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**Low Total Abundances and a Predominance of *n*- ω -Amino Acids in Enstatite Chondrites:
Implications for Thermal Stability of Amino Acids in the Inner Solar System**

Danielle N. Simkus^{1,2,3*}, José C. Aponte^{2,3}, Jamie E. Elsila², Hannah L. McLain^{2,3}, Eric T. Parker², Jason P. Dworkin², and Daniel P. Glavin²

¹NASA Postdoctoral Program at NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

²Solar System Exploration Division, Code 690, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

³Department of Physics, Catholic University of America, Washington, D.C. 20064, USA

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*Corresponding author:
Danielle N. Simkus
Solar System Exploration Division, Code 691
NASA Goddard Space Flight Center
Greenbelt, MD 20771
Phone: (301) 614-5887
danielle.n.simkus@nasa.gov

ABSTRACT

Investigating the organic contents of enstatite chondrite meteorites may offer insights into both early inner solar system and early Earth chemistry. Enstatite chondrite meteorites have highly reduced and anhydrous compositions, and their bulk isotopic compositions closely resemble terrestrial values, suggesting that their parent body asteroids accreted within the inner protoplanetary disk and were a primary contributor during Earth's late accretion (Javoy et al., 1995; Piani et al., 2020). Here, we present the first report of amino acids in enstatite chondrite meteorite samples. Three EH3 meteorites were analyzed (Dominion Range 14021, Larkman Nunatak 12001, and Larkman Nunatak 06252). The acid-hydrolyzed water extracts of the meteorites contained low abundances (1.5 – 215.9 pmol/g) of *n*- ω -amino acids (glycine, β -alanine, γ -amino-*n*-butyric acid (γ -ABA), δ -amino-*n*-valeric acid (δ -AVA), and ϵ -amino-*n*-caproic acid (ϵ -ACA)), but amino acids were not present above detection limits in the non-hydrolyzed samples. The low amino acid abundances and the predominance of *n*- ω -amino acids resembles amino acid distributions previously observed for thermally altered chondrites. These results suggest that the parent body asteroid was not conducive to the synthesis and/or preservation of α -amino acids, or free amino acids in general, and that EH3 chondrite-like material may not have been a primary contributor of diverse or abundant free amino acids to the early Earth.

1. INTRODUCTION

Enstatite chondrite meteorites or E-type chondrites (hereinafter referred to as “E chondrites”) are a distinct meteorite group defined by several unique properties including their highly chemically reduced and anhydrous compositions. The mineralogy of E chondrites consists of reduced, nearly FeO-free, silicate (essentially pure enstatite pyroxene (MgSiO_3)), Si-bearing kamacite (Fe,Ni metal), troilite (FeS), and a wide range of sulfide, nitride, phosphide, and silicide minerals that are characteristic of extremely reducing formation conditions (Anders, 1964; Mason, 1966; Keil, 1968; El Goresy, 1988; Lin and El Goresy, 2002; Kimura et al., 2005; Gannoun et al., 2011; Weisberg and Kimura, 2012). E chondrites lack hydrous minerals that would otherwise be indicative of parent body aqueous alteration, and they have low water contents (0.08 – 0.54 wt % H_2O ; Piani et al., 2020) relative to other chondrite meteorites (*e.g.*, 7.2 – 9.1 wt % H_2O for Orgueil (CI), Alais (CI), and Murchison (CM2); Piani et al., 2020). Collectively, these observations suggest

65 that the parent body asteroids of E chondrites accreted within the innermost portion of the
66 protoplanetary disk. Therefore, the compositions of E chondrites may serve as chemical records
67 of the inner solar system during its formation.

68 Not only are E chondrites potentially derived from the same vicinity as the terrestrial planets,
69 but they are also considered candidates for the building materials of Earth (Javoy et al., 1995;
70 Warren, 2011; Piani et al., 2020). E chondrites have bulk oxygen isotope compositions that can be
71 plotted on, or nearly along, the terrestrial fractionation line (Clayton et al., 1976, 1984; Javoy,
72 1995; Javoy et al., 2010), suggesting that they are potential remnants of the building blocks of the
73 terrestrial planets. Models of Earth's accretion estimate that chemically reduced meteorites similar
74 in composition to E chondrites comprised, at minimum, half of Earth's accreted material, with an
75 increasing contribution towards the later stages of accretion (Dauphas, 2017; Brasser et al., 2018;
76 Mah and Brasser, 2021). As such, investigating the organic composition of E chondrites may not
77 only provide important insights into the chemistry of the inner protoplanetary disk, but also
78 information about the organic inventory of the Earth without the delivery of hydrated and organic-
79 rich carbonaceous asteroids.

80 E chondrite meteorites are rich in carbon (0.15-0.70 weight %; Belsky and Kaplan, 1970;
81 Grady et al., 1986) and previous studies have described the analysis of graphite, insoluble organic
82 matter, and light hydrocarbons in a few thermally altered E chondrites (*e.g.*, Belsky and Kaplan,
83 1970; Cody et al., 2008; Remusat et al., 2012). However, to our knowledge, water-soluble organic
84 compounds such as amino acids have not yet been investigated in E chondrites. Amino acids are
85 the monomers of proteins in terrestrial biology and are a common target class of water-soluble
86 organic compounds in meteorite analyses due to their ubiquity in biology, numerous routes of
87 abiotic synthesis, structural variation, and the availability of sensitive analytical methods to
88 measure these species. By investigating the amino acid content of meteorite samples, we learn
89 about the possible syntheses and preservation mechanisms of these molecules within asteroid
90 parent bodies and the potential exogenous origins of amino acids on the prebiotic Earth. The bulk
91 of our current knowledge of meteoritic amino acids is based on studies of carbonaceous (C)
92 chondrite meteorite samples. To date, 96 different aliphatic amino acids have been named in the
93 Murchison CM2 carbonaceous chondrites and appear to exhibit complete structural diversity
94 (Glavin et al. 2018), though the distribution and abundances of amino acids vary widely between

95 different C chondrite groups (Pizzarello et al., 2006; Martins et al., 2007; Burton et al., 2012; Elsila
96 et al., 2016; Glavin et al., 2018). Comparative studies within and across C chondrite groups have
97 shown that a variety of factors, including the mineralogy, aqueous and thermal alteration history,
98 and post-fall terrestrial contamination, can influence the amino acid chemistry of a sample (Elsila
99 et al., 2016; Glavin et al., 2011; 2020). Expanding our amino acid database with analyses of E
100 chondrite samples opens a new window to study the prebiotic chemistry of the inner solar system
101 specifically, and allows us to assess the influence of thermal alteration, reduced oxidation state,
102 high metal contents, and lack of aqueous alteration on the synthesis and preservation of amino
103 acids. Furthermore, if E chondrite-like material did, in fact, comprise the bulk of the impactor
104 population during Earth's late accretion, the present study offers new insights into whether that
105 process would have concomitantly delivered a significant abundance of prebiotic organic matter
106 to the early Earth, or if a reservoir of water-rich objects, such as comets, was necessary to deliver
107 organic matter.

108 E chondrites are categorized into two distinct subgroups, EH and EL chondrites, which are
109 generally thought to be derived from two distinct parent body asteroids, based on differences in
110 trace element abundances that reflect distinct nebular processing (Keil, 1989). EH chondrites also
111 differ from the EL chondrites in that they tend to have smaller chondrules, lower abundances of
112 enstatite, higher abundances of sulfides, and more silicon-rich and nickel-poor metal compositions
113 (Krot et al., 2014). Although the parent bodies of E chondrites are unknown (Greenwood et al.,
114 2020), E chondrites possess spectral and density similarities to M-type asteroids (Chapman and
115 Salisbury, 1973; Shepard et al., 2010), such as Lutetia (Vernazza et al., 2011) and 16 Psyche, the
116 target of NASA's upcoming Psyche mission (Lupishko and Belskaya, 1989; Landsman et al., 2018;
117 Elkins-Tanton et al., 2020)

118 Like all chondrites, EH and EL meteorites are assigned a petrologic type, a number specifying
119 the degree of alteration experienced within the parent body asteroid (Van Schmus and Wood, 1976;
120 Weisberg et al. 2006). E chondrite petrologic types range between 3 and 6, indicating varying
121 thermal alteration histories, with petrologic type 3 representing the least altered materials, and
122 petrologic type 6 representing the most thermally altered. In the present study, we have
123 investigated the amino acid content of three EH meteorites of petrologic type 3, in order to study
124 EH chondrite samples that have experienced relatively low temperatures for this chondrite group

125 (Zhang and Sears, 1996; Kimura et al., 2005; Quirico et al. 2011) We selected Dominion Range
126 (DOM) 14021; Larkman Nunatak (LAR) 12001; and Larkman Nunatak (LAR) 06252) for this
127 study since there is sufficient mass available for destructive analyses of these specimens, and these
128 meteorites exhibit relatively minor weathering and/or fracturing. Reduced weathering/fracturing
129 minimizes the potential impact of terrestrial contamination derived from the fall and recovery, as
130 the internal mass of the meteorites tend to be better protected from terrestrial contamination.

131

132

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

134 All glassware and tools were wrapped in aluminum foil and heated at $> 500^{\circ}\text{C}$ for a
135 minimum of 6 hours before use in order to remove organic contamination. All vials were capped
136 with PTFE-lined lids. Standards and reagents were purchased from Sigma Aldrich and Fisher
137 Scientific. Ultrapure water (Millipore Milli-Q Integral 10, $18.2\text{ M}\Omega$, ≤ 3 ppb total organic carbon;
138 hereafter referred to as “ultrapure water”) was used. Stock amino acid solutions were prepared by
139 mixing individual standards (97–99% purity) in ultrapure water. The *o*-phthaldialdehyde/N-acetyl-
140 L-cysteine (OPA/NAC) reagent used for amino acid derivatization was prepared by mixing 300
141 μL 0.1 M OPA in methanol, and then adding 670 μL 0.1 M sodium borate buffer (pH 9) and 30
142 μL 1 M NAC. A 0.1 M hydrazine solution was prepared by double vacuum distillation of
143 anhydrous hydrazine (98% purity) and subsequent dilution in ultrapure water. The ammonium
144 formate buffer used for the ultra-high performance liquid chromatography with fluorescence
145 detection and time-of-flight mass spectrometry (LC-FD/ToF-MS) analyses was prepared by
146 ammonium hydroxide titration of a 50 mM formic acid solution to pH 8. Details regarding the
147 preparation of solutions and the sources of specific five-carbon (C_5) amino acids used as standards
148 are available in Glavin et al. (2006, 2011, 2020).

2.2. Sample Preparation and Amino Acid Extraction

150 Interior samples of three EH3 meteorites (DOM 14021, 2.0 g; LAR 12001, 2.2 g; LAR 06252,
151 2.5 g) were provided by the Antarctic meteorite curator at the NASA Johnson Space Center. The
152 samples were prepared for amino acid extraction within a positive pressure ISO 5 HEPA-filtered
153 laminar flow hood in an ISO ≤ 8 white room. The DOM 14021 and LAR 12001 chips did not show

154 any visible signs of weathering, while one of the LAR 06252 chips appeared to exhibit minor
155 weathering, as evidenced by a small amount of white mineral and minor rusting on the surface of
156 the sample. The individual meteorite samples were powdered using ceramic mortars and pestles,
157 and all three meteorites, especially LAR 12001, were highly indurated and resistant to powdering.
158 The powdered samples were subdivided into ~ 500 mg aliquots in flame-sealed glass ampoules,
159 each containing 1 mL of ultrapure water. To monitor background levels of amino acids in the
160 method, two procedural blanks were also carried through the meteorite extraction procedure and
161 sample work-up: one solvent blank, containing no mineral component, and one mineral analog
162 blank, consisting of ~ 500 mg of clean serpentine mineral powder (heated > 6 hours at 500°C prior
163 to the extraction step to drive off organics). All sealed ampoules were then heated in an oven set
164 at 100 °C for 24 hours.

165 **2.3. Isolation and Analysis of Amino Acids**

166 Following the hot-water extraction step, the aqueous extracts were separated from the
167 meteorite residues by centrifugation. The residues were rinsed with ultrapure water (3×0.5 mL)
168 and centrifuged after each addition of 0.5 mL ultrapure water and all of the rinses were combined
169 with the aqueous extract. For each sample, the extract was divided into two equal portions: one
170 portion for the analysis of “free” amino acids, and one portion carried through an acid-vapor
171 hydrolysis step (6 M double distilled HCl (ddHCl), 150 °C for 3 hours) to measure the “total”
172 amino acid content (free plus acid-hydrolyzable). Unhydrolyzed and acid-hydrolyzed extracts
173 were re-dissolved in ultrapure water, desalted using cation-exchange resins and derivatized using
174 OPA/NAC, following protocols described elsewhere (Glavin et al., 2006; 2011). The derivatized
175 amino acids were analyzed via LC-FD/ToF-MS using a Waters ACQUITY H Class UPLC with
176 UV fluorescence detector and a Waters Xevo G2 XS ToF-MS. The instrument parameters and
177 analytical conditions used were the same as those described elsewhere (Glavin et al., 2020). For
178 the Xevo mass calibrations, an automatically applied lock mass of a fragment (278.1141 Da) of
179 Leucine Enkephalin ($0.09 \mu\text{M}$ in 50/50 acetonitrile/water with 0.1% formic acid) with a scan time
180 of 1 second every 120 seconds was used. The capillary voltage was set to 1.2 kV. The amino acids
181 and their enantiomeric ratios were quantified from the peak areas generated from both UV
182 fluorescence (UPLC-FD, $\lambda_{\text{ex}} = 340$ nm, $\lambda_{\text{em}} = 450$ nm) and ToF-MS chromatograms by plotting
183 the accurate mass to within 10 ppm of the theoretical m/z value of each OPA/NAC derivative over

184 the elution time as described previously (Glavin et al., 2020). The reported amino acid abundances
185 are the average value of three separate LC-FD/ToF-MS measurements. The errors given are based
186 on the standard deviation of the average value of three separate measurements. Amino acid
187 abundances are blank-corrected to account for trace levels of contamination present in the blanks.

188 3. RESULTS AND DISCUSSION

189 3.1. Detection of Amino Acids in the Acid-Hydrolyzed Extracts

190 Non-hydrolyzed and acid-hydrolyzed extracts from each sample were analyzed to investigate
191 the presence of amino acids that are readily extractable in water, and amino acids generated or
192 liberated from chemical precursors or sequestered amino groups (*e.g.*, HCN, peptides, lactams,
193 hydantoins, *etc.*) during acid hydrolysis, respectively. The non-hydrolyzed extracts represent the
194 “free” water-soluble amino acid content of the meteorite, while the acid-hydrolyzed extracts
195 represent the “total” amino acid content (“free” amino acids + “precursors”). Low abundances of
196 amino acids were detected in all three hydrolyzed meteorite extracts (Table 1) while the non-
197 hydrolyzed extracts did not contain amino acids above background levels. The hydrolyzed
198 procedural blanks contained trace amounts of glycine (50 pmol), L-alanine (1 pmol), and β -alanine
199 (4 pmol) and their abundances were subtracted from the meteoritic amino acid measurements. Free
200 amino acids were not detected in any of the three E chondrite samples. While an absence of free
201 amino acids is unusual for extracts of meteorites from other classes, it is not uncommon for there
202 to be a relatively high abundance of amino acids in acid-hydrolyzed meteorite extracts. Total
203 amino acid abundances within acid-hydrolyzed samples are often a factor of two higher than that
204 of non-hydrolyzed samples (Glavin et al., 2011; 2020; Burton et al., 2012, 2013, 2015; Simkus et
205 al., 2019), indicating that a significant portion of amino acids in chondrites are bound as labile
206 precursors or synthesized via acid hydrolysis through reactions between volatile organics. This
207 observation, combined with the low overall abundances in the E chondrite samples, suggests that
208 the abundance of free water-soluble amino acids, if present, may have fallen below detection
209 limits. The lack of detection of free amino acids in the E chondrite samples could also indicate that
210 the parent body conditions were not favorable for amino acid syntheses and/or preservation, or
211 favored the cyclization or polymerization of these species. Since the formation of such bound
212 species results in the loss of a water molecule, perhaps the low water activity on the parent body
213 favored such compounds.

214 3.2. Low Total Abundances and a Predominance of *n*- ω -Amino Acids

215 The relative abundances of individual amino acids detected in the E chondrite samples
216 resembled the amino acid distributions previously observed for thermally altered R and CK
217 chondrites (Burton et al., 2015), ureilites, CV chondrites, and CO chondrites (Burton et al., 2012),
218 and thermally altered CI chondrites (Burton et al., 2014). More specifically, the amino acid
219 compositions observed in the current study primarily consisted of straight-chain, terminal-amine
220 amino acids (*n*- ω -amino acids) generally exhibiting a trend of decreasing abundance in the order
221 of: ϵ -amino-*n*-caproic acid (ϵ -ACA) > γ -amino-*n*-butyric acid (γ -ABA) > β -alanine > glycine > δ -
222 amino-*n*-valeric acid (δ -AVA). Despite this resemblance in amino acid distributions, the
223 abundances that we measured for the E chondrite samples are exceptionally low, with total
224 abundances over 10-fold lower than the most amino acid-depleted R chondrite and thermally
225 altered CI chondrite previously analyzed (Burton et al., 2014; 2015). Our ability to detect such low
226 abundances of amino acids in the present study is partly due to the relatively high sample masses
227 (~ 2 grams each) that were analyzed. The fact that the E chondrite samples are so depleted in amino
228 acids relative to these other chondrite groups suggests that their parent body conditions may have
229 been particularly unfavorable for the synthesis and/or preservation of these compounds. The
230 consistent dominance of *n*- ω -amino acids in thermally altered meteorites points towards a
231 relationship between thermal metamorphism and the predominance of these structures. Although
232 the dominance of *n*- ω -amino acids was similar, the thermally altered meteorites contained higher
233 relative amounts of free amino acids (8% to 100%) compared to the lack of free amino acids
234 observed in E chondrites (Burton et al., 2012). This suggests that the formation mechanisms may
235 be different and that the low water abundance alone is not responsible for the absence of detectable
236 free amino acids in the non-hydrolyzed EH chondrites analyzed here. The apparent absence of free
237 amino acids in E chondrites, in contrast to other thermally altered chondrites, could be partially
238 attributed to the highly reducing, high-temperature conditions of the inner solar system and
239 potentially insufficient accreted volatile molecules within the parent bodies.

240 Given the high temperatures (< 400°C, Kimura et al., 2005; < 550-600°C, Quirico et al. 2011)
241 that EH3 meteorites may have experienced during parent body thermal alteration, the
242 predominance of non- α -amino acids in the acid-hydrolyzed extracts analyzed here could reflect a
243 preferential preservation of amino acid derivatives with higher thermal stabilities. For instance, for

244 the C₄ amino acids, it has been shown that γ -ABA has a relatively low decarboxylation rate at
245 elevated temperatures in aqueous solution, in comparison to α - and β -amino-*n*-butyric acid (Li and
246 Brill, 2003a). The higher abundances of γ -ABA and non-detection of α -ABA and β -ABA in the E
247 chondrites samples may be attributable to this difference in thermal stability. Likewise, non- α -
248 amino acids that are capable of converting to lactam derivatives (such as γ -ABA and δ -AVA) are
249 relatively stable at elevated temperatures up to 400°C and are potentially preferentially preserved
250 in metamorphosed parent bodies (Cooper and Cronin, 1995; Islam et al., 2001, 2003; Li and Brill,
251 2003b; Burton et al., 2012). The absence of common α -amino acids could also indicate that
252 Strecker-cyanohydrin synthesis was not a dominant mechanism for amino acid synthesis in the E
253 chondrite parent body asteroids and that reactions such as Michael addition of β -amino acids, or
254 Fischer-Tropsch type reactions, may have played a more significant role (Elsila et al., 2016).
255 Perhaps the predominance of bound *n*- ω -amino acids could have resulted from Fischer-Tropsch
256 type reactions associated with a high-pressure impact event, as has been previously proposed for
257 other meteorites such as the Martian meteorite Roberts Massif (RBT) 04262 (Callahan et al.,
258 2013).

259 The low abundances of amino acids in the E chondrite samples, relative to chondrites that
260 contain mineralogical evidence of aqueous alteration (Burton et al., 2014; Elsila et al., 2016;
261 Glavin et al., 2018), may demonstrate the significant role that water-rock interactions play in
262 generating meteoritic amino acids. The low amino acid contents and the absence of detectable free
263 amino acids could also be indicative of the destructive effects of parent body thermal alteration on
264 amino acids and/or their precursors (e.g., aldehydes, ketones, ammonia, and cyanide). Other
265 factors could have influenced the potential for amino acid synthesis in these samples, including
266 the highly reduced mineral assemblages, low abundances of matrix minerals, high metal contents,
267 and low porosities (Macke et al., 2010; Weisberg and Kimura, 2012); determining how each of
268 these factors alone could have affected prebiotic organic synthesis would require additional
269 focused studies. E chondrites bear some resemblance to CB and CH chondrites, in terms of their
270 high metal contents, high abundances of chondrules, low abundances of calcium aluminum
271 inclusions and amoeboid olivine aggregates, and low volumes of matrix minerals (background
272 fine-grained minerals, as opposed to chondrules or inclusions), relative to other chondrite groups
273 (Krot et al., 2014; Scott and Krot, 2014). Previous analyses of CB and CH chondrite samples
274 revealed amino acid distributions similar to those observed here (*i.e.*, a predominance of non- α

275 amino acids) (Burton et al., 2013). However, the CB/CH chondrite samples contained amino acids
276 in abundances (CB: 5 – 47 nmol/g; CH: 167 – 221 nmol/g; Burton et al., 2013) that were several
277 orders of magnitude more abundant than the E chondrite values reported here (37 – 281 pmol/g).
278 The relatively high abundances of amino acids measured for CB/CH chondrites may demonstrate
279 the important role of mineral-fluid interactions for prebiotic organic synthesis; CB/CH chondrites
280 tend to have slightly higher matrix volumes (< 5 vol%), including hydrated matrix minerals and
281 clasts (Greshake et al., 2002; Krot et al., 2014), while matrix volumes of E chondrites are
282 exceptionally low (< 0.1 vol%) and anhydrous (Krot et al., 2014). Thus, it is likely that catalytic
283 reactions on hydrated matrix mineral surfaces that are absent in E chondrites may have played a
284 role in yielding relatively higher abundances of amino acids in CB and CH chondrites.

285 **3.3. Potential Terrestrial Origins of ϵ -ACA**

286 There are two sources that need to be evaluated as potential terrestrial origins for the amino
287 acids identified in this study: (1) the environment of the original fall site, including sample
288 collection and storage processes, and (2) the methodology for sample extraction and analysis in
289 the laboratory. Stable isotopic analyses (δD , and in some cases $\delta^{13}C$) can serve as a means to
290 support or refute extraterrestrial origins; however, isotopic measurements were not possible in this
291 study due to the low amino acid abundances. Likewise, the analysis of chirality to look for L-
292 excesses of protein amino acids that would be expected in biologically contaminated samples was
293 impossible with the exception of a small amount of L-alanine (1 pmol), because only achiral amino
294 acids were detected. Our assessment of the origins of amino acids in these E chondrite samples,
295 therefore, primarily relies on comparisons to blanks and previous meteorite analyses. Our analyses
296 of procedural blanks in parallel with the E chondrite samples provided confidence that the
297 methodology was not a significant source of amino acids. The amino acid content of the E
298 chondrite samples is clearly distinguishable from the procedural blanks by the predominance of *n*-
299 ω -amino acids in the meteorites (Figure 1), ruling out the laboratory as a source of these
300 compounds. The predominance of *n*- ω -amino acids in these Antarctic E chondrite samples is also
301 distinctly different from the composition of Antarctic ice previously collected and analyzed by
302 Burton et al. (2012) (Table 1). The *n*- ω -amino acids, β -alanine, γ -ABA, δ -AVA, and ϵ -ACA were
303 not detectable above 0.08 – 0.1 fmol/g (0.01 pptr) levels in the Antarctic ice samples (Burton et
304 al., 2012), in contrast to the amino acid abundances measured here for E chondrites (1.5 – 215.9

305 pmol/g). The protein amino acids, aspartic acid, glutamic acid, serine, alanine, and valine were
306 present between 0.07 and 0.6 fmol/g (0.01 and 0.05 pptr, respectively) in the Antarctic ice samples
307 (Burton et al., 2012), but were absent in the E chondrite samples studied here. These distinct
308 differences in amino acid distributions suggest that the fall and collection site is unlikely to have
309 been a significant source of *n*- ω -amino acids to the meteorite samples.

310 The most abundant amino acid detected for all three samples was ϵ -ACA, which is also the
311 degradation product upon acid hydrolysis of samples containing the nylon-6 polymer (Glavin et
312 al., 2006; Dworkin et al., 2018). This potential terrestrial source is an important consideration for
313 interpreting amino acid data in cases where samples have been exposed to nylon-6 during
314 collection, storage and/or analysis. All meteorite samples collected in Antarctica by the Antarctic
315 Search for Meteorites (ANSMET) team were initially stored in nylon bags. Once nylon was
316 identified as a potential source of terrestrial amino acids (Glavin et al., 2006) and after testing
317 different bagging materials in 2008 (Dworkin et al. 2018), ANSMET replaced the nylon sample
318 collection materials with polytetrafluoroethylene (PTFE, for example Teflon™) (Kevin Righter;
319 personal communication). Today, ANSMET collects all recovered meteorites in PTFE bags, in
320 which they are transferred to NASA's Johnson Space Center (JSC) to be dried and processed in
321 nitrogen cabinets for storage. While C chondrites and Martian meteorites are stored long-term in
322 PTFE bags, other meteorite types that are not typically targeted for soluble organic analyses, such
323 as E chondrites, are stored dry in nylon bags. The risk of contamination from the nylon bags would
324 be lower for dried meteorite samples because nylon is spread through contact transfer, which
325 becomes more efficient when wet conditions exist (Dworkin et al., 2018). However, it is worth
326 considering whether trace levels of nylon-6 polymer could still be transferred to the meteorites
327 during the process of storing dried meteorites in nylon bags. LAR 06252 was collected in
328 Antarctica in 2006. At that point in time, meteorites were collected and stored in nylon bags. The
329 LAR06252 sample was, therefore, exposed to nylon both before and after the meteorite was
330 desiccated. In contrast, LAR 12001 and DOM 14021, collected in 2012 and 2014, respectively,
331 had minimal exposure to nylon-6, which may help explain the relatively lower ϵ -ACA abundances
332 measured in these two samples.

333

4. CONCLUSIONS

334 Three EH3 chondrite samples (DOM 14021, LAR 12001, and LAR 06252) were analyzed to
335 determine their free and bound amino acid contents. All three meteorites were found to contain
336 extremely low abundances of bound amino acids and only a small suite of *n*- ω -amino acids were
337 identified as indigenous to the samples. The absence of free amino acids in these samples suggests
338 that the conditions within the E chondrite parent body or bodies were not optimal for the synthesis
339 and/or preservation of amino acids in their free form. The amino acid distributions observed here
340 for the E chondrite samples resemble those of other thermally altered chondrite groups, in terms
341 of low total abundances and the predominance of *n*- ω -amino acids (Burton et al., 2012; 2015). The
342 predominance of bound *n*- ω -amino acids in the E chondrite samples may reflect a greater
343 preservation of larger derivatives (*e.g.*, peptides, complexes, *etc.*) due to the possibly higher
344 stabilities of these structures under elevated temperatures and/or pressures.

345 These results suggest that EH3-like material bombarding the early Earth would have
346 contributed lower abundances of amino acids (or their precursors) per mass of meteorite, in
347 comparison to most other chondrite types analyzed to date. The implication of this finding is that,
348 if meteoritic delivery of amino acids constituted a significant source of amino acids or their
349 precursors to the early Earth, materials like those from the E chondrites studied here are unlikely
350 to have been a major contributor. Rather, other chondrite groups such as C chondrites would have
351 had the potential to deliver much larger quantities of prebiotic organic matter. We do consider,
352 however, that the organic compositions of EH3 meteorites are not necessarily representative of all
353 E chondrites, and that the low abundances of amino acids detected here do not rule out all E
354 chondrites as significant sources of amino acids on the early Earth. The two groups of E chondrites
355 (EH and EL chondrites), for instance, could contain entirely different total abundances and
356 distributions of amino acids, and they may not be equally relevant to Earth's late accretion (*e.g.*,
357 Mah and Brassler, 2021). Further investigation of E chondrite organic matter by conducting amino
358 acid analyses of EL samples specifically would be important to fully assess the potential influence
359 of E chondrite-like material on the chemistry of the early Earth. The present study offers valuable
360 new insights into the organic content of a chondrite group previously unstudied for soluble organic
361 matter, and demonstrates the importance of early solar system dynamics for understanding
362 implications for Earth's prebiotic chemistry.

363

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Table 1. Summary of averaged, blank-corrected amino acid abundances in 6 M ddHCl-hydrolyzed (“total”) hot-water extracts of three EH3 meteorites (in pmol/g), and in an Antarctic ice sample from the northern Graves Nunataks region (in fmol/g, converted from pptr values; Burton et al., 2012).

	DOM 14021 (EH3)	LAR 12001 (EH3)	LAR 06252 (EH3)	Antarctic ice (fmol/g; Burton et al. 2012)
D-aspartic acid	< 0.1	< 0.1	< 0.1	0.1
L-aspartic acid	< 0.1	< 0.1	< 0.1	0.1
D-glutamic acid	< 0.1	< 0.1	< 0.1	0.1
L-glutamic acid	< 0.1	< 0.1	< 0.1	< 0.1
D-serine	< 0.1	< 0.1	< 0.1	< 0.1
L-serine	< 0.1	< 0.1	< 0.1	0.5
D-threonine	< 0.1	< 0.1	< 0.1	n.d.
L-threonine	< 0.1	< 0.1	< 0.1	n.d.
glycine	< 0.1	< 0.1	3.6 ± 0.7	0.4
β-alanine	2.7 ± 0.3	< 0.1	10.7 ± 0.4	< 0.1
D-alanine	< 0.1	< 0.1	< 0.1	0.1
L-alanine	< 0.1	< 0.1	< 0.1	0.6
γ-amino- <i>n</i> -butyric acid (γ-ABA)	9.9 ± 0.7	7.4 ± 0.1	48.7 ± 0.2	< 0.1
D-β-amino- <i>n</i> -butyric acid (D-β-ABA)	< 0.1	< 0.1	< 0.1	< 0.1
L-β-amino- <i>n</i> -butyric acid (L-β-ABA)	< 0.1	< 0.1	< 0.1	< 0.1
α-aminoisobutyric acid (α-AIB)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-α-amino- <i>n</i> -butyric acid (D,L-α-ABA)	< 0.1	< 0.1	< 0.1	< 0.1
ε-amino- <i>n</i> -caproic acid (ε-ACA)	59.9 ± 0.2	27.6 ± 3.0	215.9 ± 0.1	< 0.1
3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-4-aminopentanoic acid (D,L-4-apa)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-4-amino-3-methylbutanoic acid (D,L-4-a-3-mba)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-3-amino-2-methylbutanoic acid (D,L-3-a-2-mba)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-3-amino-2-ethylpropanoic acid (D,L-3-a-2-epa)	< 0.1	< 0.1	< 0.1	< 0.1
δ-aminovaleric acid (δ-AVA)	< 0.1	< 0.1	1.5 ± 0.1	< 0.1
D,L-4-amino-2-methylbutanoic acid (D,L-4-a-2-mba)	< 0.1	< 0.1	< 0.1	< 0.1
3-amino-3-methylbutanoic acid (3-a-3-mba)	< 0.1	< 0.1	< 0.1	n.d.
D-2-amino-2-methylbutanoic acid (D-isovaline)	< 0.1	< 0.1	< 0.1	< 0.1
L-2-amino-2-methylbutanoic acid (L-isovaline)	< 0.1	< 0.1	< 0.1	< 0.1
D,L-3-aminopentanoic acid (D,L-3-apa)	< 0.1	< 0.1	< 0.1	< 0.1
D-2-amino-3-methylbutanoic acid (D-valine)	< 0.1	< 0.1	< 0.1	< 0.1
L-2-amino-3-methylbutanoic acid (L-valine)	< 0.1	< 0.1	< 0.1	< 0.1
D-2-aminopentanoic acid (D-norvaline)	< 0.1	< 0.1	< 0.1	< 0.1
L-2-aminopentanoic acid (L-norvaline)	< 0.1	< 0.1	< 0.1	< 0.1
Total	76.0 ± 0.7	36.5 ± 3.2	280.5 ± 1.4	4.2

n.d. – not determined

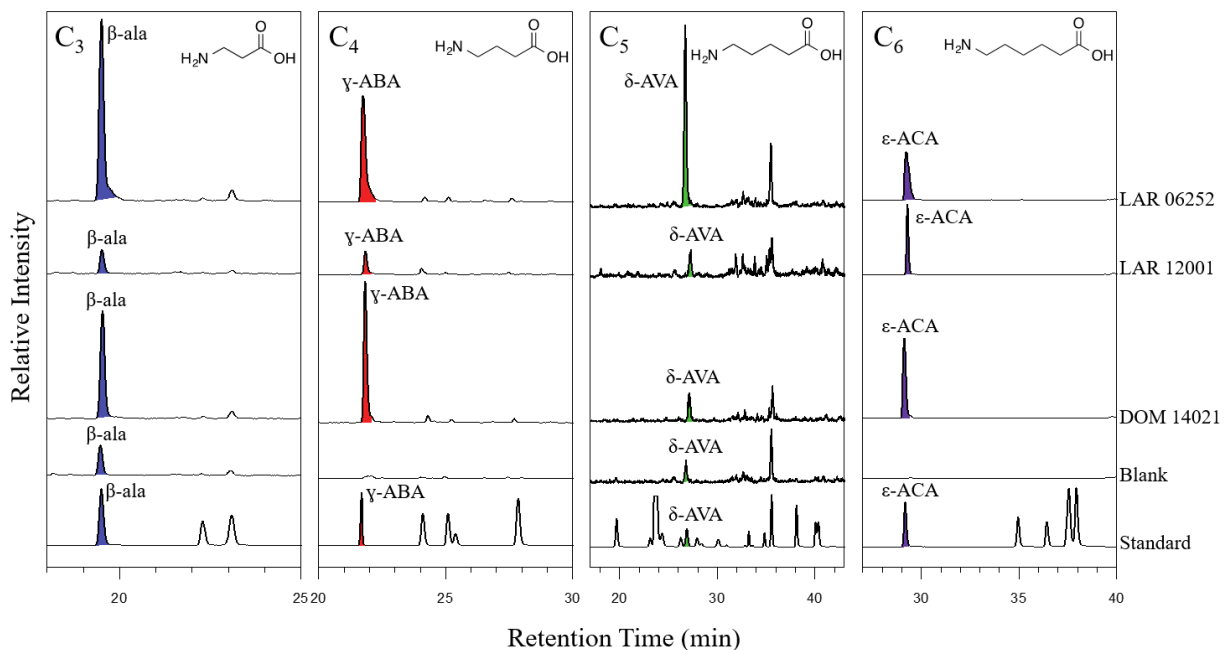


Figure 1. Representative LC-ToF-MS single ion chromatograms of 6M ddHCl-hydrolyzed EH3 chondrite samples, a procedural blank, and an amino acid standard mixture. The four panels illustrate chromatograms for C₃, ($m/z = 351.1015$), C₄ ($m/z = 365.1171$), C₅ ($m/z = 379.1328$) and C₆ ($m/z = 393.1484$) amino acids. Meteorites and blanks are ratioed to be the same mass on column. The standards are ratioed arbitrarily.

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