acid is the hydroxy acid analog of alanine, so an L-lactic acid excess may derive from the unknown mechanism leading to L-alanine excesses in some samples of the CM2 Murchison meteorite. Likewise, an abiotic mechanism to produce enantiopure D- or L-sugars is not known. In addition, the mechanism to preferentially enrich larger over smaller polyols is also not known,²⁰³ but the observed enantioenrichment of larger polyols in meteorites may be associated with amplification via polymerization reactions as has been suggested by Sandars.¹⁶⁵ The lower aqueous solubility of polyols relative to amino acids makes the crystallization enrichment methods previously discussed more difficult to invoke since you need a saturated solution.

It is possible that the coexistence of L-amino acid and D-aldonic acid excesses found in meteorites is not a coincidence. A number of mechanisms to transfer chiral preference between sugars and amino acids have been investigated. Sugar syntheses in the presence of short L-peptides²⁰⁸ and L-amino acid excesses have been observed to enrich small D-sugars^{209–212} and vice versa.³³ Though provocative, the prebiotic relevance of these reactions has been vigorously discussed in the literature. It is also possible that the chiral interaction of carbohydrates and amino acids has been important in their macromolecules^{9,213} or even potential pre-RNA precursors.²¹⁴

Studies of meteorites across different petrologic types both with and without amino acid and carbohydrate enantioenrichments may be necessary to understand if there is coincidence, correlation, or causation of chirality. However, comparisons of glycerol to erythritol ratios across CM and CR meteorites has not produced an obvious correlation.²⁰³ In stark contrast to meteorites or experimental systems, terrestrial biology shows remarkable specificity for the stereochemistry of all positions in sugars. This leads to selective uses of small numbers of polyol structural isomers and D-enantiomers for sugars similar to the isomeric selectivity and L-enantiomer preference used for amino acids in biology. These are likely the result of extensive competition in a complex ecosystem²¹⁵ and may be associated with full exploitation of biological niches, which would be readily detected by other means. Though there are notable exceptions for specific structural carbohydrates (e.g., 5–10% L-arabinose in some plants).²¹⁶

Informational macromolecules employ only two closely related aldoses (ribose and deoxyribose), and the presence of chiral impurities is detrimental to polymerization.²¹⁷ Contemporary (and probably ancient)²¹⁸ terrestrial biology also

employs a small and chemically related range of sugars in coenzymes, metabolic intermediates, and structural material. It is therefore not unreasonable to expect extraterrestrial organisms to have similar specificity over the chirality and regiochemistry of any carbohydrates it uses. However, the limited state of knowledge of the prebiotic chemical diversity of polyols across multiple meteorite types, our lack of a clear understanding of the mechanism of formation of the large, nonterrestrial D-enantiomeric enrichments that have been observed for some aldonic acids in meteorites, as well as their known chemical fragility and analytical measurement issues provide a significant challenge for *in situ* spaceflight measurements of trace polyols in extraterrestrial samples and the use of chiral asymmetry of polyols as a robust chemical biosignature.

4. ISOTOPIC MEASUREMENTS OF AMINO ACIDS AND POLYOLS

4.1. Terrestrial vs Extraterrestrial Stable Isotopic Ratios

Stable isotopic ratios reflect the formation mechanisms and environments of compounds and can thus serve as an important means of understanding the origins of observed enantiomeric excesses. In particular, the ¹³C/¹²C, ¹⁵N/¹⁴N, and D/H ratios of compounds observed in extraterrestrial environments can be used to determine whether these compounds have a biological (terrestrial contamination) or abiotic (extraterrestrial origin). Biological fractionation processes (e.g., photosynthesis) used by terrestrial life result in a strong preference for lighter isotopes,²¹⁹ for example, although amino acids isolated from a range of microorganisms possess δ¹³C values that reflect differences in metabolic pathways, all are relatively depleted in ¹³C (Table 3).²²⁰ Similarly, biological amino acids favor ¹⁴N over ¹⁵N and H over D (Table 3).^{221,222} The preference in terrestrial biology for these lighter isotopes is known as the “kinetic isotope effect”, and the resulting departure from the equilibrium isotopic ratios of a given planet can be a powerful signature for life.

In contrast to biology, meteoritic amino acids tend to be enriched in heavy isotopes^{96,223–225} (Table 3). This fact has typically been interpreted as reflecting formation of the amino acids or their precursors in cold, interstellar environments. However, not all meteoritic amino acids show heavy isotope enrichment. For example, the *n-ω*-amino acids detected in thermally altered CV and CO meteorites are depleted in ¹³C compared to amino acids in CM and CR chondrites, with δ¹³C values falling within terrestrial ranges.⁷⁰ The light carbon isotopic ratios of amino acids observed in CV and CO chondrites may reflect a higher temperature gas-phase formation, such as FTT reactions, that could occur under different conditions than those that formed amino acids in CM and CR chondrites under lower temperature aqueous conditions; FTT reactions have been shown to produce ¹³C-depleted hydrocarbons.^{226–228} Additionally, it is also possible that the formation of *n-ω*-amino acids having isotopically light values resulted from an unknown, yet specific, amount of starting materials (e.g., CO, HCN, NH₃, H₂O, etc.) that accreted inside the parent bodies of thermally altered chondrites which were not present or were present at different concentrations inside various types of parent bodies. It is important to note, however, that the isotopically light amino acids detected in the thermally altered meteorites are all achiral; all chiral amino acids present in meteorites are

isotopically enriched in ^{13}C , ^{15}N , and D relative to terrestrial biology (Table 3). Therefore, measurement of a light isotopic composition (i.e., depleted in ^{13}C , ^{15}N , and D) of chiral amino acids in an extraterrestrial sample might point to a biological origin.

The polyols that have been detected in the Murchison meteorite, including ribose,²⁰⁷ are also enriched in ^{13}C compared to terrestrial sugars^{207,229–231} (Table 3). H-isotope measurements of terrestrial sugars or polyols in meteorites have not been reported. Nevertheless, the ^{13}C enrichment in meteoritic polyols may be due to similar reasons as those cited for amino acids, such as formation from enriched interstellar precursors or formation in cold environments.

4.2. Isotopes and Enantiomeric Excesses

In addition to providing information about the formation mechanisms of meteoritic compounds, stable isotopic ratios can also help in understanding observed enantiomeric excesses of chiral molecules. Chiral compound-specific isotopic techniques allow for the measurement and comparison of isotopic ratios in individual D- and L-enantiomers. Isotopic measurements of individual enantiomers can distinguish between biological and abiotic origins of chiral asymmetry.

As discussed in Section 2.3, the first reported L-enantiomeric excesses of a meteoritic amino acid were made for alanine in the Murchison meteorite, with an L-alanine enrichment of ~33% over D-alanine.²²⁴ Because alanine is a protein amino acid, one likely cause for this excess would be terrestrial L-alanine contamination of the meteorite. In addition, since alanine forms racemic crystals and is therefore unlikely to undergo enantiomeric enrichment via crystallization,³² the detection of a 33% L-alanine excess in an extraterrestrial sample without any additional isotopic information could easily be misinterpreted as a biosignature. However, carbon and nitrogen isotopic ratios of the two alanine enantiomers in Murchison showed similarly enriched values for both, strongly suggesting an extraterrestrial, nonbiological origin for the L-excess.^{96,224,232} Similarly, L-enantiomeric excesses of aspartic acid in the Tagish Lake meteorite of up to 60% that could be misinterpreted as biology were shown to be of nonterrestrial, abiotic origin through compound-specific isotopic measurements that showed similarly enriched $\delta^{13}\text{C}$ values of +24‰ (D-aspartic) and +29‰ (L-aspartic). If terrestrial biological contamination was the source of the L-aspartic acid excess in the Tagish Lake meteorite, the $\delta^{13}\text{C}$ value of L-aspartic acid should have been significantly lower than the $\delta^{13}\text{C}$ value of D-aspartic acid, and this was not observed.²⁶

This use of isotopes to understand enantiomeric excesses can be extended to applications for biosignature detection and recognition. For this purpose, the context of isotopic measurements and differences between stable isotope ratios in enantiomers is essential. As described above with the Tagish Lake meteorite, similar isotopic ratios for two enantiomers suggest a similar origin (i.e., abiotic or biotic). Racemization does not appear to create significant carbon or nitrogen isotopic fractionation of neutral amino acids in biological proteins, although it has been speculated that partial hydrolysis of acidic protein amino acids in fossil shells can lead to small (a few per mil) differences in the carbon and nitrogen isotopic ratios with the L-enantiomer slightly enriched in ^{13}C and ^{15}N relative to the D-enantiomer.²³³ If an enantiomeric excess is observed with a corresponding significant difference in isotopic ratio, particularly with a lighter isotopic signature in the excess

enantiomer, this would be difficult to explain abiotically and could be an indicator of a biological origin of the excess. Isotopic differences between structurally similar amino acids may also indicate a biogenic origin, although in this case it would be important to consider potential differences in abiotic formation mechanisms as well.

The isotopic composition of organic material relative to the inorganic material in the sample may also be a marker of biological origin, although again this must be interpreted carefully. A lighter isotopic composition of organics compared to inorganics may result from biological fractionation, but this requires understanding of the isotopic composition of various reservoirs and food sources, as well as knowledge of metabolic processes. For example, it is possible that microorganisms in a sample could become isotopically enriched compared to the typically light isotopic compositions that are characteristic of terrestrial biology by incorporating ^{13}C enriched carbon from inorganic material (e.g., carbonate) or organic matter of exogenous, nonbiological origins in the sample. Although the isotopic composition of organics on its own may not definitively point to a specific origin, the combination of compound-specific isotopic composition with the context of isomeric and enantiomeric distributions can still serve as a powerful biosignature.

5. PROPOSED FRAMEWORK FOR USING CHIRALITY AS A BIOSIGNATURE

Based on our current understanding of both terrestrial biochemistry and abiotic chemistry from carbonaceous meteorites and laboratory experiments, we propose three criteria that must be met to establish a credible biological origin of asymmetric amino acids or polyols detected in extraterrestrial environments. These criteria serve as a guide for a set of measurements that should be made on future life detection missions to establish the origin of any chiral asymmetry detected and expand beyond the search for >20% enantiomeric excesses as a biosignature proposed previously.²⁵ Chiral amino acids and sugars detected in an extraterrestrial sample that show enantiomeric excess (L > D or D > L) display structural isomer preference, are enriched in the lighter isotopes (^{12}C , ^{14}N , and H) relative to inorganic material in the same sample as illustrated by the overlapping region in the Venn diagram (Figure 5), would provide the strongest evidence for a biological origin. It should be re-emphasized that chiral asymmetry of amino acids, sugars, or other chiral molecules in an extraterrestrial sample is only one of several biosignatures that would likely be required to establish unambiguous evidence of extraterrestrial life.

5.1. Detection of Chiral Asymmetry

It has been proposed that the detection of enantiomeric excesses of >20% in multiple amino acid types would provide a high likelihood of being an extraterrestrial biosignature provided that terrestrial contamination could be ruled out.²⁵ This enantiomeric excess threshold is based on the largest L-excesses of the α -dialkyl amino acid isovaline that have been found in carbonaceous meteorites.²⁴ However, we argue that it is best not to specify an absolute enantiomeric excess threshold to meet a biosignature requirement since several nonterrestrial amino acids and aldonic acids in meteorites of nonbiological origin have enantiomeric excesses that greatly exceed 20%. In addition, any chiral amino acids or sugars from extinct life could have racemized or decomposed significantly over time,

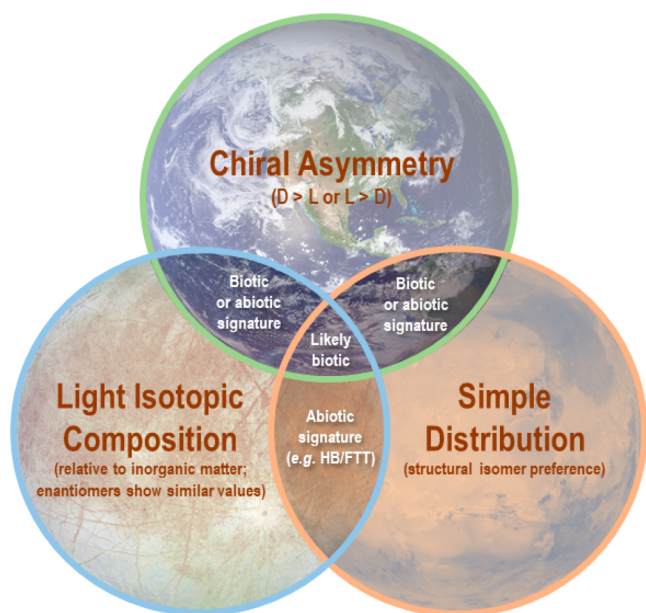


Figure 5. Venn diagram showing the three key molecular attributes of amino acids and sugars (chiral asymmetry, simple distribution with structural isomer preference, and a light isotopic composition) needed to establish a likely biotic signature. Images adapted from NASA - NSSDC, ID number: P-48040; NASA/JPL-Caltech/USGS, ID number: PIA00407; NASA/Visible Earth – MODIS, The Blue Marble.

erasing any initial homochiral signatures. Furthermore, depending on the specific amino acids and sugars displaying the enantiomeric excesses and their isotopic compositions, abiotic enantioenrichment mechanisms such as asymmetric autocatalysis³⁰ or amplification during crystallization³² may also be possible and could lead to false positives. One strategy

to identify amino acids of biological origin would be to search for enantiomeric excesses present in known racemic-crystal-forming amino acids that are usually present as racemic or near racemic mixtures in meteorites such as alanine, valine, β -amino-*n*-butyric acid and whose enantiomeric excesses do not appear to change significantly as a result of nonbiological processes.²⁶

Several hypothetical relative enantiomeric abundances of amino acids covering the range of possibilities that could be measured in an extraterrestrial sample are shown in Figure 6. By far, the most intriguing possible evidence of extraterrestrial biotic chemistry would be the detection of D-amino acid excesses indicating extant (D \gg L) or extinct (D > L) life, since as yet no D-enantiomeric excesses of amino acids with a single asymmetric carbon have been found in meteorites. This would be a very exciting discovery, suggesting a biological origin and perhaps a second, independent origin of life in our Solar System. Similarly, the detection of enantiomeric excesses of a suite of L-sugars in an extraterrestrial sample would also provide evidence of biology that evolved independently from Earth's. However, based on our current knowledge of prebiotic organic chemistry in meteorites and the potential mechanisms for chiral symmetry breaking during Solar System formation, a case can be made that the probability of finding amino acids and sugars with the opposite handedness as life on Earth is very low, given that the prebiotic inventory of these molecules in our Solar System from which life could emerge appears to have been biased toward L-amino acids and D-aldehydic acids from the very beginning. In any case, although the discovery of such excesses would be suggestive of life, it would be important to understand their context, particularly through measurements of isomeric distributions and isotopic ratios.

Large L-amino acid excesses (L \gg D, $L_{ee} > \sim 60\%$) could also provide an indication of extant but rare or recently extinct biology, provided that the amino acids displaying the L-

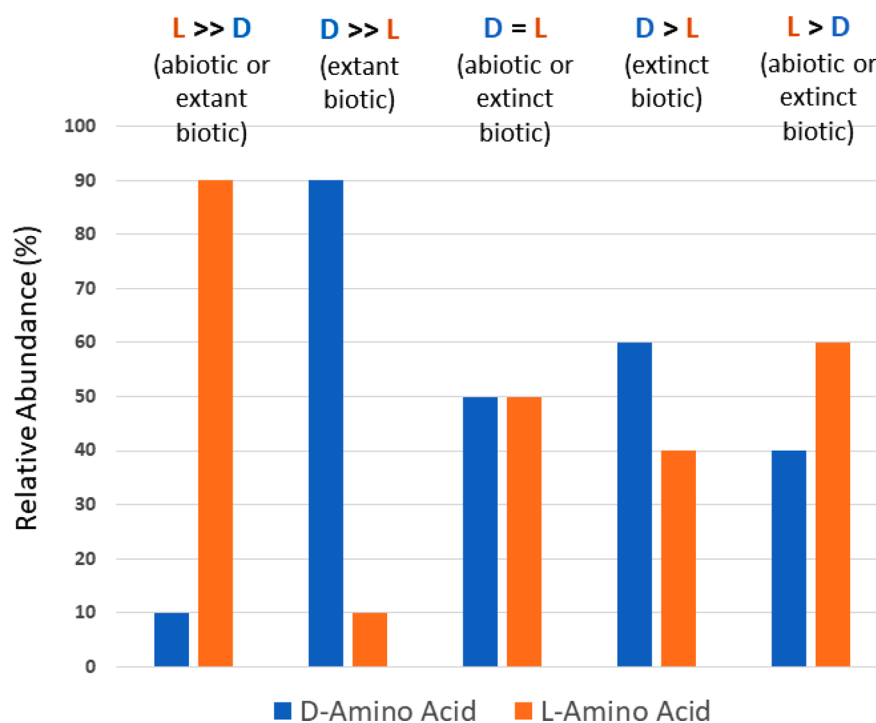


Figure 6. Some hypothetical relative abundances of D- and L-amino acid enantiomers and their possible biotic or abiotic origins.

enrichment are not among the amino acids that are also known to have large L-excesses formed by abiotic processes in meteorites. Multiple amino acids with L- or D-enantiomeric excesses that correlate to racemization rates, rather than plausible enrichment mechanisms (e.g., conglomerate crystallization) would be stronger evidence of extant or recently extinct life. For example, first order rate constants (k) for the interconversion of the L- and D-enantiomers of several protein amino acids including isoleucine, alanine, and aspartic acid have been measured for both wet and dry (desiccated) lake sediments with the following equation: $\ln[(1 + D/L)/(1 - D/L)] - \text{constant} = 2 \cdot k \cdot t$, where t = time and D/L is the amino acid enantiomeric ratio.¹⁰⁵ Isoleucine epimerization has one of the slowest amino acid racemization rates, while alanine racemization is about 3× faster and aspartic acid is approximately 7–9× faster than isoleucine.^{105,112} If we assume that these three protein amino acids were biological in origin and initially mostly L prior to extinction, then racemization of the L-amino acids to D-amino acids over time would lead to different enantiomeric ratios with D/L aspartic acid > D/L alanine > D/L isoleucine as has been observed in marine sediments.¹⁰⁵ In contrast, the enantiomeric ratios of the same amino acids produced by nonbiological processes in meteorites typically display a different order with D/L alanine > D/L aspartic acid \sim D/L isoleucine as has been observed in Murchison and other carbonaceous meteorites (Table 1). However, these observations are general trends under modern terrestrial ocean conditions. It would be crucial to experimentally measure the different racemization and decomposition rates of target compounds under the relevant local extraterrestrial conditions over time (e.g., temperature, pH, activity, radiation, etc.) to assess the likelihood of a biological origin.

Smaller L-amino acid excesses ($L > D$, $L_{ee} < 20\%$), even if present in multiple amino acid types, would be a much less convincing signature of extinct life, since both abiotic chemistry and terrestrial L-amino acid contamination would have to be ruled out first. Establishing the origin of racemic mixtures ($D = L$) of amino acids or sugars would be extremely challenging since both abiotic and extinct biotic origins would be possible. Although the enantiomeric ratios of ribose recently detected in carbonaceous meteorites²⁰⁷ and ribose and other aldopentoses synthesized in interstellar ice analog irradiation experiments¹⁹⁷ have not yet been measured, the detection of large D-aldonic acid excesses in the CM2 Murchison meteorite and the CR2 GRA 95229 meteorites of nonbiological origin that range from 33 to 100%²⁸ presents a significant challenge in the search for evidence of D-sugar or D-sugar acid excesses of biological origin. One exception would be the detection of large enantiomeric excesses of D- or L-glyceric acid, a common biological three carbon sugar acid present as D-glyceric acid in terrestrial biology that is also the most abundant sugar acid of nonbiological origin in the Murchison meteorite but is not present in enantiomeric excess above analytical uncertainty within Murchison.²⁸

5.2. Simple Distribution

Since biochemistry on Earth has evolved to use only ~ 20 coded amino acids in proteins with the same isomeric structure (α) and chirality (L), despite the likely presence of a much broader diversity of prebiotic amino acids that would have been available on the early Earth, the identification of a simple distribution of amino acids with a strong isomeric preference

could be a signature of biochemistry. There is one important caveat here. At elevated temperatures and pressures, abiotic chemistry (e.g., HB/FTT synthesis, hydrothermal reactions) can also result in a simple distribution of amino acids with structural isomeric preference and light carbon isotope values.^{14,70} However, even under these conditions, the n - ω -amino acids produced are all achiral, so the detection of a simple distribution of chiral amino acids with isomeric preference could be a biosignature. It is also worth noting that other abiotic chemical reactions at lower temperatures and pressures, such as those that occurred in the Miller spark discharge experiments, also resulted in the synthesis of a limited set of both achiral and chiral amino acids (34 amino acids identified to date, Table 1); however, only racemic amino acid mixtures were produced in these experiments and the nonprotein α -, β -, and γ -amino acids synthesized did not display any isomeric preference, with relative abundances similar to those found in meteorites.^{15–17}

In summary, the detection of a simple distribution of chiral amino acids displaying isomeric preference in an extraterrestrial sample could be a strong indicator of extinct or extant biotic chemistry, especially if large enantiomeric excesses and light stable C-, N-, and H-isotopic compositions are also observed.

5.3. Isotopic Composition

Stable hydrogen, carbon, and nitrogen isotopic ratios (δD , $\delta^{13}C$, and $\delta^{15}N$) of organic compounds and their enantiomers can reveal important information about their origin and formation pathways. The isotopic compositions of amino acids and sugars derive from both their precursor molecules and their formation environments and pathways. As previously discussed, many extraterrestrial chiral amino acids and aldonic acids found in carbonaceous meteorites are typically enriched in heavy isotopes (D, ^{13}C , and ^{15}N) relative to biologically derived terrestrial compounds which is a reflection of the cold environments in which these meteoritic compounds or their chemical precursors were formed.^{223,234,237} The D/H and $^{15}N/^{14}N$ ratios of amino acids in meteorites fall well outside the terrestrial range and in most cases the $^{13}C/^{12}C$ ratio of meteoritic amino acids is also higher than what is found in terrestrial biology (Table 3). Organic compounds found in biology are depleted in ^{13}C , ^{15}N , and D which can be attributed to kinetic effects during biological reactions (e.g., photosynthesis, bacterial processes) where the lighter isotope is enriched in the reaction product relative to the substrate.²³⁸ Assuming similar kinetic effects would act to fractionate isotopes toward lighter isotopic compositions in an extraterrestrial biotic system, then the detection of nonequilibrium isotopic compositions of amino acids or polyols that are depleted in ^{13}C , ^{15}N , and D in an extraterrestrial sample relative to the inorganic substrate, could be an important marker of biochemistry.

One caveat is that some straight-chained n - ω -amino acids found in thermally altered meteorites and possibly formed by FTT processes also have light carbon isotope values ($\delta^{13}C \sim -25\%$) that fall within the known terrestrial amino acid range of $\delta^{13}C = -70$ to $+11\%$ (Table 3). However, these n - ω -amino acids are all achiral and not likely to be predominant in extraterrestrial biochemical systems that require homochiral molecules. Moreover, all of the nonbiological chiral amino acids measured in meteorites to date have isotopic compositions that are heavily enriched in ^{13}C , ^{15}N , and D

relative to terrestrial biology, and their enantiomers have similar isotopic values. This is an important observation since it implies that the detection of isotopically depleted chiral amino acids or sugars found in an extraterrestrial sample relative to the inorganic substrate would be a biosignature. Finally, if these chiral amino acids and sugars also possessed large enantiomeric excesses, the presence of an extant biochemistry could be inferred.

Thus, both the molecular and environmental context of the analyte must be understood to use isotopic ratios as biomarkers.

6. RELEVANT PAST, CURRENT AND FUTURE MISSIONS

In situ and sample return missions to high priority Solar System targets such as comets, primitive asteroids, Mars, Ceres, and the outer planet ocean worlds will continue to contribute to our knowledge of the origin and evolution of organic material, including a much deeper understanding of the organic chemistry that preceded and/or evolved independently from life on Earth. Robotic missions can dramatically reduce the terrestrial organic contamination of a sample by controlling and carefully documenting the sample exposure history to contaminants²³⁹ in a way that is impossible with meteorites that are rapidly contaminated after their fall to Earth. Sample return missions enable scientists to use state-of-the-art ground-based analytical instruments to analyze the returned samples without the resource constraints (mass, power, volume, data rate, etc.) inherent to *in situ* analyses. Moreover, ground-based measurements give scientists an enormous amount of flexibility to make changes to analytical procedures or instrument parameters to fine-tune measurements and utilize new technologies over decades, which are not possible for *in situ* spaceflight missions.

Sample return missions from comets such as NASA's Stardust mission and from carbonaceous asteroids including JAXA's Hayabusa2 and NASA's Origins, Spectral Interpretation, Resource Identification, Security-Regolith Explorer (OSIRIS-REx) missions that will return pristine material from the surface of the carbon-rich asteroids Ryugu and Bennu to Earth in late 2020 and 2023, respectively, will provide unique opportunities to analyze extraterrestrial material, yielding valuable information about the effects of the main alteration processes of primitive organics including aqueous alteration, heating, and radiation.²⁴⁰ Analysis of these samples, as well as those from future comet nucleus return missions, will greatly advance our understanding of the origin of chiral amino acid and sugar asymmetry in the early Solar System, and how subsequent parent body processes altered their initial D/L ratios due to their much lower levels of terrestrial contamination compared with meteorite samples recovered on Earth. Finally, the analysis of materials returned from primitive bodies will provide important constraints on the range of possible abiotic organic chemistry needed to help guide our search for chemical biosignatures on Mars and other potentially habitable environments such as the outer planet ocean worlds.

6.1. Comets

Comets represent the most primitive Solar System materials that are available for organic analysis. Studies of cometary material have occurred through both *in situ* and sample return missions. NASA's Stardust mission, which flew through the

coma of comet 81P/Wild (Wild 2) and returned a total mass of ~1 mg of cometary and interstellar dust grains to Earth on January 15, 2006,²⁴¹ allowed for the first detailed laboratory analyses of this material. Studies of the returned cometary material revealed the presence of one amino acid (glycine) and two amines (methylamine and ethylamine).^{242,243} Carbon isotopic ratios were required to confirm the extraterrestrial origin of the glycine detected in elevated abundances on the collector tray aerogel and foils.²⁴² Although this represented the first detection of a cometary amino acid, the amines identified were all achiral, with no enantiomers to provide chiral information.

The European Space Agency's Rosetta mission to comet 67P/Churyumov-Gerasimenko (67P/C-G) confirmed and extended these observations of cometary organics. The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument also identified glycine, methylamine, and ethylamine in the coma of 67P/C-G.²⁴⁴ As with Stardust, only achiral molecules were observed by ROSINA; in both cases, sampling was limited to the smaller, more volatile molecules present in the comets' comae, without access to the more refractory organic materials present in the nucleus. In contrast, Rosetta's Philae lander was planned to land on and directly sample the nucleus, with its Cometary Sampling and Composition (COSAC) instrument package specially designed for the detection of complex organic molecules, including amino acid chirality measurements.²⁴⁵ The failure of the anchoring harpoons on Philae, however, and the subsequent bounce of the lander to its final resting place on an area of the comet with hard and rugged terrain,²⁴⁶ meant that the planned drilling and delivery of nucleus surface material to COSAC was not possible. COSAC did carry out analyses of volatile material released from dust ejected into the instrument inlet shortly after the first bounce on the cometary surface, detecting methylamine, ethylamine, and several other volatile organic compounds,²⁴⁷ but the planned wet chemistry experiment and GCMS analyses of the refractory organic component of the comet nucleus, including an investigation of the possible presence of chiral amino acids and sugars, were not possible and remain an unstudied area for the future.

Future comet nucleus sample return missions would provide the primitive refractory and volatile material from the comet nucleus needed to establish whether comets contain chiral molecules and, if so, the magnitude and preference of any initial enantiomeric excesses present in the early Solar System. Comets that originated in the outer Solar System represent a distinct chemical environment from asteroids or other small bodies in the inner Solar System that were altered by heating, with a presumed lower level of aqueous activity over their history compared to asteroids due to colder temperatures.²⁴⁸ A detailed comparison of primitive comet nucleus material with asteroidal material, as measured through analyses both of meteorites and of returned samples (Section 6.2), will greatly improve our understanding of the initial chiral asymmetry in our Solar System and the role of aqueous alteration in the amplification of enantiomeric excesses. The cold temperature history of comets should also better preserve relatively unstable sugars or other organic compounds formed in ices that could be destroyed or significantly altered during parent body processing on asteroids.

6.2. Asteroid Sample Return and Ceres

In 2010 JAXA's Hayabusa spacecraft²⁴⁹ returned 1,534 particles from the surface of near-Earth spectral type S asteroid (25143) Itokawa.²⁵⁰ The particles are organic-depleted and similar to type LL5/6 meteorites²⁵¹. Two-dimensional high-performance liquid chromatography and time-of-flight-secondary ion mass spectrometry measurements of solvent extracts of 50–100 μm diameter grains from Itokawa found no amino acids or any other organic compounds above procedural blank levels.²⁵¹ JAXA's Hayabusa2 and NASA's OSIRIS-REx missions will collect and return more material from the near-Earth carbonaceous asteroids (162173) Ryugu and (101955) Bennu, respectively, which should be much more organic-rich than asteroid Itokawa. Hayabusa2 will eventually return grains and gas collected from two different sites on Ryugu totaling ~ 100 mg in sample mass, while OSIRIS-REx is expected to return 60–2,000 g of surface material collected from one sampling site.

Ryugu is a rare spectral type C_g 1 km diameter, spinning-top shaped macroporous rubble pile (density = 1.19 ± 0.02 g/cm³) asteroid²⁵² with a low albedo (4.5 ± 0.2 at 550 nm)²⁵³ and relatively featureless infrared spectrum, with indications of a very weak global hydration feature at 2.72 μm .²⁵⁴ The near-infrared spectra of Ryugu are characteristic of thermally metamorphosed or shocked CI or CM type carbonaceous chondrites and reminiscent of the CI1 Ivuna meteorite after heating to 500 °C. Although previous amino acid analyses of the CI1 chondrites Orgueil and Ivuna have revealed part-per-million (ppm) levels of primarily glycine and β -alanine,⁶⁵ thermally altered CI chondrites that have been heated at 500–600 °C are essentially devoid of indigenous amino acids.²⁵⁵ Asteroid Bennu, a 490 m diameter, spectral type B asteroid, is also a spinning-top shaped rubble pile^{256–258} with a porosity of 40–50% inferred from its relatively low density (1.19 ± 0.013 g/cm³),^{259,260} and a low albedo (4.4 ± 0.2 at 550 nm).²⁶¹ Bennu also has a relatively featureless infrared spectrum, but with much stronger indications of a global hydration band at 2.74 μm reminiscent of a mildly heated and relatively altered CM carbonaceous chondrite of petrographic subtype <2.5 based on the alteration scale developed for CMs by Rubin et al.²⁶² Aqueously altered CM carbonaceous chondrites typically show a more complex distribution of amino acids than CI1 chondrites and also possess large L-isovaline and other L-amino acid enrichments believed to the result of parent body alteration.⁴⁹ Aldonic acids with large D-enantiomer enrichments and racemic alditols have also been identified in the CM2s Murchison and Murray as well as CR2 meteorites²⁸ but have not been reported in more altered CI and CM type 1 chondrites. Although the 2.7 μm hydration feature of Bennu²⁶³ is significantly stronger than that of Ryugu,²⁵⁴ consistent with a higher degree of thermal alteration of Ryugu, it is also possible that space weathering has reduced the intensity of the hydration feature in the infrared accessible depth of these asteroids.²⁶⁴ Therefore, the strength of the near-infrared features may not reflect the actual concentration of water and complex organics in the returned samples that will include subsurface material. The return of samples from Ryugu and Bennu will provide a unique opportunity to evaluate the effects of parent body processing on the distributions and enantiomeric abundances of amino acids and other prebiotic molecules in carbon-rich asteroids.

Unlike meteorites recovered from terrestrial finds and even soon after observed falls, asteroid samples returned by

spacecraft have a much more limited exposure to terrestrial contamination, and the potential sources of contamination have been archived and are available for study if needed.²³⁹ Robotic asteroid sample return missions avoid the uncertainties of the extent of biological contamination from sample exposure to air and soil, liquid water or ice, and during collection by humans, and take advantage of rigorous spacecraft hardware cleaning procedures and contamination knowledge. Such clean samples provide researchers the ability to study them without intrusive biology.²⁶⁵ As such, the concerns about chiral asymmetry or changes in the distribution and isotopic compositions of amino acids and sugars introduced by biological contamination, as discussed throughout this manuscript, are significantly reduced. Therefore, samples returned from the carbonaceous asteroids Ryugu and Bennu will provide the first opportunity to investigate the extent of chiral asymmetry in amino acids and sugars produced solely by nonbiological processes.

(1) Ceres is the largest object in the asteroid belt (between Mars and Jupiter) with an average radius of about 470 km and mass of 10^{21} kg.²⁶⁶ Ceres is classified as a Dwarf Planet, and its surface shows similarities to type C or G asteroids based on IR spectral analyses,²⁶⁷ similar to Bennu and Ryugu. These types of carbon-rich asteroids are believed to most closely resemble CM and CI meteorites in collections on Earth, and *in situ* observations of Ceres from the Dawn mission broadly support this relationship.²⁶⁸ However, due to its orders of magnitude larger size, Ceres does have many notable differences from Bennu and Ryugu and other carbon-rich asteroids. In particular, Ceres has undergone some differentiation and is thought to have a core composed of hydrated silicate minerals.²⁶⁶ Data also reveal that Ceres contains significant amounts of water ice ($\sim 25\%$ on average), including within a meter of its surface ($\sim 20\%$) and throughout its ~ 30 km crust.²⁶⁹ Furthermore, numerical modeling of Ceres' high water content, driven initially by radiogenic heating and subsequent serpentinization, suggests it had a global muddy ocean for ~ 3 billion years and could still have several subsurface "mud sea" regions today.²⁷⁰

Characterization of the surface composition of Ceres have revealed regions that contain exposed ice, high concentrations of aliphatic organics (up to 10 wt % and higher) compared to carbonaceous meteorites, and ammoniated clays, serpentines, and carbonates.^{271–275} Taken together, the data from Dawn reveal that Ceres has experienced recent geologically activity with a potentially water-rich history throughout much of its 4.5 billion-year lifetime. It seems certain, then, that at a minimum Ceres has hosted abiotic chemistry comparable to what has been observed in carbonaceous meteorites. Thus, it would be expected that Ceres samples would also contain ppb to ppm levels of a diverse suite of amino acids and other organic compounds. Moreover, if the aqueously mediated amplification mechanisms for amino acid enantiomeric excesses are correct, it is reasonable to expect that analysis of surface and subsurface samples from Ceres would also contain amino acids in enantiomeric excess, regardless of whether life was ever present. In summary, Ceres offers a unique environment to explore planetary-scale water-rock interactions with potentially advanced prebiotic chemistry on a body with similarities to both carbonaceous asteroids and outer Solar System ocean worlds.

6.3. Mars Exploration and Sample Return

The exploration of habitable environments on Mars, including an assessment of the preservation potential for complex organics of either abiotic or biological origin is a key goal of the Mars Science Laboratory (MSL) mission, which has been exploring Gale Crater with the Curiosity rover since it landed there on August 6, 2012.²⁷⁶ The Curiosity rover analytical payload includes the Sample Analysis at Mars (SAM) instrument suite²⁷⁷ that is conducting the most extensive search for volatiles and organic compounds on the surface of Mars since the Viking lander missions using a combination of wet chemistry and pyrolysis gas chromatography mass spectrometry. Given the extremely cold and dry surface conditions presently on Mars, it is expected that amino acid hydrolysis and racemization would be extremely slow and any chiral or isotopic signatures of extinct life could be preserved for billions of years assuming average temperatures <250 K.^{104,113}

Even in the absence of indigenous biological or abiotic chemistry on Mars, exogenous organic matter delivered by micrometeorites and interplanetary dust particles³⁴ should have accumulated on the martian surface due to the continuous meteorite influx. It has been estimated that the martian regolith could contain 60 parts-per-million (ppm) total organic carbon from exogenous sources²⁷⁸ assuming a constant flux of carbonaceous micrometeorites of $\sim 2.4 \times 10^8$ g/yr²⁷⁹ to the martian surface over its entire history, an average micrometeorite organic carbon content of ~ 10 wt %, ²⁸⁰ efficient mixing of a ~ 100 m regolith, and no degradation of the organic material over time, although some degradation is inevitable given the known surface radiation and oxidative environment.^{281–283} Benner et al.²⁸⁴ predicted that nonvolatile organic salts derived from the oxidation of meteoritic organic matter would accumulate in the upper meter of the martian surface with benzenecarboxylate concentrations up to ~ 500 ppm by weight.

SAM evolved gas measurements of sedimentary rocks in Gale Crater have detected low temperature CO₂ and CO releases consistent with the presence of oxidized organic matter (~ 160 to 2,400 ppm of C_(CO₂)) that may be derived from the combustion or thermal decarboxylation of organic acid salts in the samples.²⁸⁵ Despite these relatively high total carbon concentrations measured by SAM, the only reduced organic molecules that have been identified so far by the SAM gas chromatograph mass spectrometer include sub-ppm levels of several chlorinated methanes, dichloroalkanes, and chlorobenzene that result from reactions between perchlorates and organics during pyrolysis,²⁸⁶ and sub-ppm to ppm levels of a variety of S-containing organic molecules including methanethiol, dimethylsulfide, thiophene, and methylthiophenes released at elevated temperatures due to possible breakdown of more refractory macromolecular organic material.²⁸⁷

In order to target less volatile and refractory organic compounds with reduced thermal degradation during pyrolysis and combustion, the SAM instrument also includes a “one-pot” wet chemistry experiment where the solid sample is exposed directly to a derivatization agent [*N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) mixed with dimethylformamide (DMF) or tetramethylammonium hydroxide (TMAH) in methanol] prior to pyrolysis and GCMS analysis.^{277,288,289} Although lab experiments with MTBSTFA that simulate the SAM-like wet chemistry protocols have shown that amino acids can be extracted from Mars analog

materials and identified above picomole levels,²⁸⁸ enantiomeric separation and stable isotopic analyses of MTBSTFA amino acid derivatives are not possible. In addition, reactions between iron oxides and hydrated minerals present on Mars with MTBSTFA can greatly reduce the derivatization efficiency of amino acids and other organic acids,²⁸⁸ and peptide or protein bound amino acids cannot be detected since acid hydrolysis of the sample prior to MTBSTFA derivatization would be required.

The first full SAM MTBSTFA wet chemistry experiment on a scooped sample of the Bagnold dune material called Ogunquit Beach detected several higher molecular weight MTBSTFA reaction products;^{290,291} however, no amino acid derivatives were identified above the SAM GCMS background levels.²⁹¹ Based on the measured radiolytic constants of pure amino acids exposed to γ radiation,²⁹² the destruction of amino acids and other organic compounds in the martian near-surface by ionizing radiation may be rapid on geological time scales. Pavlov et al.²⁹³ calculated that the abundances of complex organics with molecular masses >100 Da at a depth of ~ 5 cm below the surface would be reduced by a factor of 1000 in less than a billion years of ionizing radiation exposure. If the radiolysis constants from amino acids and clay mineral mixtures are used,²⁹⁴ the Pavlov et al.²⁹³ model predicts near complete destruction of amino acids in the martian near-surface on time scales of tens of millions of years.

Conversely, recent analysis of the martian shergottite Roberts Massif (RBT) 04262 showed evidence for part-per-billion (ppb) levels of several nonterrestrial, straight-chained, amine-terminal *n*- ω -amino acids including glycine, β -alanine, and γ -amino-*n*-butyric acid in the meteorite.²⁹⁵ It is possible that the amino acids in the RBT 04262 meteorite were synthesized by abiotic HB/FTT reactions of trapped gases during igneous processing on Mars or after impact ejection. A light carbon isotope value ($\delta^{13}\text{C} \sim -24\%$) was measured for β -alanine in RBT 04262 which is in the range of carbon isotopic measurements of reduced macromolecular organic matter of igneous origin found in 12 other martian meteorites²⁹⁶ and is also consistent with ¹³C-depletions observed previously in hydrocarbons produced by HB/FTT reactions²⁹⁷ and abiotic synthesis of organic compounds under hydrothermal conditions.²⁹⁸ Although the simple distribution of *n*- ω -amino acids in RBT 04262 shows isomeric preference and has a light carbon isotopic composition, the amino acids are all achiral and therefore do not meet all three criteria for a biological origin. Nevertheless, the detection of indigenous amino acids in a martian meteorite is a surprising result and may indicate that radiolysis is not as destructive on the surface of Mars as has been modeled previously.²⁹⁹ It is also possible that the depth of the sample excavated by the impacts that liberated all of these meteorites from Mars may have been beyond the range of ionizing radiation exposure. The RBT 04262 results provide a unique reference of abiotic amino acid chemistry on Mars that will be very useful in the future search for chiral molecules of possible biological origin.

The ExoMars mission scheduled for launch in July 2020 is planning to deliver a Russian lander and a European rover, named Rosalind Franklin, to the surface of Mars at Oxia Planum, an ancient Noachian sedimentary environment with one of the largest exposures of clay-bearing rocks on Mars. The rover includes a robotic drill designed to acquire samples below the intense radiation surface layer down to a depth of ~ 2 m and deliver the samples to a suite of analytical

instruments to investigate the habitability of Mars and search for chemical biosignatures, including amino acids.³⁰⁰ One of the rover payload instruments called the Mars Organic Molecule Analyzer (MOMA) will carry out a broad and highly sensitive search for organic molecules with laser desorption mass spectrometry and gas chromatography mass spectrometry.³⁰¹ The MOMA instrument also contains a wet chemistry experiment package that includes the *N,N*-dimethylformamide-dimethyl acetyl (DMF-DMA) derivatization reagent designed specifically for the detection of chiral amino acids and measurement of their enantiomeric composition at ppm concentrations or higher.^{301,302} If successful, the ExoMars 2020 mission and MOMA will be the first mission to sample material from the martian subsurface that has not been exposed to intense ionizing radiation and will make the first *in situ* measurements of amino acid chirality on Mars or any other Solar System body. Like SAM, the MOMA instrument does not have the ability to make compound specific stable isotopic measurements. Therefore, establishing an unambiguous origin of any chiral amino acid asymmetry on Mars, if detected by MOMA, will be challenging.

NASA is also planning to launch a rover to Mars in the same time frame as the ExoMars mission, with a primary goal of assessing past habitability and searching for evidence of ancient life on Mars including the potential for preservation of biosignatures in near-surface materials using a variety of *in situ* imaging and spectroscopy techniques.³⁰³ The Mars 2020 rover will be landed in Jezero Crater, an ancient lake-delta system that includes clays and carbonates that may have collected and preserved ancient organic molecules and other signs of microbial life that flowed into the crater billions of years ago. Although the Mars 2020 rover does not have an analytical laboratory to make bulk mineralogical and chemical composition measurements of drill and scoop samples like Curiosity, Mars 2020 will collect and cache dozens of surface sample cores for possible future return to Earth.³⁰³ Another sample return opportunity from the vicinity of Mars is JAXA's Martian Moons Exploration (MMX) mission³⁰⁴ which is currently scheduled to launch in 2024 and aims to collect surface samples from Mars' moon Phobos and return them to Earth in 2029. Although Phobos may be a captured asteroid or was formed *in situ* from the debris disk generated from a giant impact on Mars,³⁰⁵ the returned sample could contain martian dust and other surface materials released from Mars for billions of years.

With the detection of indigenous organic matter in sedimentary rocks on Mars,^{286,287} Curiosity has significantly advanced our understanding of the preservation of potential chemical biosignatures on the martian surface. However, given the complexity of robotic spacecraft operations on Mars, and the known analytical challenges associated with *in situ* extraction and characterization of trace reduced organic compounds in ancient rocks, coordinated state-of-the-art laboratory measurements of returned surface and subsurface samples from Mars that would include spatially resolved chemical, mineralogical, and isotopic studies and molecule specific stable isotopic and enantiomeric measurements will be required to firmly establish the origin of complex organic matter. Ultimately, sample return may be our best chance of identifying chemical biosignatures from a past or present martian biota if one ever existed on Mars.

7. CONCLUSIONS

The search for definitive evidence of extinct or extant signs of life in our Solar System will require a suite of measurements that focus on identifying the characteristic features of life (i.e., potential biosignatures). The homochirality of amino acids and sugars is one of many unique features of life on Earth that will be investigated in the search for chemical evidence of extraterrestrial life. The detection of chiral asymmetry in amino acids or other organic compounds will need to be carefully interpreted in the context of other key observations. The previously proposed "Ladder of Life Detection" threshold for biotic chemistry based on the degree of amino acid asymmetry (>20% enantiomeric excess of a few amino acids²⁵) is insufficient based on our current knowledge of prebiotic chemistry in meteorites and experimental evidence for nonbiological enantioenrichment processes that can produce even larger enantiomeric excesses. Instead of providing an absolute enantiomeric excess value threshold that might be indicative of biotic chemistry and that could be dependent on the specific compound as well as the enantiomeric preference ($L > D$ or $D > L$), we propose a set of criteria that can be used to help discriminate between biological or nonbiological origins of chiral asymmetry. The most compelling case of a biological origin of chiral asymmetry would be the detection of a limited distribution of chiral compounds with the opposite handedness as life on Earth that display structural isomeric preference and whose individual enantiomers have isotopic compositions that are similarly depleted in ¹³C, ¹⁵N, and D relative to inorganic material in the same sample.

There are many exciting *in situ* and sample return missions currently in flight or under development that will conduct detailed investigations of prebiotic chemistry as well as a robust search for extinct or extant chemical biosignatures, including chirality measurements. At present, *in situ* sample extraction and analysis of polyols as well as chiral molecule enantiomer-specific stable isotopic measurements are beyond the capabilities of spaceflight instrumentation. Significant advances in spaceflight-qualified sample extraction, purification, derivatization, and chromatographic separation technologies coupled with high-resolution mass spectrometry are needed to make these measurements. Given the complexity and limited duration of spaceflight operations and the analytical challenges associated with *in situ* measurements of complex organics in extraterrestrial samples, returning samples to Earth may ultimately provide the best chance to firmly establish the origin of chiral asymmetry and other potential biosignatures in our Solar System.

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Notes

The authors declare no competing financial interest.

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Daniel Glavin earned a B.S. in physics from the University of California at San Diego in 1996 and a Ph.D. in earth sciences from the

Scraps Institution of Oceanography in 2001 where he studied the amino acid and nucleobase composition of meteorites and exogenous delivery as a mechanism for delivering prebiotic organic compounds to the early Earth. He joined the 2002–03 Antarctic Search for Meteorites (ANSMET) team that recovered over 900 meteorites in Antarctica. In 2003, Dr. Glavin joined the NASA Goddard Space Flight Center in Greenbelt, Maryland, where he later cofounded the Astrobiology Analytical Laboratory at NASA Goddard. He was selected to be a Participating Scientist on the Mars Science Laboratory (MSL) mission in 2011 and was part of the team that discovered the first evidence of indigenous organic compounds on Mars using the Sample Analysis at Mars (SAM) instrument. He became NASA Goddard's Associate Director for Strategic Science in the Solar System Exploration Division in 2014. Dr. Glavin is a Co-Investigator on the OSIRIS-REx asteroid sample return mission. In recognition of Dr. Glavin's meteorite research, the International Astronomical Union named an asteroid after him, asteroid (24480) Glavin. He has received numerous awards including the 2007 NASA Goddard Internal Research and Development Innovator of the Year Award, the 2010 Nier Prize from the Meteoritical Society, and the 2014 NASA Robert H. Goddard Exceptional Achievement Award for Science.

Aaron Burton earned both his B.S. in biochemistry (2005) and Ph.D. in chemistry (2010) from Portland State University in Portland, Oregon. He was a NASA Postdoctoral Program Fellow in the Astrobiology Analytical Laboratory at the NASA Goddard Space Flight Center in 2010 and started an organic geochemistry laboratory at the NASA Johnson Space Center (JSC) in 2013. Dr. Burton's research at JSC focuses on investigating links between meteorite mineralogy and organic molecule content, as well as the effects of impact, hydrothermal, and magmatic processes on biologically relevant organic molecules. Burton is a Co-Investigator on the SHERLOC instrument that is part of the Mars 2020 mission instrument payload and was part of the team that demonstrated sequencing DNA and RNA works just as well off-planet on the ISS as it does on Earth. He has received several awards including NASA's Exceptional Achievement Medal in 2017.

Jamie Elsila earned a B.A. in chemistry from Kalamazoo College in 1996 and a Ph.D. in chemistry from Stanford in 2004. She joined the Astrobiology Analytical Laboratory at NASA Goddard in 2007, where her research focuses on the stable isotopic signatures of extraterrestrial organic compounds, including amino acids in carbonaceous chondrites, lunar samples, and cometary material returned by the Stardust mission. She is also a Co-Investigator of the Goddard Center for Astrobiology node of the NASA Astrobiology Institute and a collaborator on the OSIRIS-REx asteroid sample return mission; in recognition of her contributions, the International Astronomical Union named asteroid (117657) Jamieelsila after her. Her awards include NASA's Early Career Achievement Medal and the Robert H. Goddard Award for Exceptional Achievement in Science.

José Carlos Aponte was born in Lima, Peru, where he obtained his B.Sc. in chemistry. In 2005 he moved to Louisville, Kentucky, where he pursued his Ph.D. in organic chemistry and natural products working on the isolation and synthesis of bioactive molecules from Peruvian medicinal plants. He then went to Brown University as a postdoctoral fellow, where he researched the isolation of organic compounds from meteorites. In 2012 José became a NASA Astrobiology Institute postdoctoral fellow and moved to Maryland, where he is currently a Research Associate working at the Astrochemistry Analytical Laboratory at NASA Goddard Space Flight Center. For his collaboration with the OSIRIS-REx mission and his research on meteorites, the 2017 Asteroid (2005 EY161) was

renamed as asteroid (117652) Joséaponte by the International Astronomical Union.

Jason Dworkin was a high school intern at the University of Houston studying potentially prebiotic coenzymes until 1987. He earned an A.B. in biochemistry from Occidental College in 1991 and a Ph.D. in biochemistry from the University of California at San Diego in 1997, where he studied potential pre-RNA chemistry. He conducted postdoctoral research at NASA Ames Research Center studying laboratory presolar ice chemistry. In 2002, Dr. Dworkin joined the NASA Goddard Space Flight Center in Greenbelt, Maryland, where he cofounded the Astrobiology Analytical Laboratory at NASA Goddard. He became NASA Goddard's Chief of Astrochemistry in 2009. Dr. Dworkin is the project scientist on the OSIRIS-REx asteroid sample return mission. In recognition of Dr. Dworkin's contamination control and meteorite research, the International Astronomical Union named an asteroid after him, asteroid (27347) Dworkin. He has received numerous awards including the 2012 NASA Outstanding Leadership Medal, the American Chemical Society 2015 Maryland Chemist of the Year award, and the 2017 NASA Silver Achievement Medal (Team).

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