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The effects of parent body processes on amino acids in carbonaceous chondrites

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Abstract–To investigate the effect of parent body processes on the abundance, distribution, and enantiomeric composition of amino acids in carbonaceous chondrites, the water extracts from nine different powdered CI, CM, and CR carbonaceous chondrites were analyzed for amino acids by ultra performance liquid chromatography-fluorescence detection and time-of-flight mass spectrometry (UPLC-FD/ToF-MS). Four aqueously altered type 1 carbonaceous chondrites including Orgueil (CI1), Meteorite Hills (MET) 01070 (CM1), Scott Glacier (SCO) 06043 (CM1), and Grosvenor Mountains (GRO) 95577 (CR1) were analyzed using this technique for the first time. Analyses of these meteorites revealed low levels of two- to five-carbon acyclic amino alkanoic acids with concentrations ranging from approximately 1 to 2,700 parts-per-billion (ppb). The type 1 carbonaceous chondrites have a distinct distribution of the five-carbon (C_5) amino acids with much higher relative abundances of the γ- and δ-amino acids compared to the type 2 and type 3 carbonaceous chondrites, which are dominated by α-amino acids. Much higher amino acid abundances were found in the CM2 chondrites Murchison, Lonewolf Nunataks (LON) 94102, and Lewis Cliffs (LEW) 90500, the CR2 Elephant Moraine (EET) 92042, and the CR3 Queen Alexandra Range (QUE) 99177. For example, α-aminoisobutyric acid (α-AIB) and isovaline were approximately 100 to 1000 times more abundant in the type 2 and 3 chondrites compared to the more aqueously altered type 1 chondrites. Most of the chiral amino acids identified in these meteorites were racemic, indicating an extraterrestrial abiotic origin. However, nonracemic isovaline was observed in the aqueously altered carbonaceous chondrites Murchison, Orgueil, SCO 06043, and GRO 95577 with L-isovaline excesses ranging from approximately 11 to 19%, whereas the most pristine, unaltered carbonaceous chondrites analyzed in this study had no detectable L-isovaline excesses. These results are consistent with the theory that aqueous alteration played an important role in amplification of small initial left handed isovaline excesses on the parent bodies.

INTRODUCTION

Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on Earth. The delivery of organic compounds by carbonaceous chondrites to the early Earth and other planetary bodies could have been an important source of prebiotic compounds required for the emergence of life as we know it (Chyba and Sagan 1992). The carbonaceous chondrite class represents roughly 4% of all meteorite falls (Grady 2000) and is subdivided into separate groups (CI, CM, CR, CV, CO, CH, CB, and CK) based on differences in elemental composition and mineralogy (Sears and Dodd 1988). In addition, a number is given after the carbonaceous chondrite group based on their petrologic histories (i.e., degree of mineralogical or textural modification of the meteorite by aqueous and/or thermal alteration on the parent body), where type 1 chondrites represent the most altered by low temperature aqueous alteration and type 3 the least aqueously altered (Van Schmus and Hayes 1974; McSween 1979). Petrographic types 4 to 6 refer to carbonaceous chondrites with increasing thermal alteration. Carbonaceous chondrites represent a very primitive class of meteorite that generally contain 2 to 5 wt% of carbon, most of which is from organic

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matter (Sephton 2002). More than 70% of the organic carbon is in the form of an insoluble kerogen-like macromolecule that is structurally complex (Sephton et al. 2000; Cody and Alexander 2005), while the remaining solvent extractable organic carbon is comprised of a complex mixture of organics that includes amino acids.

The amino acid compositions of a variety of carbonaceous chondrites, in particular the CMs, have been studied extensively because these prebiotic molecules are essential components of life as the monomers of proteins and enzymes. Over 80 different amino acids have been named in the CM chondrites Murchison and Murray, comprising a mixture of 2- to 8-carbon cyclic and acyclic monoamino alkanoic and alkanedioic acids of nearly complete structural diversity, many of which are rare or absent in the terrestrial biosphere (Cronin and Pizzarello 1983, 1986; Cronin and Chang 1993; Botta and Bada 2002; Sephton 2002). Recent studies of organic compounds in solvent extracts of the Murchison meteorite by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry have detected thousands of different molecular compositions and likely millions of diverse structures (Schmitt-Kopplin et al. 2010). Therefore, it is likely that previous amino acid analyses of Murchison have greatly underestimated the chemical complexity of this meteorite due to a lack of sensitivity and standards. Amino acids have also been identified in the more aqueously altered CI1 carbonaceous chondrites Orgueil and Ivuna, and these two meteorites have a relatively simple distribution of amino acids (predominantly β-alanine [BALA] and glycine) that is distinct from the complex mixture of amino acids found in the CMs Murchison and Murray (Ehrenfreund et al. 2001). CR chondrites are believed to contain the most primitive insoluble organic matter (IOM) of any carbonaceous chondrite group (Cody and Alexander 2005), and it has recently been discovered that two Antarctic CR2 chondrites, Elephant Moraine (EET) 92042 and Graves Nunataks (GRA) 95229 have the highest amino acid abundances of any meteorite analyzed to date (Martins et al. 2007; Pizzarello et al. 2008). One of the most primitive CR chondrites, the CR3 Queen Alexandra Range (QUE) 99177 has also been observed to have a similarly high abundance and distribution of five-carbon amino acids compared to EET 92042 (Glavin and Dworkin 2009).

Most amino acids found in carbonaceous chondrites are structurally chiral, meaning they possess two nonsuperimposable mirror image structures or enantiomers (by convention: S, left, L and R, right, D). With a few very rare exceptions, only L-amino acids are found in biology, whereas amino acids formed by abiotic processes are racemic (equal mixtures of L- and D-enantiomers). Therefore, the molecular structure of these compounds can be a very useful tool to help discriminate between biotic and abiotic (nonbiological) origins of amino acids in meteorites. The first analyses of interior pieces of the Murchison meteorite shortly after its fall found that the chiral amino acids were racemic (D/L = 1), indicating that the amino acids were indigenous to the meteorite and very little, if any, terrestrial amino acid contamination of the meteorite had occurred (Kvenvolden et al. 1970, 1971). One major discovery is the finding of nonracemic α-dialkyl amino acids in the CM chondrites Murchison and Murray, with slight to significant L-isovaline excesses ranging from 0 to 15.2% (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Pizzarello et al. 2003). These results are difficult to explain since the abiotic formation of isovaline and other α-dialkyl amino acids (e.g., by Strecker synthesis) on the CM parent body should produce racemic mixtures. In contrast to the α-hydrogen protein amino acids common to all life on Earth, nonbiological α-dialkyl amino acids such as isovaline found in meteorites are not prone to geologically rapid racemization (conversion of one enantiomer to the other) under aqueous or radiogenic conditions (Pollock et al. 1975). Therefore, the initial enantiomeric ratios of these amino acids are more likely to have been preserved since the time of their formation. The finding of L-amino acid excesses in Murchison and Murray could point toward a possible prebiotic contribution to the origin of biological homochirality by the delivery of extraterrestrial organic material from asteroids and comets to the early Earth.

Amino acid analyses by high performance liquid chromatography with fluorescence detection (HPLC-FD) of the Antarctic type 1 CM carbonaceous chondrites Meteorite Hills (MET) 01070, Allan Hills (ALH) 88045, and LaPaz Icefield 02277, and the only known type 1 CR chondrite Grosvenor Mountains (GRO) 95577 have been reported (Botta et al. 2007; Martins et al. 2007). The very low amino acid abundances in these meteorites compared to CM2 and CR2 chondrites was suggested to be a result of chemical oxidation during an extended aqueous alteration phase on the parent bodies (Martins et al. 2007). It has been suggested that aqueous alteration on the parent body may also play an important role in the enrichment of L-isovaline observed in the CI1 Orgueil and CM2 Murchison meteorites (Glavin and Dworkin 2009) by asymmetric amplification via crystallization (Blackmond 2004; Klussmann et al. 2006) or asymmetric autocatalytic reactions (Soai et al. 1995). Additional measurements of the enantiomeric ratio of isovaline in other aqueously altered type 1 chondrites are necessary to test this hypothesis. Precise abundances and enantiomeric

Table 1. Peak identification numbers and abbreviations for amino acids detected in the chromatograms of the standards, procedural blanks, and meteorite extracts. The number of carbons (#C) for the aliphatic amino acids is also shown.

Peak	Amino acid	#C
1	D-aspartic acid	
2	L-aspartic acid	
3	L-glutamic acid	
4	D-glutamic acid	
5	D-serine	
6	L-serine	
7	D-threonine	
8	L-threonine	
9	Glycine	2
10	β-alanine (BALA)	3
11	D-alanine	3
12	L-alanine	3
13	γ-amino-*n*-butyric acid (γ-ABA)	4
14	D-β-amino-*n*-butyric acid (D-β-ABA)	
15	L-β-amino-*n*-butyric acid (L-β-ABA)	
16	α-aminoisobutyric acid (α-AIB)	
17	D,L-α-amino-*n*-butyric acid (D,L-α-ABA)	
18	3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa)	5
19	D,L-4-aminopentanoic acid (D,L-4-apa)	
20	D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba)	5
21	D,L-3-amino-2-methylbutanoic acid (D,L-3-a-2-mba)	5
22	D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa)	5
23	5-aminopentanoic acid (5-apa)	5
24	D,L-4-amino-2-methylbutanoic acid (D,L-4-a-2-mba)	5
25	3-amino-3-methylbutanoic acid (3-a-3-mba)	5
26	D-2-amino-2-methylbutanoic acid (D-isovaline)	5
27	D,L-3-aminopentanoic acid (D,L-3-apa)	5
28	L-2-amino-2-methylbutanoic acid (L-isovaline)	5
29	L-2-amino-3-methylbutanoic acid (L-valine)	5
30	D-2-amino-3-methylbutanoic acid (D-valine)	5
31	D-2-aminopentanoic acid (D-norvaline)	5
32	L-2-aminopentanoic acid (L-norvaline)	
33	ε-amino-*n*-caproic acid (EACA)	6
34	D,L-isoleucine	6
35	D,L-leucine	6
I.S.	D,L-norleucine (internal standard)	6
X	Desalting or nonfluorescent mass artifact	

ratios for isovaline and other five-carbon (C_5) amino acids were not determined in the previous analyses of CM1 and CR1 chondrites (Botta et al. 2007; Martins et al. 2007). In addition, the compound assignments of the amino acids extracted from these chondrites were based solely on derivatization chemistry and chromatographic retention time without confirmation by high-resolution mass spectrometry. To our knowledge, amino acid analyses of any kind have not been previously reported for the CM1 chondrite Scott Glacier (SCO) 06043.

To continue to investigate the potential role of aqueous alteration in amino acid decomposition, amplification of L-isovaline enantiomeric excess, and changes in the relative distributions of amino acids in carbonaceous chondrites, we analyzed the type 1 carbonaceous chondrites Orgueil (CI1), SCO 06043 (CM1), MET 01070 (CM1), and GRO 95577 (CR1) and compared our measurements with data from several less altered type 2 and type 3 CM and CR carbonaceous chondrites including Murchison (CM2), Lewis Cliffs (LEW) 90500 (CM2), Lonewolf Nunataks (LON) 94102 (CM2), EET 92042 (CR2), and QUE 99177 (CR3), using the identical extraction and analytical technique. The CR3 chondrite QUE 99177 was originally classified as a CR2, but analyses of presolar grains and the carbon isotopic composition of organic matter in this meteorite indicate that QUE 99177 is less altered than other CR2 chondrites and is the most primitive CR chondrite analyzed to date (Floss and Stadermann 2009). Although LON 94102 has been classified as a CM2, it is a relatively unaltered meteorite, with oxygen isotope values that fall at the low end (i.e., least hydrated) of the CM chondrites (Clayton and Mayeda 1999). Amino acid abundances and enantiomeric ratios were determined using a highly sensitive and selective ultra performance liquid chromatography fluorescence detection and time of flight mass spectrometry (UPLC-FD/ToF-MS) technique (Johnson et al. 2008; Glavin and Dworkin 2009) coupled with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization. All of the UPLC-FD/ToF-MS results presented here for the CR1 and CM1 meteorites and one sample of the CM2 Murchison meteorite (USNM 5453) have not previously been reported. For comparison, some of the amino acid data for the CI Orgueil, the CM's Murchison (USNM 6650), LEW 90500, and LON 94102 and the CR's EET 92042 and QUE 99177 shown in Tables 2–5 were taken from previous studies (Glavin et al. 2006; Glavin and Dworkin 2009).

MATERIALS AND METHODS

Meteorite Samples and Controls

The amino acid extracts of the CI, CM, and CR carbonaceous chondrites analyzed in this study were obtained from interior chips that did not contain any visual evidence of fusion crust. All of the meteorite samples were received as chips and were separately crushed into fine powders (estimated < 150 μm) and

Table 2. Summary of the total (free + bound) abundances of the two- to six-carbon amino acids identified in the acid-hydrolyzed, hot-water extracts of CI, CM, and CR carbonaceous chondrites[a].

	CI1	CM1		CM2				CR1	CR2	CR3
	Orgueil	MET 01070	SCO 06043	Murchison USNM 5453	Murchison USNM 6650	LEW 90500	LON 94102	GRO 95577	EET 92042	QUE 99177
Amino acids	This study	This study	This study	This study	Glavin et al. (2006)		This study	This study	This study	This study
D-aspartic acid	54 ± 31	< 1	< 1	189 ± 14	120 ± 16	127 ± 24	118 ± 63	< 8	1,028 ± 157	546 ± 214
L-aspartic acid	55 ± 28	< 2	< 2	281 ± 23	132 ± 15	151 ± 73	112 ± 41	< 2	1,016 ± 145	536 ± 170
D-glutamic acid	47 ± 16	< 2	< 1	503 ± 82	343 ± 44	317 ± 55	534 ± 193	< 9	10,088 ± 1,973	3,517 ± 602
L-glutamic acid	83 ± 22	< 2	< 3	819 ± 113	357 ± 42	316 ± 55	552 ± 191	< 1	10,180 ± 1,743	3,442 ± 537
D-serine	< 1	< 1	< 3	n.d.	48 ± 9	219 ± 151	99 ± 69	< 4	2,584 ± 1,420	685 ± 426
L-serine	< 1	< 2	< 2	n.d.	46 ± 9	235 ± 163	92 ± 30	< 3	2,266 ± 1,237	609 ± 379
Glycine	865 ± 450	105 ± 15	48 ± 10	2,606 ± 717	1,995 ± 122	1,448 ± 682	3,391 ± 1,029	278 ± 76	54,527 ± 15,365	14,134 ± 3,376
D-alanine	80 ± 17	18 ± 2	10 ± 1	592 ± 99	623 ± 6	343 ± 171	823 ± 295	46 ± 16	40,107 ± 9,275	3,589 ± 455
L-alanine	94 ± 22	21 ± 3	10 ± 2	718 ± 160	659 ± 84	352 ± 161	745 ± 286	35 ± 5	41,326 ± 7,477	3,544 ± 594
β-alanine	2,732 ± 675	187 ± 34	122 ± 45	1,081 ± 243	1,419 ± 157	442 ± 238	821 ± 343	295 ± 98	4,161 ± 1,182	1,954 ± 332
D,L-α-ABA[b]	71 ± 49	23 ± 4	4 ± 1	622 ± 128	403 ± 156	431 ± 159	896 ± 300	45 ± 10	20,859 ± 5,653	3,300 ± 637
D-β-ABA	221 ± 110	26 ± 4	18 ± 3	349 ± 58	233 ± 17	155 ± 16	279 ± 110	70 ± 10	2,855 ± 580	585 ± 127
L-β-ABA	181 ± 59	25 ± 2	18 ± 2	320 ± 41	256 ± 15	172 ± 40	178 ± 81	60 ± 9	3,160 ± 852	679 ± 203
γ-ABA	281 ± 131	46 ± 13	54 ± 12	979 ± 97	1,460 ± 213	164 ± 21	470 ± 115	140 ± 12	2,620 ± 982	1,322 ± 115
α-AIB	343 ± 140	37 ± 10	30 ± 9	5,124 ± 2,487	3,182 ± 620	2,706 ± 377	753 ± 413	175 ± 15	56,825 ± 15,592	14,246 ± 3,249
EACA	108 ± 103	2,014 ± 86	954 ± 147	490 ± 148	268 ± 123	386 ± 169	9,265 ± 370	3,914 ± 573	51,371 ± 13,566	2,529 ± 311
C_5 amino acids (from Table 3)	1,600	220	350	7,300	3,100	1,800	5,900	500	65,000	28,000
Free amino acids[c] (% Free)[d]	n.d.	340 (48%)	250 (38%)	11,000 (52%)	7,100 (51%)	4,200 (45%)	8,400 (53%)	830 (52%)	205,000 (64%)	40,000 (49%)
Total (free + bound) amino acids[c]	6,700	710	660	21,000	14,000	9,400	16,000	1,600	320,000	81,000

[a]All values are reported in parts-per-billion (ppb) on a bulk sample basis. Extracts were analyzed by OPA/NAC derivatization (1 and 15 min) and UPLC separation with UV fluorescence and time of flight mass spectrometry (ToF-MS) detection. For the LC-ToF-MS data, the mono-isotopic masses of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a serpentine blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of 4 to 8 separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n - 1)^{-1/2}$.

[b]Enantiomers could not be separated under the chromatographic conditions.

[c]Amino acid concentrations rounded to two significant digits. The EACA concentrations were not included in the sum of the individual amino acid concentrations.

[d]Percent free amino acids in the nonhydrolyzed extracts were calculated by dividing the free amino acid concentration by the total (free + bound) amino acid concentration measured in the acid-hydrolyzed extracts.

n.d. = not determined.

Table 3. Summary of the total (free + bound) abundances of the five-carbon (C_5) α-, β-, γ-, and δ-amino acids in the acid-hydrolyzed, hot-water extracts of CI, CM, and CR type carbonaceous chondrites[a].

	CI1	CM1		CM2				CR1	CR2	CR3
	Orgueil	MET 01070	SCO 06043	Murchison USNM5453	Murchison USNM6650	LEW 90500	LON 94102	GRO 95577	EET 92042	QUE 99177
C_5 amino acids	Glavin and Dworkin (2009)	This study	This study	This study	Glavin and Dworkin (2009)			This study	Glavin and Dworkin (2009)	
α										
D-norvaline	13 ± 1	< 0.2	0.6 ± 0.2	59 ± 4	18 ± 2	9 ± 1	259 ± 20	2.2 ± 0.1	3,275 ± 391	960 ± 60
L-norvaline	14 ± 1	< 0.2	0.8 ± 0.2	59 ± 3	19 ± 2	9 ± 1	263 ± 17	1.8 ± 0.2	3,231 ± 351	967 ± 68
D-isovaline	36 ± 3	< 0.4	3.3 ± 0.4	1263 ± 125	993 ± 43	652 ± 15	332 ± 19	14.6 ± 1.7	14,446 ± 625	5,534 ± 210
L-isovaline	49 ± 2	< 0.5	4.6 ± 0.5	2058 ± 220	1,444 ± 66	696 ± 20	348 ± 21	18.2 ± 2.0	14,164 ± 1,038	5,564 ± 92
D-valine	22 ± 6	< 0.3	2.6 ± 1.1	160 ± 5	105 ± 15	48 ± 6	357 ± 20	5.5 ± 0.1	7,217 ± 427	3,442 ± 208
L-valine	56 ± 2	< 10[e]	< 14[e]	< 330[e]	111 ± 28	55 ± 8	480 ± 21	< 12[e]	7,647 ± 500	3,861 ± 137
β										
D,L-3-apa[c]	181 ± 11	5.9 ± 0.6	10 ± 1	158 ± 19	37 ± 4	36 ± 2	178 ± 9	41 ± 4	2,077 ± 177	804 ± 25
D,L- and allo-3-a-2-mba[c]	64 ± 4	5.2 ± 0.3	9.5 ± 0.6	158 ± 20	26 ± 5	24 ± 4	162 ± 7	29 ± 2	2,161 ± 102	962 ± 29
3-a-3-mba[d]	< 30	< 3	< 3	< 66	< 14	< 14	< 150	< 4	< 286	< 250
3-a-2,2-dmpa	69 ± 3	5.7 ± 0.5	23 ± 2	195 ± 16	36 ± 3	21 ± 1	320 ± 13	13 ± 1	539 ± 21	315 ± 20
D,L-3-a-2-epa[b]	171 ± 14	11 ± 1	25 ± 6	470 ± 233	37 ± 2	24 ± 3	534 ± 34	88 ± 31	1,393 ± 127	774 ± 59
γ										
D,L-4-apa[c]	283 ± 24	21 ± 2	33 ± 2	444 ± 47	84 ± 12	78 ± 9	475 ± 31	75 ± 4	2,968 ± 212	1,293 ± 90
D,L-4-a-2-mba[b]	173 ± 11	50 ± 2	61 ± 1	553 ± 58	67 ± 8	75 ± 3	733 ± 38	62 ± 5	2,396 ± 311	1,485 ± 60
D,L-4-a-3-mba[b]	325 ± 17	62 ± 15	102 ± 21	984 ± 180	103 ± 7	68 ± 2	973 ± 23	111 ± 23	2,137 ± 75	1,472 ± 87
δ										
5-apa	140 ± 19	63 ± 12	73 ± 12	341 ± 59	50 ± 5	48 ± 5	480 ± 24	39 ± 6	973 ± 93	570 ± 17
Total C_5 amino acids[f]	1,600	220	350	7,300	3,100	1,800	5,900	500	65,000	28,000

[a]All values are reported in parts-per-billion (ppb) on a bulk sample basis. Extracts were analyzed by OPA/NAC derivatization (15 min) and LC-FD/ToF-MS. For the ToF-MS data, the mono-isotopic masses (m/z 379.13) of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The uncertainties (δx) are based on the standard deviation of the average value of 4 to 8 separate measurements (n) with a standard error, $\delta x = \sigma_x \cdot (n - 1)^{-1/2}$. For isovaline, the reported values represent the average of 8 to 23 separate measurements.

[b]Enantiomers could not be separated under the chromatographic conditions.

[c]Enantiomers were separated but could not be identified due to the lack of optically pure standards.

[d]3-a-3-mba coelutes with one of the enantiomers of D,L-4-apa, therefore upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two D,L-4-apa enantiomers.

[e]Peak detected above blank levels, however only upper limit reported due to unidentified coeluting peak X (see Figs. 1 and 2).

[f]Total (free + bound) amino acid abundances rounded to two significant digits.

Table 4. Amino acid enantiomeric ratios (D/L) measured in the carbonaceous chondrites[a].

Amino acids[b]	CI1	CM1		CM2				CR1	CR2	CR3
	Orgueil	MET 01070	SCO 06043	Murchison USNM 5453	Murchison USNM 6650	LEW 90500	LON 94102	GRO 95577	EET 92042	QUE 99177
	This study	This study	This study	This study	Glavin et al. (2006)		This study	This study	This study	This study
Aspartic acid	0.98 ± 0.12	n.d.	n.d.	0.67 ± 0.07	0.91 ± 0.16	0.84 ± 0.24	1.05 ± 0.13	n.d.	1.01 ± 0.10	1.02 ± 0.15
Glutamic acid	0.57 ± 0.24	n.d.	n.d.	0.61 ± 0.13	0.96 ± 0.17	1.00 ± 0.20	0.97 ± 0.18	n.d.	0.99 ± 0.06	1.02 ± 0.24
Serine	n.d.	n.d.	n.d.	n.d.	1.04 ± 0.18	0.93 ± 0.19	1.08 ± 0.10	n.d.	1.14 ± 0.18	1.12 ± 0.19
Alanine	0.85 ± 0.27	0.86 ± 0.16	1.00 ± 0.22	0.82 ± 0.23	0.95 ± 0.12	0.97 ± 0.16	1.10 ± 0.15	1.31 ± 0.29	0.97 ± 0.28	1.01 ± 0.11
Valine	> 0.4	n.d.	> 0.2	> 0.5	0.95 ± 0.17	0.87 ± 0.17	0.74 ± 0.05	> 0.5	0.94 ± 0.08	0.89 ± 0.06
β-ABA	1.22 ± 0.23	1.04 ± 0.18	1.00 ± 0.20	1.09 ± 0.23	0.91 ± 0.09	0.90 ± 0.23	1.56 ± 0.30	1.17 ± 0.24	0.90 ± 0.31	0.86 ± 0.22
Norvaline	0.93 ± 0.10	n.d.	0.75 ± 0.21	1.00 ± 0.08	0.95 ± 0.15	1.00 ± 0.16	0.98 ± 0.10	1.22 ± 0.15	1.01 ± 0.16	0.99 ± 0.09
Isovaline	0.73 ± 0.07	n.d.	0.72 ± 0.12	0.61 ± 0.09	0.69 ± 0.04	0.94 ± 0.03	0.95 ± 0.08	0.80 ± 0.13	1.02 ± 0.09	0.99 ± 0.04

[a]The uncertainties ranged from ±0.05 to ±0.3 and are based on the absolute errors shown in Tables 2 and 3.
[b]The protein amino acids are italicized.
n.d. = ratio could not be determined due to low amino acid abundances.

Table 5. Summary of the L-enantiomer excesses for total isovaline in CI, CM, and CR carbonaceous chondrites and two racemic standards[a].

Sample	Isovaline L_{ee} (%)	Isovaline δx (n)	β-Ala/Gly ratio	Reference
Orgueil (CI1)	15.2	±4.0 (8)	2.7	Glavin and Dworkin (2009)
SCO 06043 (CM1)	16.5	±7.5 (8)	2.1	This study
MET 01070 (CM1)	n.d.	n.d.	1.5	This study
GRO 95577 (CR1)	11.0	±7.2 (8)	0.89	This study
Murchison (CM2)	17.2	±6.7 (8)	0.35	This study
	18.5	±2.6 (20)	0.60	Glavin and Dworkin (2009)
	0–15.2[c]	±0.2–1.3 (5–33)[c]	–	Pizzarello et al. (2003)
LEW 90500 (CM2)	3.3	±1.8 (23)	0.26	Glavin and Dworkin (2009)
LON 94102 (CM2)	2.4	±4.1 (8)	0.20	Glavin and Dworkin (2009)
EET 92042 (CR2)	−1.0	±4.3 (8)	0.06	Glavin and Dworkin (2009)
QUE 99177 (CR3)	0.3	±2.1 (8)	0.12	Glavin and Dworkin (2009)
Racemic standard[b]	−2.3	±1.3 (14)	–	Glavin and Dworkin (2009)
	−3.9	±1.2 (10)	–	This study

[a]The L_{ee} and errors (δx) shown are based on the absolute values and uncertainties taken from Table 3 for n separate measurements ranging from 8 to 20 propagated through the equation L_{ee} (%) = $(L - D)/(L + D) \times 100$.
[b]Used for L_{ee} correction of the meteorite samples.
[c]Range of L_{ee} values and errors previously reported for several different fragments of the Murchison meteorite by Pizzarello et al. (2003). The errors are based on 5–33 separate measurements for multiple samples.
n.d. = not determined due to extremely low isovaline concentrations.

manually homogenized by using a mortar and pestle in a positive pressure high efficiency particulate air (HEPA) filtered laminar flow hood (AirClean). We analyzed only one CI chondrite Orgueil for this study (total mass 1.0 g) which was provided by the Musée National, Paris (petrographic type 1); less altered CI chondrites (type 2 or type 3) have not yet been identified. For the CMs, both type 1 and 2 chondrites were analyzed. The CR chondrites analyzed in this study represent the entire range of aqueous alteration (type 1–3). Two different pieces of the CM2 Murchison meteorite were provided by the Smithsonian National Museum of Natural History, Washington, D.C. (USNM 6650, total mass 6.3 g; USNM 5453, total mass 15.2 g). The Antarctic meteorites studied were collected by Antarctic Search for Meteorites (ANSMET) field teams and are designated by the geographic area where they were found and a five digit number, the first two digits of which indicate the collection season year. In addition, the specific daughter split, parent rock number, and mass of each chip allocated for this study are also shown in parentheses. The Antarctic CM2 chondrites LEW 90500 (specific 69, parent 1, total mass 5.0 g) and LON 94102 (specific 19, parent 7, total mass 0.6 g), the CR1 chondrite GRO 95577 (specific 46, parent 10, total mass 0.5 g), CR2 chondrite EET 92042 (specific 58, parent 0, total mass 0.6 g), CR3 chondrite QUE 99177 (specific 29, parent 10, total mass 0.5 g), and the CM1 chondrites MET 01070 (specific 34, parent 0, total mass 0.5 g) and SCO 06043 (specific 8, parent 0, total mass 0.5 g) were provided by the Antarctic meteorite curator at the NASA Johnson Space Center in Houston, TX. As controls, a crushed serpentine (a hydrated magnesium silicate) sample that had been heated at 500 °C in air overnight and amino acid standards were carried through the identical extraction procedure as the meteorite samples.

Chemicals and Reagents

Most of the chemicals and reagents used in this study were purchased from Sigma-Aldrich. A stock amino acid solution (approximately 10^{-5} to 10^{-6} M) was prepared by mixing individual standards (97–99% purity) in Millipore water (see Fig. 1). The OPA/NAC reagent used for amino acid derivatization was prepared by dissolving 4 mg OPA in 300 μL methanol (Optima grade), and then adding 685 μL 0.1 M sodium borate buffer (pH 9) and 15 μL 1 M NAC. A 0.1 M hydrazine (NH_2NH_2) solution was prepared by vacuum distillation of concentrated anhydrous hydrazine (98% purity) and subsequent dilution in Millipore water. The HCl was double-distilled, and the ammonium formate buffer used in the UPLC-FD/ToF-MS analyses was prepared by ammonia titration (95% purity) of a 50 mM formic acid solution to pH 8. A 10 μM phenolphthalein solution in acetonitrile with 0.1% formic acid was used for internal mass calibration of the ToF-MS.

A separate standard solution containing all of the acyclic C_5 α-, β-, γ-, and δ-amino alkanoic acids (see Fig. 2) was prepared by weighing each individual standard using a microbalance and mixing them in

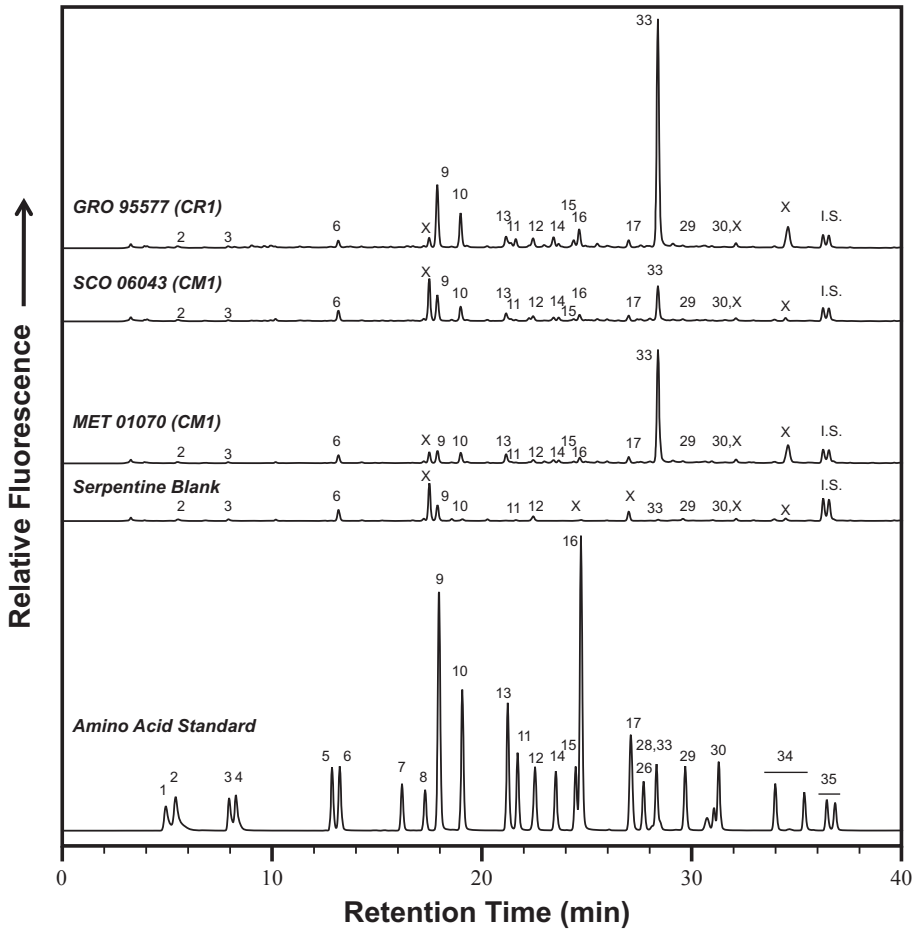

Fig. 1. The 0–40 min region of the LC-FD chromatograms. OPA/NAC derivatization (15 min) of the amino acid standard and of the 6 M HCl-hydrolyzed, hot-water extracts of the serpentine blank and the type 1 chondrites MET 01070, SCO 06043, and GRO 95577 are shown. Similar chromatograms were obtained for the nonhydrolyzed extracts. Peaks in the chromatograms that did not correspond to the same UV fluorescence and mass retention times of the standard amino acids tested were not identified. The identities of the peaks are given in Table 1.

Millipore water at a concentration of approximately 10^{-5} to 10^{-6} M. Individual D- and L-2-amino-2-methylbutanoic acid (2-a-2-mba, isovaline) were purchased from Acros Organics (>99% purity), and a racemic mixture (D = L) was prepared by mixing the appropriate volumes of each individual solution. DL-2-aminopentanoic acid (2-apa, norvaline), DL-2-amino-3-methylbutanoic acid (2-a-3-mba, valine), and 5-aminopentanoic acid (5-apa) standards were purchased from Sigma-Aldrich (97–99% purity). DL-3-aminopentanoic acid (3-apa) was from AzaN (97% purity). 3-amino-3-methylbutanoic acid (3-a-3-mba), 3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa), DL-3-amino-2-methylbutanoic acid (3-a-2-mba and allo-3-a-2-mba, 4 stereoisomers), DL-4-aminopentanoic acid (4-apa), DL-4-amino-3-methylbutanoic acid (4-a-3-mba), L-3-amino-2-ethylpropanoic acid (3-a-2-epa), DL-4-amino-2-methylbutanoic acid (4-a-2-mba) were individually synthesized and provided by S. Pizzarello (ASU), S. Miller (UCSD), S. Davies (Oxford), and R. Duke (U. Sydney). The L-3-a-2-epa was mostly racemized by 6 M HCl acid vapor hydrolysis (150 °C for 1 week).

Extraction Procedure

All glassware, ceramics, and sample handling tools were rinsed with Millipore Direct Q3 UV (18.2 MΩ, <5 ppb total organic carbon) ultrapure water, wrapped in aluminum foil and then heated in a furnace at 500 °C overnight. A portion of each powdered meteorite sample (approximately 0.1 to 0.2 g) was flame sealed separately in a glass ampoule with 1 mL of Millipore water and extracted at 100 °C for 24 h. Half of the water supernatants were then subjected to a 6 M HCl acid vapor hydrolysis procedure at 150 °C for 3 h to determine total hydrolyzable amino acid content (Glavin et al. 2006). The acid-hydrolyzed, hot-water

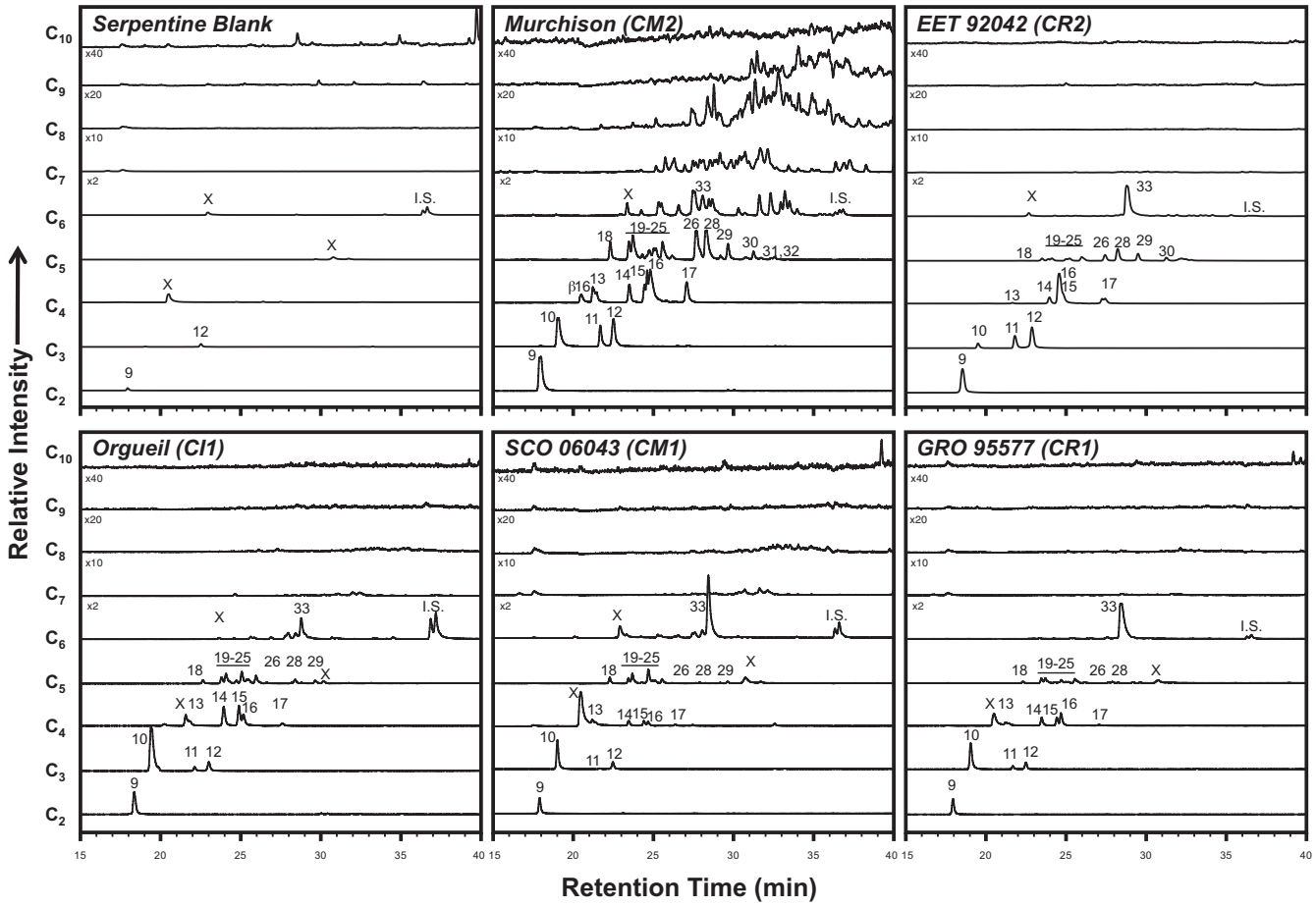

Fig. 2. The 15–40 min region of the LC-ToF-MS single ion chromatograms (C_2: m/z = 337.09; C_3: m/z = 351.10; C_4: m/z = 365.12; C_5: m/z = 379.13; C_6: m/z = 393.15; C_7: m/z = 407.16; C_8: m/z = 421.18; C_9: m/z = 435.20; and C_{10}: m/z = 449.21) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the standard mix and of the 6M HCl-hydrolyzed, hot-water extracts of Orgueil, MET 01070, GRO 95577, Murchison (USNM 5453), EET 92042 and the serpentine blank are shown. Similar single ion chromatograms were obtained for the nonhydrolyzed extracts. Peaks were identified by comparison of the retention time and molecular mass to those in amino acid standards run on the same day. Peak identifications are given in Table 1.

extracts were desalted by using cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, BIO-RAD), and the amino acids recovered by elution with 2 M NH_4OH (prepared from Millipore water) and NH_3(g) (AirProducts, in vacuo). During ion exchange column loading, a DL-norleucine internal standard was added to each sample to estimate the amino acid recoveries from desalting and OPA/NAC derivatization. The nonhydrolyzed extracts of the meteorite samples were taken through the identical desalting procedure in parallel with the acid-hydrolyzed extracts. After desalting, the amino acids in the NH_4OH eluates were dried under vacuum to remove excess ammonia; the residues were then redissolved in 100 μL of Millipore water, transferred to sterile microcentrifuge tubes, and stored at −20 °C prior to analysis. Based on our analysis of amine standards taken through the entire extraction procedure, it is likely that a significant fraction of simple volatile amines including indigenous ammonia, methylamine, ethylamine, and propylamines were lost from the meteorite extracts during evaporation of the NH_4OH eluates; therefore, these compounds were not quantified. However, it is important to note that no decomposition or thermal degradation of amino acids during the extraction procedure was observed after comparison of the peak areas in amino acid standards taken through the identical hot water extraction and acid hydrolysis treatment as the meteorite samples.

UPLC-FD/ToF-MS Amino Acid Analyses

Prior to analysis, 10 μL of each meteorite extract, procedural blank, or standard was added to 10 μL of 0.1 M sodium borate buffer at room temperature and

then derivatized by adding 5 μL of OPA/NAC. The OPA/NAC reaction was quenched after 1 or 15 min with 75 μL of 0.1 M aqueous hydrazine, and 25 μL of the solution was immediately injected into a Waters ACQUITY UPLC with a fluorescence detector and Waters LCT Premier time-of-flight mass spectrometer using positive electrospray ionization. The details of the ToF-MS settings and the amino acid quantification methods used, and the range of linear response for these analyses are described elsewhere (Glavin et al. 2006). The remaining derivatized sample (and a parallel derivatized standard) was stored in a −86 °C freezer for repeat analyses. We have found through monitoring standards that OPA/NAC amino acid derivatives are stable for up to 1 week at −86 °C without significant degradation. Each derivatized sample was analyzed using our standard tandem LC column conditions for initial two- to ten-carbon (C_2–C_{10}) amino acid separation and characterization (Glavin et al. 2010). The first column was a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm bead) followed by a second Waters BEH Phenyl-Hexyl column (2.1 × 150 mm, 1.7 μm bead). The conditions for separation of the OPA/NAC amino acid derivatives at 30 °C were as follows: flow rate, 150 μL min^{-1}; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). The following day a different gradient using the same columns and buffers optimized specifically for the separation of the five-carbon (C_5) amino acids was used to analyze the same derivatized extract on the same columns (Glavin and Dworkin 2009).

Amino acid abundances and their enantiomeric ratios in the meteorite extracts were determined by comparison of the peak areas generated from the UV fluorescence detector and ToF-MS of the OPA/NAC amino acid derivatives to the corresponding peak areas of standards under the same chromatographic conditions on the same day (see Figs. 1–3). Amino acid peak identifications are given in Table 1. In addition to identifying the major fluorescent peaks present in the UPLC-FD/ToF-MS chromatograms by retention time, we also searched for the masses of the OPA/NAC derivatives corresponding to C_2–C_{10} amino acids by plotting the mass of each amino acid derivative over the elution time (see Fig. 2). The total amino acid concentrations in parts-per-billion (ppb) by bulk sample weight, the enantiomeric ratios, and L-isovaline excesses measured for the meteorite extracts reported in Tables 2–5 represent the average of between four and twenty-three separate analyses. The highly sensitive and selective UPLC-FD/ToF-MS technique employed in this study has a detection limit for amino acids that is a factor of approximately 10^3 times lower than for current state-of-the-art gas chromatography-mass spectrometer (GC-MS) measurements (Glavin et al. 2006). However, due to the extremely low amino acid abundances and limited sample mass available for the CM1 and CR1 carbonaceous chondrites analyzed in this study, GC-MS analyses and compound specific isotopic measurements for these meteorites were not possible.

RESULTS AND DISCUSSION

Amino Acid Analyses of the Carbonaceous Chondrites

UPLC-FD Measurements and Total Amino Acid Abundances

Typical UPLC-FD chromatograms of the 6 M HCl-hydrolyzed, hot-water extracts from the CM1 chondrites SCO 06043 and MET 01070, the CR1 chondrite GRO 95577, the serpentine blank, and an amino acid standard mixture are shown in Fig. 1. Similar UPLC-FD chromatograms were obtained for the other meteorite samples. The amino acid peak numbers correspond to the designations given in Table 1. Peaks in the meteorite extracts were only identified as amino acids if the retention time of the UV fluorescence peak coincided with the corresponding mass peak of the OPA/NAC derivatized amino acid standard (see Figs. 1 and 2). Several peaks labeled with an "X" in the fluorescence chromatograms for the meteorite samples and the serpentine blank are unidentified primary amine compounds from either the chemical workup or analytical artifacts that did not interfere with amino acid identification and quantification (Fig. 1). All of the identified amino acids and corresponding abundances are given in Tables 2 and 3. The absolute abundances reported were corrected for the desalting and derivatization recoveries using the D,L-norleucine internal standard; the recoveries ranged from 60–80% for the meteorite samples studied. Many other amino acid peaks were detected in the meteorite extracts (e.g., see Murchison in Fig. 2), but were not identified due to a lack of amino acid standards. All of the Antarctic meteorite samples revealed high intensity peaks (see Figs. 1 and 2, peak no. 33) corresponding to the C_6 amino acid ε-amino-*n*-caproic acid (EACA). This finding is consistent with a previous analysis of Antarctic CM2 chondrites and the most likely source of EACA is terrestrial contamination from the Nylon-6 storage bags used during sample collection and curation of Antarctic meteorites (Glavin et al. 2006). The abundance of EACA in the Antarctic meteorites ranged from approximately 400 to 51,000 ppb (Table 2), suggesting that exposure of these meteorites to Nylon-6 contamination is variable. It should be emphasized that

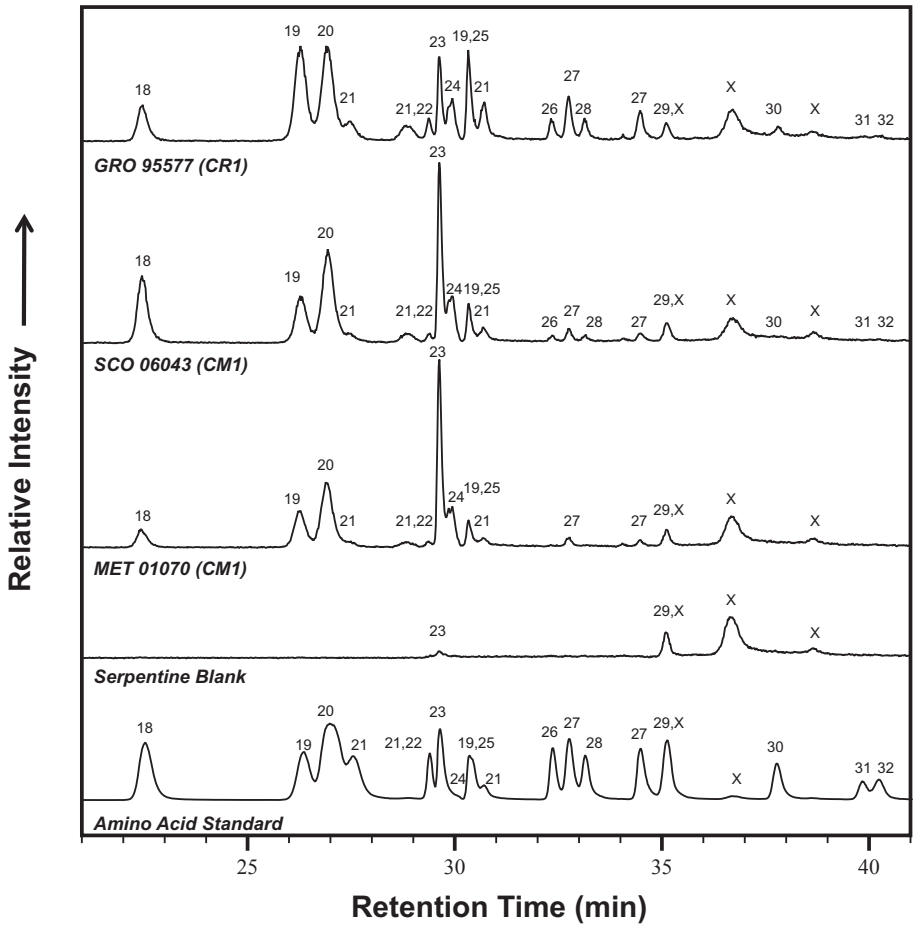

Fig. 3. The 20–41 min region of the LC-ToF-MS single ion chromatograms of the C_5 amino acids (m/z = 379.13 ± 0.02) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the standard mix and of the 6M HCl-hydrolyzed, hot-water extracts of the serpentine blank and the MET 01070, SCO 06043, and GRO 95577 meteorites are shown. Similar LC-ToF-MS single ion chromatograms were obtained for the nonhydrolyzed extracts. The peaks were identified by comparison of the retention time and exact molecular mass to those in the C_5 amino acid standard run on the same day. Peak identifications are given in Table 1.

the EACA contamination in these meteorites did not interfere with the ability to detect trace levels of other amino acids present in the samples. Since EACA is a potential terrestrial contaminant and its abundance is highly variable in meteorites, we excluded this amino acid from the total amino acid abundances and the ratio of free to total amino acids reported in Table 2.

Much lower abundances ranging from 4 to 295 ppb of the amino acids glycine, α-alanine, BALA, α-, β-, and γ-amino-*n*-butyric acid (ABA), and α-aminoisobutyric acid (α-AIB) were found in the aqueously altered chondrites MET 01070, SCO 06043, and GRO 95577 (Table 2). The abundances of α-AIB in these type 1 chondrites (30 to 175 ppb) are 100 to 1,000 times lower than the α-AIB abundances found in the CM2 Murchison and the CR2 EET 92042 (Table 2). A total amino acid abundance of approximately 16,000 ppb was measured in LON 94102, which is in the range of amino acid abundances previously measured in the CM2 chondrites Murchison and LEW 90500 (Table 2). Previous bulk oxygen isotope data (Clayton and Mayeda 1999), as well as hydrogen, carbon, and nitrogen isotopic analysis of the IOM of LON 94102 suggest that this meteorite is among the least altered of the CM chondrites (Alexander et al. 2010).

From Table 2, the low total amino acid abundances measured in MET 01070 (approximately 710 ppb) and GRO 95577 (approximately 1,600 ppb) are consistent with previous amino acid analyses of these type 1 chondrites (Botta et al. 2007; Martins et al. 2007). Although aspartic acid, glutamic acid, and serine have all been identified previously in these meteorites, we were unable to confirm their presence above serpentine blank levels (Fig. 1, Table 2). These amino acids are

difficult to identify by mass due to the low abundances and poor ionization of these compounds during the UPLC-ToF-MS analysis. The CM1 chondrite SCO 06043 has a very similar amino acid composition and total abundance (660 ppb) compared to MET 01070 (Table 2). The total amino acid abundance of the CI1 Orgueil (6,700 ppb) is higher than the CM1 and CR1 meteorites studied (Table 2). These Orgueil results are consistent with amino acid abundances measured in a previous HPLC-FD analysis of a different fragment of this meteorite (Ehrenfreund et al. 2001). Overall, the total amino acid abundances found in these aqueously altered type 1 chondrites are lower than those found in the less altered CM and CR type 2 and 3 chondrites which ranged from approximately 9,400 ppb for the CM2 LEW 90500 up to 320,000 ppb for the CR2 chondrite EET 92042 (Table 2). High amino acid concentrations ranging from 180,000 to 249,000 ppb have previously been reported for the CR2 meteorites EET 92042 and GRA 95229 (Martins et al. 2007; Pizzarello et al. 2008), but these values did not contain many of the C_5 amino acids that we included in our total amino acid abundance calculations reported in Tables 2 and 3. We found that the primitive CR3 chondrite QUE 99177 had a similar distribution of amino acids compared to EET 92042, but the total amino acid abundance of QUE 99177 (81,000 ppb) was lower than in EET 92042 (Table 2).

UPLC-FD/ToF-MS Measurements of C_2 to C_{10} Amino Acids

We investigated the masses corresponding to the OPA/NAC derivatives of the acyclic C_2 to C_{10} amino alkanoic acids in the sample extracts (see Fig. 2). Only trace levels (<10 ppb) of glycine (peak 9) and L-alanine (peak 12) in the serpentine procedural blank were measured by UPLC-FD/ToF-MS (Fig. 2), which indicates that minimal amino acid contamination of the meteorite samples occurred during the processing procedure. A few small unidentified nonfluorescent peaks were detected in both the serpentine blank and meteorite sample extracts and are marked with an "X" (Fig. 2). Based on the UPLC-FD/ToF-MS data, the Murchison meteorite contains a very large diversity of amino acids with evidence for C_2 up to C_{10} acyclic amino alkanoic acid isomers detected above background (Fig. 2). The masses plotted in Fig. 3 represent a 0.02 Da window (the peak width at half maximum) centered around the corresponding theoretical masses of the mono-protonated positive ions of C_2 to C_{10} OPA/NAC amino acid derivatives, and not the masses of the individual unlabeled amino acids. Based on the total ToF-MS areas in Fig. 3 (data not shown), the C_{10} amino acids in Murchison are a factor of 10–20 times less abundant than the area of each of the C_2 through C_6 amino acids.

Amino acids with carbon numbers exceeding C_{10} may also be present in Murchison, but these were not observed with confidence above the detection limit of the UPLC-ToF-MS instrument under the conditions employed. This may either be a result of meteorite chemistry or biases in the extraction and workup for the more hydrophilic amino acids. Diamino acids have also been identified in Murchison meteorite extracts using GC-MS (Meierhenrich et al. 2004). OPA derivatives of diamino acids have been separated using HPLC (Satyanarayana et al. 2001); however, our OPA/NAC derivatization and UPLC-FD/ToF-MS analytical technique was not optimized for the identification of these compounds. Nevertheless, these results are consistent with previous analyses of the Murchison meteorite that have identified over 80 amino acids, including both cyclic and acyclic primary α-amino alkanoic and alkanedioic acids with carbon numbers ranging from C_2 up to C_8 (Cronin et al. 1981; Cronin and Pizzarello 1983, 1986; Cronin and Chang 1993). To our knowledge, this study is the first report of amino acids in the Murchison meteorite that exceed C_8. Based on our UPLC-FD/ToF-MS data and the numerous possible structural isomers and enantiomers for amino acids with carbon numbers up to C_{10}, the Murchison meteorite likely contains hundreds of individual amino acids. Unfortunately, due to their low abundance, incomplete separation, and a lack of standards, the identity of many specific compounds cannot be confirmed. Future optimization of our LC separation conditions and synthesis of amino acid standards that are not commercially available will be required to determine the identities of the detected C_6 to C_{10} amino acids in Murchison and other carbonaceous meteorites.

Several unidentified peaks above background also appeared in the *m/z* 393.15 mass window of the Murchison extract, corresponding to the C_6 amino acid isomers (Fig. 2); however, we only confirmed the identity of two of these peaks: (EACA, peak 33) and the norleucine internal standard (I.S.) used to estimate amino acid desalting recoveries. For EET 92042, the intensity of the EACA peak was so high that the I.S. peak is present, but not easily visible at the scale shown (Fig. 2). A few of the unidentified C_6 amino acid peaks were also present in the type 1 chondrites Orgueil and SCO 06043; however, the total number of C_6 isomers is clearly less in these carbonaceous chondrites compared to Murchison (Fig. 2). In contrast to Murchison, the CR chondrites GRO 95577 and EET 92042 did not contain any evidence for amino acids with more than six carbons above serpentine blank levels (Fig. 2). This finding is particularly surprising for EET 92042, which

contains the highest reported amino acid abundance of any meteorite to date (Martins et al. 2007). The Orgueil and SCO 06043 meteorite extracts contain some evidence for the presence of C_7 and C_8 amino acids above serpentine background levels; however, the intensity of these amino acid peaks are reduced compared to Murchison (Fig. 2). These data are consistent with earlier studies showing reduced amino acid abundances in more aqueously altered type 1 carbonaceous chondrites compared to type 2 chondrites (Botta et al. 2007; Martins et al. 2007).

The UPLC-FD/ToF-MS instrument was specifically optimized for separation of the C_5 acyclic amino alkanoic acids and the retention times for all possible C_5 amino acid isomers and enantiomers were identified based on the analysis of standards (Fig. 3). The UPLC-FD/ToF-MS chromatograms centered at m/z 379.1328 ± 0.02 (the peak width at half maximum) correspond to the C_5 amino acids in the standard, the serpentine blank, and the MET 01070, SCO 06043, and GRO 95577 meteorite extracts (Fig. 3). Chromatograms showing the C_5 amino acid distributions in Orgueil, Murchison, LON 94102, EET 92042, and QUE 99177 are not shown here, but have been published previously (Glavin and Dworkin 2009). Although complete separation of all 23 possible C_5 amino acid isomers and enantiomers could not be achieved under the chromatographic conditions employed, all of the C_5 amino acids were accounted for and we observed no interference or coelution of the D- and L-enantiomers of isovaline, valine, norvaline, and 3-aminopentanoic acid (3-apa) with other C_5 amino acids. As with a number of rare C_5 amino acids, the D- and L-enantiomers of 3-apa were clearly separated (Fig. 3), however they could not be identified due to the lack of optically pure 3-apa standards.

A comparison of the individual and total abundances of the C_5 amino acids in the meteorites is shown in Table 3. The only C_5 amino acid that could not be quantified in any of the meteorite extracts due to coelution was 3-amino-3-methylbutanoic acid (3-a-3-mba); therefore, only upper limits are given for 3-a-3-mba. The total abundances of all other C_5 amino acids were determined by comparing the peak areas with standards (Table 3). The CM1 chondrites MET 01070 and SCO 06043 and the CR1 chondrite GRO 95577 had low total C_5 amino acid abundances ranging from 220 to 500 ppb, much lower than found in the CM2 and CR2/3 chondrites (Table 3). The most likely explanation for the low abundances in type 1 chondrites is decomposition of amino acids during aqueous alteration on the meteorite parent body. This is not surprising, since the decomposition of aliphatic moieties in the free and macromolecular organic matter by low temperature chemical oxidation during aqueous alteration on the parent body could result in the low amino acid levels observed in the type 1 chondrites (Sephton et al. 2004; Cody and Alexander 2005). Thermal decomposition by α-decarboxylation of α-amino acids to CO_2 and the corresponding primary amine during aqueous alteration on the parent body is another possibility (Simmonds et al. 1972); however, as noted previously, many of the volatile amines produced from α-decarboxylation (including the butylamines from the C_5 amino acids) were not detected in our UPLC-FD/ToF-MS analyses of the meteorite extracts and may have been lost during chemical workup.

Presence of Free versus Bound Amino Acids

It has been shown previously that acid hydrolysis of the water extracts from carbonaceous meteorites will readily release bound amino acids. These bound amino acids have their amino group chemically protected and are not subject to OPA/NAC derivatization or exist as a precursor to the amino acid and would have a different mass and retention time compared to the OPA/NAC labeled amino acid. The increase in amino acid concentration in the hydrolyzed extracts observed in many carbonaceous chondrites is believed to be a result of derivatives and/or acid-labile precursors that are converted to amino acids after acid hydrolysis. For example, in the Murchison meteorite most of the acid-labile precursors are low molecular weight derivatives including mono- and dicarboxylic acid amides, hydroxy acid amides, lactams, caboxylactams, *N*-acetylamino acids, and substituted hydantoins (Cronin 1976a,b; Cooper and Cronin 1995).

Analysis of the nonhydrolyzed water extracts of the CM1s SCO 06043 and MET 01070, and the CR1 GRO 95577 showed a similar distribution of free amino acids compared to the total (free + bound) amino acids in the acid-hydrolyzed extracts. From the UPLC-FD/ToF-MS data (not shown), we calculated the total abundance of free amino acids (not including EACA) in the nonhydrolyzed extracts (Table 2). The results are similar to previous analyses of the CM2 chondrites Murchison, LEW 90500, and ALH 83100 (Glavin et al. 2006) and the CM1 chondrites MET 01070 and ALH 88045 (Botta et al. 2007) which reported that free amino acids on average represent approximately 40 to 50% of the total acid-hydrolyzable amino acid abundance. In contrast, Pizzarello and coworkers found that the abundance of amino acids in the relatively unaltered Antarctic CR2 chondrite GRA 95229 hot water extract did not increase substantially after acid hydrolysis, with free amino acids representing over 70% of the total amino acid abundance on average (Pizzarello et al. 2008). We also measured a high relative abundance of

free amino acids (free/total = 64%) in another Antarctic CR2 chondrite EET 92042 (Table 2). It is possible that bound amino acids are more resistant to oxidation during aqueous alteration than free amino acids, resulting in a lower free/total amino acid ratio in more aqueously altered chondrites. However, if this were true we would expect a higher ratio of free to total amino acids in the less altered CR3 chondrite QUE 99177 compared to the CR2 EET 92042, and this was not observed (Table 2). Amino acid analyses of the nonhydrolyzed water extracts from additional carbonaceous chondrites that experienced minimal aqueous alteration will be required to further investigate this hypothesis.

Unusual Amino Acids and Enantiomeric Measurements

The presence of nonprotein amino acids in meteorites that are not common on Earth, such as α-AIB and isovaline, has often been used to argue that these amino acids are indigenous to the meteorites and not terrestrial contaminants. In fact, the majority of the 80+ amino acids identified in the Murchison meteorite are either rare or nonexistent in terrestrial proteins (Cronin and Chang 1993). The high relative abundances of α-AIB and isovaline in Murchison and other Antarctic CM2 and CR2 chondrites (Table 2) compared to the most common protein amino acids provide additional support of an extraterrestrial origin for these amino acids. For the Antarctic meteorites, the Antarctic ice is a very unlikely source of these two nonprotein amino acids. Amino acid analysis of Antarctic ice from the ALH region revealed only ppb levels of the protein amino acids glycine, L-aspartic acid, L-serine, L-glutamic acid, and L-alanine and no evidence for α-AIB and isovaline above the 2 parts-per-trillion (ppt) detection limit (Mcdonald and Bada 1995; Bada et al. 1998). Trace levels of α-AIB (46 ppt) were recently identified in an Antarctic ice sample from LaPaz using very similar methods to those reported here, although the source of this amino acid remains uncertain (Glavin et al. 2006). In addition, contamination of the Murchison meteorite by terrestrial α-AIB or isovaline from the landing site environment is also unlikely since these amino acids were not identified above the 10 ppb detection limit in surface and subsurface (20–30 cm) soil samples collected from the Murchison fall site (Kvenvolden et al. 2000). For the Murchison meteorite, stable isotope analyses of α-AIB and isovaline have shown enrichments of D, ^{15}N, and ^{13}C that fall well outside the range for terrestrial amino acids and indicate an extraterrestrial origin (Engel et al. 1990; Engel and Macko 1997; Pizzarello et al., 2004b; Pizzarello and Huang 2005).

Although α-AIB and isovaline are not among the 20 genetically encoded amino acids, they are present in a variety of terrestrial fungal polypeptides (named peptaibols) that are biosynthesized through nonribosomal enzymatic pathways (Kleinkauf and Von Dohren 1996; Brückner et al. 2009); therefore, presence of these amino acids alone does not prove an extraterrestrial origin. Additional data, such as the distribution of the entire suite of amino acids, chirality, or stable isotopes are required to completely rule out a biological source of α-AIB and isovaline in meteorites. This becomes particularly important (and difficult) for meteorites with extremely low abundances of α-AIB and isovaline and where only a limited mass of sample is available for analysis (e.g., MET 01070, SCO 06043, and GRO 95577). For these meteorites, compound-specific stable isotopic measurements of α-AIB and isovaline could help determine the origin of these amino acids. However, given the low amino acid abundances in the type 1 chondrites, this analysis is particularly challenging, if not impossible, with current instrumentation and would require a significant fraction of the available sample. For example, recent analysis of material returned from NASA's Stardust mission showed the ability to perform compound-specific carbon isotope analysis from 0.7 nmol of glycine (Elsila et al. 2009). A similar isotopic analysis of D-isovaline would require a minimum of approximately 0.25 nmol on column. Based on this detection limit and the measured abundances of D-isovaline in SCO 06043 and GRO 95577 of 3.3 ppb and 14.6 ppb (Table 3), we would require 29 g and 6.3 g of meteorite, respectively. Given the total recovered mass of 27.6 g for SCO 06043 and 106.2 g of GRO 95577, there is not enough material available for isotopic measurement of D-isovaline in SCO 06043 and roughly 6% of the total available mass of GRO 95577 would have to be requested for destructive analysis. Given that GRO 95577 is the only known CR1 carbonaceous chondrite, obtaining this much sample appears prohibitive. Therefore, until the sensitivity of analytical techniques for isotopic measurements can be improved, amino acid enantiomeric measurements and comparisons of the amino acid distributions with possible terrestrial sources are the only ways to establish the origin of amino acids in these type 1 chondrites.

D/L Enantiomeric Ratios

Chirality is another important measurement tool to help discriminate between biotic and abiotic origins of amino acids in meteorites, even if present at low abundances. On Earth, biology almost exclusively uses L-amino acids, whereas abiotic syntheses result in equal mixtures of L- and D-amino acids. Furthermore, protein amino acids will readily racemize (approach D/L = 1)

on geologically short time scales (Bada 1972). Therefore, if we assume that the protein amino acids found in carbonaceous chondrites were racemic (D/L approximately 1) prior to their fall to Earth, then their current D/L ratios can be used to determine the relative degree of terrestrial L-amino acid contamination they have experienced on Earth. The enantiomeric ratios (D/L) for aspartic and glutamic acids, serine, alanine, β-ABA, valine, norvaline, and isovaline are reported in Table 4 when abundances permitted quantitation.

The enantiomeric ratios measured for the protein amino acids (italicized in Table 4) in the CM chondrites Murchison (USNM 6650), LEW 90500, and LON 94102, and the CR chondrites EET 92042 and QUE 99177 were mostly found to be racemic (D/L approximately 0.9 to 1.0) within analytical errors (±0.05 to 0.3, Table 4), indicating that these amino acids are primarily abiotic in origin and not the result of terrestrial contamination. However, a lower D/L ratio for glutamic acid of 0.57 measured in Orgueil (Table 4) may indicate that some terrestrial L-glutamic acid is present in this meteorite. The relatively low D/L ratios of aspartic and glutamic acids in Murchison (USNM 5453) of 0.67 and 0.61, indicate that this fragment has a higher degree of terrestrial L-protein amino acid contamination than the other Murchison sample used in this study (USNM 6650) which has much higher D/L ratios for aspartic and glutamic acids (D/L = 0.91 and 0.96, respectively) (Table 4). Despite these significant differences in D/L aspartic and glutamic acid ratios in the two samples of Murchison, the nonprotein amino acids β-ABA, norvaline, and isovaline in these samples had identical D/L ratios within errors (Table 4), suggesting that terrestrial contamination is an unlikely source for these nonprotein amino acids. Although aspartic and glutamic acids were not detected in MET 01070, SCO 06043, and GRO 95577, the D/L ratio for alanine measured in these meteorites was racemic (D/L approximately 1) within analytical uncertainties (Table 4), indicating both an extraterrestrial origin for alanine and low levels of terrestrial L-amino acid contamination in these meteorites.

Although the D- and L-enantiomers of valine were separated using the LC conditions employed, there was a relatively large unidentified nonfluorescent coeluting isobaric contaminant at approximately the same retention time as L-valine in some of the analyses including the serpentine blank (Fig. 3), which may have led to erroneously high L-valine abundances, and hence lower D/L valine ratios (approximately 0.2 to 0.5) for Orgueil, Murchison (USNM 5453), SCO 06043, and GRO 95577 (Table 4). Therefore, lower limits were placed on these ratios. The nonprotein amino acids β-ABA and norvaline detected in these meteorites were racemic (D/L approximately 1) within analytical error, indicating an abiotic origin for these amino acids (Table 4). One notable exception was the enantiomeric ratio of the nonprotein amino acid isovaline, which ranged from 0.61 to 0.80 in Orgueil, SCO 06043, GRO 95577, and Murchison (Table 4). Terrestrial isovaline contamination of these meteorites after falling to Earth is highly unlikely since no isovaline was detected in any of the relevant collection site environments or any of the laboratory procedural blanks. Although some fungal peptide contamination of both D- and L-isovaline cannot be completely ruled out, it is important to note that isovaline is most commonly found in the D-configuration in fungal peptides (Keller et al. 1990; Brückner et al. 2009), which would increase (and not decrease) the D/L isovaline ratio. In addition, many common fungal peptides also contain L-alanine (D/L approximately 0.06) at similar abundances to isovaline (Brückner et al. 2009); therefore, if any significant fungal peptide contamination of the meteorites had occurred, the D/L alanine ratios in these meteorites should have been affected as well. However, the D/L alanine ratios in all of the meteorites analyzed were racemic within analytical errors showing no evidence for significant terrestrial L-alanine contamination (Table 4). The detection of nonracemic D/L isovaline ratios corresponding to L-isovaline excesses in Murchison and other carbonaceous chondrites have been reported previously (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Pizzarello et al. 2003, 2008; Glavin and Dworkin 2009). Possible mechanisms for the origin of the L-isovaline asymmetry observed in some carbonaceous chondrites are discussed below.

Variability in Amino Acid Distributions and Formation Pathways

Comparisons of the relative amino acid abundances between different groups of carbonaceous meteorites can be a powerful way to elucidate synthetic pathways for the formation of amino acids and to understand the trends between amino acid composition and degree of aqueous alteration on the meteorite parent body (Glavin et al. 2006; Botta et al. 2007; Martins et al. 2007). For example, the CI1 chondrites Orgueil and Ivuna were found to have a relatively simple distribution of amino acids (predominantly β-alanine) compared to the complex distribution of α-amino acids (predominantly glycine, isovaline, and α-AIB) found in the CM2 meteorites Murchison and Murray believed to have formed by Strecker synthesis (Peltzer et al. 1984; Ehrenfreund et al. 2001). Since β-alanine is not produced directly by the Strecker-cyanohydrin pathway, it was argued that this amino acid must have formed by an alternate synthetic route (Ehrenfreund et al. 2001),

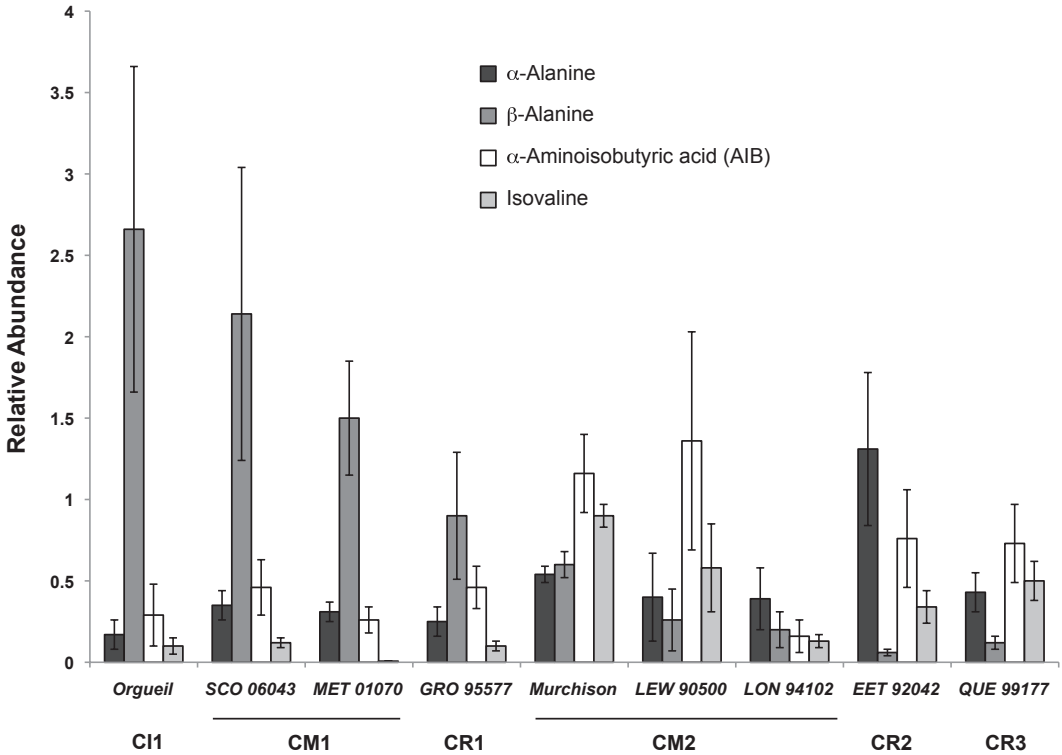

Fig. 4. A comparison of the relative molar abundances (glycine = 1.0) of alanine, β-alanine, α-aminoisobutyric acid, and isovaline in the 6M HCl-hydrolyzed, hot-water extracts of the carbonaceous meteorites investigated in this study. The relative abundances were calculated from the data in Table 2 after correcting for the molecular weights of each amino acid. The uncertainties were calculated by standard error propagation of the absolute errors in Table 2. The amino acid data for Murchison (USNM 6650) and LEW 90500 were taken from Glavin et al. (2006).

such as Michael addition of ammonia to cyanoacetylene (Miller 1957). Based on this amino acid evidence it was concluded that the Orgueil and Ivuna meteorites must have originated on a chemically distinct parent body from the CMs, possibly an extinct comet (Ehrenfreund et al. 2001).

A subsequent comparison of the relative abundances of β-alanine and α-AIB in Orgueil with four CM2 meteorites showed that the relative abundances of both β-alanine and α-AIB tracked with the degree of aqueous alteration of the meteorites, with the more altered Orgueil meteorite having the highest β-alanine and lowest α-AIB relative abundances (Glavin et al. 2006). Although a similar trend was also observed for the CR1 chondrite GRO 95577 and the less altered CR2s EET 92042 and GRA 955229 (Martins et al. 2007), there was no clear trend with aqueous alteration found in relative α-AIB and β-alanine abundances in a previous study of CM1 and CM2 chondrites (Botta et al. 2007). One potential problem with comparing amino acid abundance data from these different studies is that the meteorites were analyzed in different laboratories at different times using different instrumentation and different peak integration procedures. In addition, sample heterogeneity must also be accounted for when drawing comparisons between laboratories. Here for the first time we compare the relative abundances of amino acids collected on a suite of CI, CM, and CR carbonaceous chondrites that cover the entire range of aqueous alteration (petrographic types 1–3) using the identical extraction, analytical, and quantitation techniques in the same laboratory.

Relative Abundance of β-alanine as an Indicator for Aqueous Alteration

A comparison of the relative molar abundances (glycine = 1.0) of α-alanine (D+L enantiomers), β-alanine, α-AIB, and isovaline (D+L enantiomers) measured in nine different carbonaceous chondrites is shown in Fig. 4. The order of carbonaceous chondrites in Fig. 4 are based on the approximate degree of aqueous alteration inferred from mineralogical and isotopic evidence with the most altered CI1 Orgueil and other type 1 chondrites on the left and the most primitive, least altered CR chondrites on the right (Zolensky and McSween 1988; Kallemeyn et al. 1994; Zolensky and Browning 1994). The relative degree of aqueous alteration among carbonaceous chondrites within the

same group and of the same petrologic type (e.g., the difference in degree of alteration between the three CM2 chondrites shown in Fig. 4) is less certain, although recent isotopic analyses of the IOM in LON 94102 suggests that this meteorite is less altered than Murchison (Alexander et al. 2010). Based on the data in Fig. 4, there appears to be a correlation between the relative abundance of β-alanine and degree of aqueous alteration in the meteorites studied. The relative abundance of β-alanine increases from a β-alanine/glycine ratio of approximately 0.1 to 0.2 for the least altered CR chondrites EET 92042 and QUE 99177 up to approximately 2.7 for the most aqueously altered CI1 Orgueil. We also find that within the corresponding CM and CR chondrite groups, the type 1 chondrites have a much higher relative abundance of β-alanine compared to the less altered type 2 chondrites (Fig. 4). Thus, in addition to mineralogy and isotopic measurements, the relative abundance of β-alanine should also be considered when comparing the degree of aqueous alteration between carbonaceous chondrites.

In contrast to β-alanine, there do not appear to be any strong trends in relative α-alanine, α-AIB, and isovaline abundances with aqueous alteration (Fig. 4). However, it is worth noting that the relative abundances of α-AIB and isovaline tend to be higher in carbonaceous chondrites that experienced less aqueous alteration (Fig. 4). The relative abundance of α-alanine ranged from 0.2 for Orgueil up to 1.3 for EET 92042. The high α-alanine abundance in EET 92042 was not observed in QUE 99177 and cannot be explained by a large contribution of terrestrial L-alanine contamination since the D/L alanine ratio in EET 92042 was 0.97 (Table 4). Assuming that Strecker synthesis was the primary mechanism for the formation of α-alanine in EET 92042 and QUE 99177, it is possible that the parent body of EET 92042 had a higher ratio of acetaldehyde to formaldehyde (the Strecker precursors for formation of α-alanine and glycine, respectively) compared to QUE 99177.

The weakly altered CM2 chondrite LON 94102 is clearly different compared to the other more altered CM2 chondrites (or any other meteorite analyzed in this study) and appears to follow the opposite trend in relative α-AIB and isovaline abundances, with lower α-AIB/glycine and isovaline/glycine ratios compared to Murchison and LEW 90500 (Fig. 4). One possibility for the low α-AIB and isovaline abundances in LON 94102 is that this meteorite originated from a chemically distinct parent body from other CM chondrites that was depleted in acetone and 2-butanone, the ketone precursors required for the formation of α-AIB and isovaline, respectively, by Strecker-cyanohydrin synthesis. However, based on a variety of petrologic properties of eleven different CM chondrites that show similar bulk compositions, it has been suggested that textural differences seen among individual CM chondrites may reflect progressive alteration of similar hypothetical CM3 starting materials in different regions of the same parent body (Rubin et al. 2007). Therefore, we cannot rule out the possibility that the relative abundances of amino acids in LON 94102 are typical for weakly altered CM chondrites. Comparing the relative distribution of amino acids in LON 94102 to other weakly altered CM2 chondrites, such as QUE 97990 and Yamato (Y)-791198 (Metzler et al. 1992; Rubin et al. 2007; Chizmadia and Brearley 2008; Maeda et al. 2009), may help confirm this hypothesis. Previous amino acid analyses found more than ten times the relative molar abundance of α-AIB (α-AIB/glycine = 2.7 to 3.5) in Y-791198 (Shimoyama et al. 1985; Shimoyama and Ogasawara 2002) compared to what we observed in LON 94102 in this study (Fig. 4). However, it should be pointed out that we have not yet analyzed Y-791198 using the same UPLC-FD/ToF-MS technique used for LON 94102. To our knowledge, no amino acid measurements have been reported yet for QUE 97990.

The similarity in the distributions of α-alanine, β-alanine, α-AIB, and isovaline among type 1 chondrites across three separate carbonaceous chondrite groups (CI, CM, and CR) that are distinct from the less altered type 2 and type 3 chondrites (Fig. 4), may point toward degree of aqueous alteration, rather than unique parent body chemical compositions, as an explanation for the amino acid variations observed in these chondrites. Although the high relative abundance of β-alanine and the simple distribution of amino acids found in the CI1 chondrites Orgueil and Ivuna has been attributed to a distinct chemical composition on the CI parent body compared to the CM parent body (Ehrenfreund et al. 2001), the amino acid data from this study suggest that this might not be the case, and extended aqueous alteration, rather than differences in the chemical composition of the parent body, may be responsible for the high relative abundance of β-alanine over other α-amino acids in CI1 chondrites.

Possible Formation Pathways for Amino Acids Found in Meteorites

As stated above, β-amino acids cannot be formed by the Strecker mechanism, but can be synthesized by Michael addition of ammonia to α,β-unsaturated nitriles followed by reduction/hydrolysis in water, a mechanism that was proposed for the formation of β-alanine in spark discharge experiments (Miller 1957). For example, the formation of β-alanine by Michael addition of ammonia to cyanoacetylene during aqueous alteration on the parent bodies of CI, CM, and CR chondrites may have occurred. The reaction of HCN, NH_3, and carbonyl compounds

(aldehydes and ketones) leads to the formation of α-amino, imino, and α-hydroxy acids in aqueous solution via the Strecker-cyanohydrin pathway and all of these expected Strecker byproducts have been identified in the Murchison meteorite (Peltzer and Bada 1978; Peltzer et al. 1984; Lerner and Cooper 2005). Alternative sources for the amino acids in carbonaceous chondrites such as irradiation of ices formed in the interstellar medium (Bernstein et al. 2002; Elsila et al. 2007; Hudson et al. 2008) and Fischer-Tropsch Type (FTT) catalysis (Hayatsu et al. 1971) that do not require aqueous activity for their formation in the parent body have also been proposed. Several α-amino acids and one β-amino acid (β-alanine) have been synthesized by Fischer-Tropsch, however, no γ- or δ-amino acids were reported (Yoshino et al. 1971). Additional studies of the Fischer-Tropsch based synthesis of amino acids are clearly needed using modern analytical methods to ascertain the distribution of amino acids produced by this process. Some meteoritic γ- and δ-amino acids found in Murchison could be produced from the hydrolysis of lactams that have been identified in this meteorite (Cooper and Cronin 1995; Pizzarello et al. 2006). Although FTT products are expected to be predominantly straight-chain hydrocarbons (Hayatsu and Anders 1981), the opposite is found for the carbonaceous chondrites where branched-carbon chain amino acid isomers dominate over straight-carbon chain isomers (e.g., Murchison, LEW 90500, EET 92042, QUE 99177, GRA 95229) or are approximately equal abundance (Orgueil, MET 01070, SCO 06043, GRO 95577, LON 94102) (see Fig. 5b) (Martins et al. 2007). The predominance of branched over straight-chain amino acid isomers has also been observed in Murchison and suggests that ion and radical stability was important during carbon chain formation of the interstellar amino acid precursors (Cronin and Chang 1993; Herbst 1995). Identifying variations in the structure of C_5 amino acids in meteorites has also been used to help constrain parent body processes for the formation of these compounds (Glavin et al. 2010).

Variations in C_5 Amino Acid Structure Between Carbonaceous Chondrite Groups

For this study, we calculated the relative molar abundances of the C_5 amino acid isomers in each meteorite as a function of amine position (α-, β-, γ, or δ-) and valeric acid carbon chain structure (*n*-, *sec*-, *iso*-, or *tert*-) to determine if any synthetic relationships or chemical patterns exist between the CI, CM, and CR chondrite groups. These results, normalized to the total number of possible structural isomers, are illustrated in Figs. 5a and 5b. The dashed line corresponding to a relative abundance of 1 indicates the expected ratio if there was an equal probability of forming all of the C_5 amino acid isomers. Therefore, for the purposes of this discussion, enhanced and depleted relative abundances refer to values that fall above and below the dashed line, respectively. The high relative abundances of C_5 α-amino acids compared to β-, γ-, and δ-amino acids in the CM chondrites Murchison and LEW 90500 and the CR chondrites EET 92042 and QUE 99177 provide strong evidence that the C_5 α-amino acids in these meteorites were formed by Strecker-cyanohydrin synthesis (Fig. 5a). However, the opposite trend is observed for the more aqueously altered type 1 chondrites Orgueil, SCO 06043, MET 01070 and GRO 95577, which have a much higher relative abundance of the γ- and δ-amino acids compared to the α- and β-amino acids (Fig. 5b). One possibility is that more extensive aqueous alteration in the type 1 carbonaceous chondrites results in an increase in the rate of hydrolysis of amino acid precursors yielding elevated levels of γ- and δ-amino acids in these carbonaceous chondrites. As mentioned earlier, some meteoritic γ- and δ-amino acids found in Murchison could have been produced directly from the hydrolysis of lactams present in the meteorite (Cooper and Cronin 1995; Pizzarello et al. 2006). It is possible that the high abundances of C_5 γ- and δ-amino acids detected in type 1 carbonaceous chondrites could have formed from lactams by a similar process; however, lactams contain secondary (and not primary) amines and we are unable to confirm the presence of these compounds in the nonhydrolyzed meteorite extracts using our analytical method. Another possible explanation for the high relative abundances of C_5 γ- and δ- amino acids is that these amino acids are more stable to thermal decomposition than the α- and β-amino acids. For example, it has been shown previously for the C_4 amino acids that α- and β-aminobutyric acid have much higher decarboxylation rates than γ-aminobutyric acid in aqueous solution at elevated temperatures (Li and Brill 2003). Future experiments will be required to determine if the relative abundances of the C_5 amino acids measured in this study reflect a similar amino acid decarboxylation rate trend.

In general, the relative abundances of the C_5 β-amino acids in the type 1 chondrites seem to be slightly higher than in the type 2 and type 3 chondrites (Fig. 5a); however, unlike the C_3 amino acid β-alanine, we see no clear trend in C_5 β-amino acid abundance with degree of alteration in the meteorites analyzed. LON 94102 has a unique C_5 amino acid distribution compared to the other CM2 chondrites and is only slightly enriched in α-, γ-, and δ-amino acids compared to β-amino acids. One possible explanation for this observation is that LON 94102 experienced more aqueous alteration than Murchison and LEW 90500 leading to an increased relative abundance of γ- and

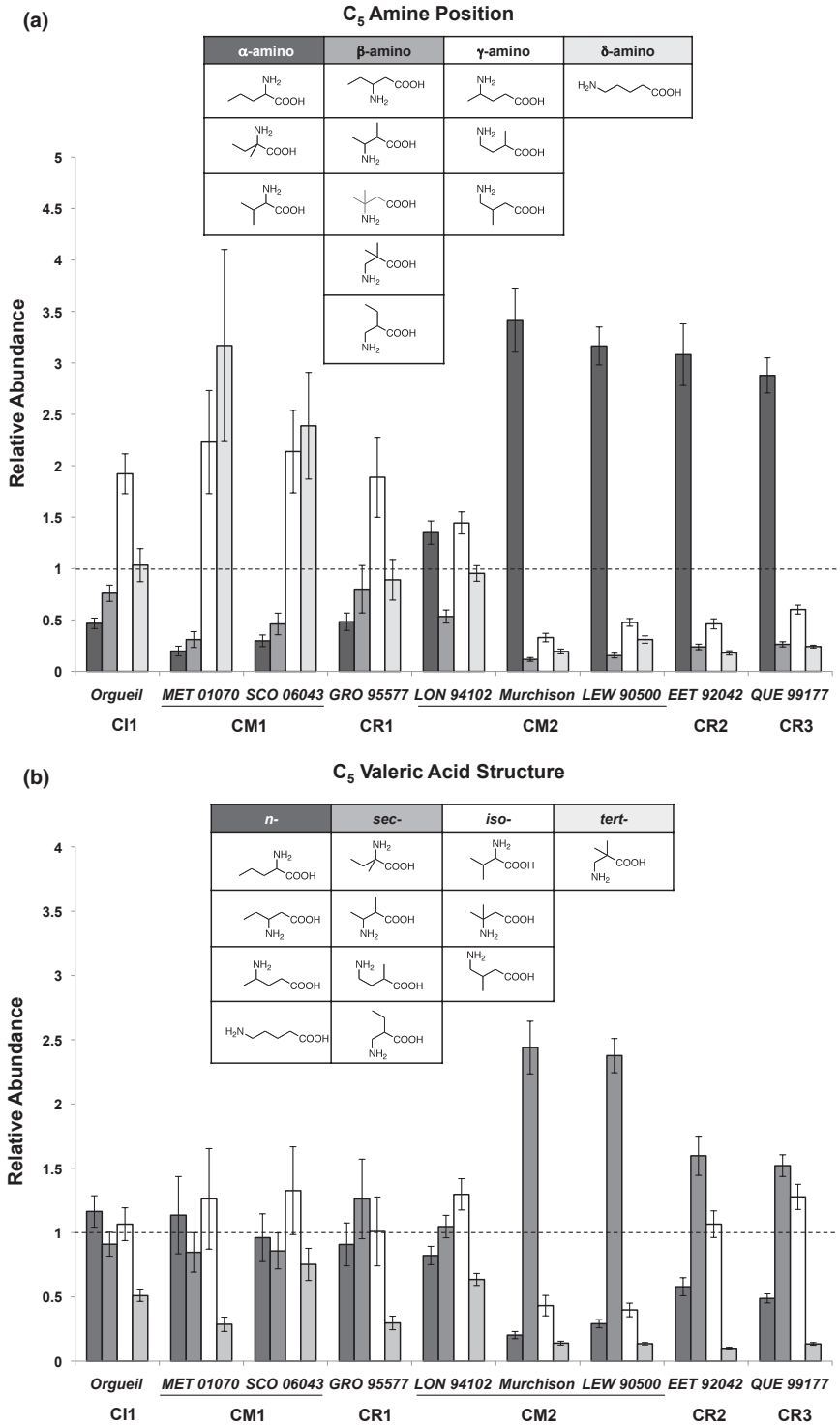

Fig. 5. A comparison of the relative molar abundances of the C_5 amino acids in CI, CM, and CR carbonaceous chondrites as a function of (a) amine position (α-, β-, γ-, and δ-) and (b) valeric acid carbon chain backbone (*n*-, *sec*-, *iso*-, and *tert*-) normalized to the total number of possible structural isomers. The dashed line corresponds to the expected relative abundance if the amino acids were formed by a completely random synthetic process. The relative abundance data for MET 01070, SCO 06043, and GRO 95577 is from this study. The data for Orgueil, LON 94102, Murchison (USNM 6650), LEW 90500, EET 92042, and QUE 99177 taken from Glavin and Dworkin (2009) are shown for comparison. It is apparent from the data that in most cases there is structural similarity in C_5 amino acid relative abundances within a single meteorite group. However, based on our amino acid relative abundance data, LON 94102 appears to be distinct from other CM2 chondrites.

δ-amino acids due to their slower decomposition rates and/or increased production from the hydrolysis of lactams in LON 94102. However, bulk oxygen isotope data (see Fig. 4 of Clayton and Mayeda 1999) and recent isotopic analysis of the IOM in LON 94102 indicates that this meteorite is much less, not more, altered than Murchison and LEW 90500 (Alexander et al. 2010). Therefore, an alternate explanation is that LON 94102 originated on a chemically distinct parent body from these CM2 chondrites.

A comparison of the relative abundances of the C_5 amino acids as a function of carbon-chain (valeric acid) structure yields additional insight into the mechanism of formation of these amino acids. As illustrated in Fig. 5b, we find a predominance of branched-chain (*sec*- and *iso*-) over straight-chain (*n*-) C_5 amino acids in the CMs Murchison and LEW 90500 and the CRs EET 92042 and QUE 99177. However, this is not the case for the aqueously altered type 1 chondrites Orgueil, MET 01070, SCO 06043, and GRO 95577 where branched-chain amino acids are not favored over the straight-chain acids and roughly equal abundances of the *n*-, *sec*-, and *iso*-valeric acid structures are observed with only a slight depletion of *tert*-valeric acid (Fig. 5b). Once again, we find that LON 94102 has a distinct distribution of C_5 amino acids compared to other CM2 and CR2 chondrites with respect to the valeric acid chain structure with a distribution that is very similar to the type 1 chondrites. Since LON 94102 has been classified as a CM2, the relative distribution of C_5 amino acids in this meteorite is puzzling. With the exception of LON 94102, we conclude that aqueous alteration on the parent bodies of CM and CR chondrites changes the distributions of C_5 amino acids from predominately α-amino acids to predominately γ- and δ-amino acids with relative enrichments in the *n*- and *tert*-valeric acid structures. Although at present we have not identified the mechanism(s) responsible for the variations seen in the C_5 amino acid distributions for these carbonaceous chondrites, parent body alteration seems to be the most reasonable explanation.

Evidence for Amplification of L-Isovaline Asymmetry During Aqueous Alteration

Although nearly racemic mixtures (D/L approximately 0.9 to 1.0) were measured for several chiral protein and nonprotein amino acids in at least one pristine sample of Murchison (Table 4), small L-enantiomeric excesses ranging from 1.0 to 9.2% have previously been measured for several nonprotein α-dialkyl amino acids in the Murchison and Murray meteorites including 2-amino-2,3-dimethyl-pentanoic acid, isovaline, α-methylisoleucine, α-methylnorvaline, α-methylnorleucine, and α-methylvaline (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Pizzarello et al. 2003). In contrast to α-hydrogen amino acids, these α-dialkyl amino acids are highly resistant to racemization (conversion of one enantiomer to the other); therefore, small enantiomeric excesses should be preserved for these amino acids since the time of formation. However, the detection of enantiomeric enrichments of approximately 12–14% in the C_6 amino acid diastereomers L-isoleucine and D-alloisoleucine in the Antarctic CR meteorite GRA 95229 that may have derived from asymmetry in their C_5 aldehyde precursor (Pizzarello et al. 2008), suggests that aqueous alteration did not lead to extensive racemization of the aldehydes on the parent body. L-isovaline excesses ranging from 0 to 15.2% were measured in several different samples of the Murchison meteorite from the Smithsonian Institution (USNM 5341) and Arizona State University (ASU 828 and ASU ′70) collections using GC-MS with significant variations between meteorite fragments (Pizzarello et al. 2003). The large L-isovaline excesses in Murchison were later confirmed in our laboratory by LC-FD/ToF-MS analysis of another sample of Murchison (USNM 5560), and L-isovaline excesses up to 15% were also found for the first time in the CI Orgueil (Glavin and Dworkin 2009). The large L-isovaline excesses observed in Murchison and Orgueil would not likely have obtained their asymmetry by the same mechanisms as L-isoleucine and D-alloisoleucine, since the Strecker precursor for isovaline (2-butanone), is achiral.

It has been proposed that the L-enantiomeric excesses of the α-dialkyl amino acids found in Murchison and Murray could be the result of asymmetric photolytic decomposition of the amino acids or their precursors by UV circularly polarized light (UV-CPL) in the presolar cloud (Bonner and Rubenstein 1987). Polarized photons of synchrotron radiation derived from strong magnetic fields around neutron stars or scattered from interstellar dust in star forming regions have also been suggested as alternative sources of the amino acid asymmetry found in meteorites (Bonner 1991; Bailey et al. 1998; Fukue et al. 2009). Chiral amino acid symmetry breaking and enantiomeric enrichment of 2–3% by UV CPL photodestruction of solid leucine has been demonstrated in the laboratory (Flores et al. 1977). Similar experiments have also shown that small 0.5% excesses of D- and L-alanine can be produced by R-UV-CPL and L-UV-CPL, respectively (Takano et al. 2007). However, in order to produce the largest ≥15% left handed excess previously reported for isovaline in Murchison (Pizzarello et al. 2003; Glavin and Dworkin 2009), more than 99% of the compound would have to be destroyed

by UV-CPL (Flores et al. 1977). Therefore, UV-CPL as the sole mechanism for enantiomeric enrichment seems unlikely given the high concentrations of isovaline found in Murchison and Murray and chemical evidence that isovaline and other α-amino acids formed by Strecker-cyanohydrin synthesis during aqueous alteration in the CM parent body (Peltzer and Bada 1978), thus shielded from circularly polarized radiation. It should also be noted that similarities in the carbon isotopic variation with chain length in Murchison observed for α-methyl-α-amino acids including isovaline and for α-hydrogen amino acids provides additional evidence that these amino acids did not form by distinct chemical pathways (Pizzarello et al. 2004). Other possible mechanisms for breaking amino acid symmetry include physical processes, such as crystallization (Kondepudi et al. 1990). Asymmetric autocatalysis (the Soai reaction) provided the first experimental evidence that small initial imbalances can be amplified under aqueous conditions to produce large enantiomeric excesses up to 90% (Soai et al. 1995). Recently, it has also been shown that several protein amino acids that form racemic compounds and have nonzero eutectic values can result in significant asymmetric amplification from a small initial imbalance due to the equilibrium solid-liquid phase behavior of amino acids in solution (Blackmond 2004; Klussmann et al. 2006). The eutectic value of isovaline has not been reported and it remains unclear whether or not this amplification mechanism is even relevant under parent body conditions. Nevertheless, since the more aqueously altered CM and CI chondrites Murchison and Orgueil have high L-isovaline enantiomeric excesses (L_{ee} approximately 15 to 19%), and the most primitive unaltered Antarctic CR chondrites EET 92042 and QUE 99177 have very small or no L-isovaline enrichment (Pizzarello et al. 2008; Glavin and Dworkin 2009), it is likely that aqueous alteration played some role in the amplification of L-isovaline excesses on the meteorite parent body.

Although the current isovaline enantiomeric data for these meteorites suggest that there may be a relationship between enantiomeric enrichment and degree of aqueous alteration (Glavin and Dworkin 2009), additional isovaline enantiomeric measurements are needed to firmly establish a trend, especially for the type 1 carbonaceous chondrites. In order to further investigate the source of L-isovaline excesses in carbonaceous chondrites, we expanded our search for isovaline asymmetry to include CM and CR aqueously altered type 1 chondrites. We found that the CM1 SCO 06043 and the CR1 GRO 95577 carbonaceous chondrites both had significant L-isovaline excesses, with values of 16.5 ± 7.5% and 11.0 ± 7.2%, respectively (Table 5). These excesses agree with previous measurements of isovaline in the CI1 Orgueil (L_{ee} = 15.2 ± 4.0%). Isovaline was not detected in the CM1 MET 01070 above the 0.5 ppb level (Table 3). Similarly large L-isovaline excesses of 17.2 ± 6.7% and 18.5 ± 2.6% were also found for the two Murchison meteorite samples USNM 5453 and USNM 6650, respectively (Table 5). However, only slight L-excesses were observed in the CM2 LEW 90500 (3.3 ± 1.8%), and no detectable L-isovaline excesses (within analytical uncertainty based on the standard deviation of the mean) were found in LON 94102 (2.4 ± 4.1%), EET 92042 (−1.0 ± 4.3%), and QUE 99177 (0.3 ± 2.1%) (Glavin and Dworkin 2009). It should be emphasized that these results do not rule out circularly polarized radiation as a possible source of a small initial L-isovaline asymmetry in these weakly altered meteorites that is within our analytical error of a few percent. The errors in the L_{ee} values were calculated by standard error propagation of the absolute uncertainties of the total D- and L-isovaline concentrations reported in Table 3. We are currently unable to resolve small excesses (< 2–3%) on complex or dilute samples using our UPLC-FD/ToF-MS technique with sufficient confidence.

We have previously shown that the β-alanine/glycine molar ratio (which is approximately proportional to the β-alanine/α-AIB ratio presented in (Glavin and Dworkin 2009) found in carbonaceous meteorites can be used as an indicator for the extent of parent body aqueous alteration and that the magnitude of the L-isovaline excesses in CI, CM, and CR meteorites was correlated with the relative abundance of β-alanine (Glavin et al. 2006; Glavin and Dworkin 2009). The β-ala/glycine ratios and L-isovaline excesses for the meteorites studied are shown in Table 5. In general, the more altered meteorites have larger L-isovaline excesses and higher relative abundances of β-alanine, while the less altered meteorites have smaller L-isovaline excesses and lower β-alanine abundances. The exception is the Murchison meteorite which has the highest L-isovaline excess, but is less altered than the type 1 chondrites. The relative abundance ratios in these meteorites should be interpreted with caution since they were not corrected for the potential contribution of terrestrial glycine contamination, which could vary between meteorite samples.

The delivery of amino acids by carbonaceous chondrites to the early Earth could have been an important source of the Earth's prebiotic organic inventory (Chyba and Sagan 1992). Although α-dialkyl amino acids such as isovaline are not common in the terrestrial biosphere, these amino acids are highly resistant to racemization and may have been well suited as catalysts for transferring their asymmetry to the

α-hydrogen protein amino acids or other prebiotic compounds, such as sugars (Pizzarello and Weber 2004) common to all terrestrial life. There may have also been primordial chiral asymmetry in the α-hydrogen amino acids, but all evidence of this would have been long erased by racemization. Based on the results of this study, it seems increasingly likely that most aqueously altered carbonaceous chondrites possess L-isovaline asymmetry. The fact that only L-amino acid excesses (no D-excesses) have been found in carbonaceous meteorites analyzed so far may indicate that the origin of life on Earth and possibly elsewhere in our solar system was biased toward L-amino acid homochirality from the very beginning.

CONCLUSIONS

The purpose of this study was to compare the distribution and enantiomeric composition of amino acids found in CI, CM, and CR carbonaceous chondrites that cover a wide range of aqueous alteration states. The type 1 chondrites MET 01070, SCO 06043, and GRO 95577 had not previously been analyzed for amino acids using the highly sensitive and selective liquid chromatography time of flight mass spectrometry technique. For the first time, amino acids were extracted from a set of carbonaceous chondrites and analyzed by UPLC-FD/ToF-MS using the same analytical and quantitation methods in a single laboratory. A comparison of the amino acid abundances and enantiomeric ratios of isovaline in the nine carbonaceous chondrites studied led to the following five observations.

1. The total amino acid abundances found in the type 1 chondrites MET 01070, SCO 06043, and GRO 95577 were much lower than in the corresponding type 2 meteorites from the same carbonaceous chondrite group.
2. The relative abundance of β-alanine in the type 1 chondrites is much higher than in less altered type 2 carbonaceous chondrites. The β-alanine/glycine ratio appears to be a good chemical indicator to help assess the relative degree of aqueous alteration in CI, CM, and CR chondrites.
3. The relative abundances of the C_5 amino acids show that the less altered type 2 chondrites are dominated by α-amino acids with branched-chain isomers favored over straight-chain isomers; this is consistent with formation by Strecker synthesis. In contrast, the aqueously altered type 1 chondrites are enriched in γ- and δ-amino acids with no apparent enrichment of branched versus straight-chain isomers.
4. In general, the distribution of amino acids in LON 94102 do not match well with the CM2 chondrites Murchison and LEW 90500, possibly indicating that this CM2 meteorite originated on a chemically distinct parent body.
5. Large enrichments in L-isovaline of up to 11–19% were observed in the aqueously altered type 1 chondrites and in Murchison, exceeding those found in other less altered type 2 and type 3 chondrites from the respective chondrite groups.

The differences in the amino acid abundances, distributions, and L-isovaline asymmetry found in CI, CM, and CR type carbonaceous chondrites are best explained by differences in the degree of aqueous alteration on the respective meteorite parent bodies. In contrast to previous studies of CM1 and CM2 chondrites, we observe distinct differences in relative amino acid abundances between type 1 and 2 CM chondrites that we believe are best explained by aqueous alteration, and are likely not the result of chemical compositional differences between distinct CM parent bodies. One notable exception is the weakly altered CM2 chondrite LON 94102, which has a C_5 amino acid distribution that does not fit well with other type 2 chondrites, but more closely resembles the type 1 chondrites. For LON 94102, we cannot rule out the possibility that this meteorite did originate from a parent body that was chemically distinct from that of the other CM2s. The finding of large L-isovaline excesses in the most altered type 1 chondrites, but not in the most pristine unaltered type 2 and type 3 CRs provides additional support that amplification of a small L-isovaline excess occurred during an aqueous alteration phase on the parent bodies of these carbonaceous chondrites. We recognize that aqueous processing on the parent body cannot explain all of the compositional differences and patterns we observe in the meteorites. Finally, to gain a more thorough understanding for the mechanisms responsible for the differences seen in amino acid composition between CI, CM, and CR chondrites, laboratory investigations of the synthesis and decomposition of amino acids under realistic parent body conditions should be carried out.

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